CONCRETE ADMIXTURES HANDBOOK

Properties, Science, and Technology

Second Edition

Edited by

V. S. Ramachandran

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National Research Council Canada
Ottawa, Ontario, Canada

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DEDICATION

Dedicated to my brother Sampath
my mentor and benefactor
during the critical period of my
academic career

About the Editor

Dr. V. S. Ramachandran is Distinguished Researcher at the Institute for Research in Construction, National Research Council Canada, Ottawa, Canada. In 1968 he joined the Council as a research officer and was Head of the Building Materials Section for ten years until December, 1991.

He has been engaged in research for 42 years and has made significant contributions in catalysis, clay mineralogy, lime, gypsum, thermal analysis, cement chemistry and concrete technology. He has published six books and has also contributed 17 chapters to books. Also to his credit, he has 200 publications.

He is a Fellow of the Royal Society of Chemistry, the Ceramic Society (U.K.) and the American Ceramic Society. He is also a member of the American Society for Testing and Materials, the American Concrete Institute and the International Confederation of Thermal Analysis. He is a member of the editorial board of the Journal of Materials and Structures, France, and the Editor of the Journal of Materials in Civil Engineering. He is a member of the technical committee of RILEM organization in France, and also a member of the Concrete Research Council of the American Concrete Institute. In addition, Dr. Ramachandran is a recipient of numerous awards and honors for his scientific accomplishments in the concrete and ceramic fields.

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Preface to the Second Edition

Since the publication of the first edition ten years ago, important developments have taken place in the use of admixtures in concrete. The increased role and development of admixtures in concrete technology is evidenced by reports in a number of conferences, publications in the literature, and novel admixtures available in the market place.

This edition contains eighteen chapters compared to ten chapters in the first edition. All the chapters in the first edition have been updated. Some chapters needed modifications to a much greater extent than others, reflecting the relative advances made in the science and technology of different groups of admixtures.

The addition of eight new chapters in the second edition was necessary because of the increasing importance and development of some admixtures in concrete practice. Although individual chapters refer to standards and specifications on admixtures, those interested only in the standards or the techniques commonly applied in research related to the investigation of admixtures in concrete may find the second chapter on "Research Techniques, Standards and Specifications" useful. Admixtures are not inert as may be presumed. They may chemically interact with the constituents of concrete and affect the properties of the fresh and hardened concrete and its durability. The third chapter deals with these aspects. Many attempts have been made to develop new admixtures recently and it was thought that a chapter should be devoted to describing them. Chapter 4 pertains to a description of the more recent developments in chemical admixtures. Fly ash and slag concretes have been used in practice over a number of years. Incorporation of higher-than-normal dosages of superplasticizers has made it possible to fabricate concretes containing high volumes of supplementary cementing materials. Chapter 12 on "High Volume Fly

Ash and Slag Concrete" provides comprehensive information on such concretes. The annual outlay for repair and restoration of concrete has substantially increased recently. It was determined that it is important to provide information on the types of repair materials, concrete, and techniques used for this purpose from the viewpoint of the use of admixtures. Chapter 13 on "Admixtures for Repair and Restoration of Concrete" emphasizes the precautions to be taken in the use and applications of admixtures for this purpose. Depending on the materials and exposure conditions, concrete may deteriorate and there has been widespread concern, particularly about the alkali-aggregate expansion reactions and corrosion of concrete. In view of the importance of counteracting these forms of deterioration, a separate chapter on "Alkali-Aggregate Expansion and Corrosion Inhibiting Admixtures" was included in the second edition. Batching and dispensing of admixtures are indispensable parts of admixture usage and therefore a separate chapter (Chapter 16) was introduced in this edition. There has been an increasing interest in oil well cements and this necessitated inclusion of a separate chapter (Chapter 18) on the use of admixtures in these cements.

In such a voluminous treatise as this, although written by internationally known experts, it is quite possible that some pertinent information has been excluded or is missing. In addition, some duplication of information occurs in some of the chapters. This was intentional because some specific chapters may only be of interest to specialized groups, and they will provide enough self-contained information so that gleaning through other chapters may not be required.

The second edition, I believe, is more comprehensive than the first edition and contains the latest knowledge on concrete admixtures. This edition should serve as a reference for the engineer, scientist, architect, concrete technologist, manufacturer, and user of concrete admixtures.

I am indebted to the following sources for granting me permission to incorporate a substantial amount of matter from their publications in the chapters I was involved in. They include: Heyden & Son, Applied Science Publishers, CANMET-Canada, Pergamon Press, American Concrete Institute, ASTM, CRC Press, Thomas Telford Publications, National Council for Cement and Building Materials (India), RILEM (France), Transportation Research Board (USA), Chapman and Hall, Cement Association of Japan, British Cement Association, Nihon University (Japan), Elsevier Publications, John Wiley & Sons, The Society of Materials Science (Japan), The Concrete Society (UK), Industria Italiana Del Cemento, Silicates Industrielle (Belgium), and American Ceramic Society. References to the above and other sources from which the tables and figures were derived have been indicated in the book.

July 1, 1995 V. S. Ramachandran
Ottawa, Canada

Preface to the First Edition

Admixtures are ingredients that are added to the concrete batch immediately before or during mixing. They confer certain beneficial effects to concrete, including enhanced frost and sulfate resistance, controlled setting and hardening, improved workability, increased strength, etc. Special concretes can be made using coloring pigments, polymer latexes, expansion or gas-producing admixtures and flocculating agents. It is estimated that 80% of concrete produced in North America contains one or more types of admixtures. Admixtures are being used increasingly in many other countries.

I have been reviewing the admixture literature for the American Ceramic Society for the past seven years and am impressed with the tremendous amount of activity in this field. In the years 1976–1981 for example, at least 550 patents pertained to admixture formulations. In spite of extensive investigations, the use of admixtures in many instances is based more on art than science.

Few books are available that serve as a source of reference for all admixtures. There is a need for a book which deals with the science, properties, specifications, dispensing, availability, limitations, patents and other aspects of the commonly used admixtures. This handbook is intended to serve such a purpose. It represents the concerted efforts of several internationally known experts. Although every attempt has been made to present as much information as possible on each of the admixtures, some compromise was inevitable because of space limitations, lack of specific information and of course the editor's discretion. A uniform treatment of all the chapters although beneficial could not be followed fully, because some specific information was not available or it would have meant sacrificing some quality.

The book is divided into 10 chapters and all the important admixtures are included. Each chapter contains a list of important recent references that should be a useful guide for further reading. A chapter on "Cement Science" was included to describe the most recent concepts so that the information presented in subsequent chapters could easily be followed. The last chapter on "Patents" describes how a variety of materials (natural, synthesized or waste) can be utilized as admixtures for various purposes.

The handbook is intended for the scientist, technologist and the practitioner. It should be of use as reference material for the engineer, architect, concrete technologist, manufacturer and use of concrete and concrete admixtures. It is also intended for use by cement scientists, material scientists and students of concrete technology.

I would like to express my thanks to Mr. C. B. Crawford, Director of Building Research, National Research Council of Canada, for his permission and encouragement to write the book. Mrs. D. M. Naudain acted as a very efficient secretary in this project and F. Crupi, K. Nadon, J. D. Scott and Doreen Charron were very kind in providing me with excellent drawings and figures for chapters 1, 2, and 4 and my thanks are due them. I am also indebted to Heyden & Son Ltd. and Applied Science Publishers who permitted me to incorporate some material from their publications into chapters 1, 2, and 4.

My deep interest in writing started some 25 years ago and has not yet diminished. This interest could not have been sustained but for the tremendous encouragement, understanding, patience and assistance of my wife Vasundhara.

Ottawa
March 1984

V. S. Ramachandran

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Concrete Science

V. S. Ramachandran and Rolf F. Feldman

1.0 INTRODUCTION

Concrete, a composite material made with cement, aggregates, admixtures and water comprises in quantity the largest of all man-made materials. Although aggregates make up three fourths of the volume of concrete, the active constituent of concrete is cement paste, and the properties and performance of concrete are largely determined by the properties of the cement paste. Admixtures in concrete confer some beneficial effects such as acceleration, retardation, air entrainment, water reduction, plasticity, etc., and these effects are due to their action on cement.

In this chapter, important aspects of the physical, chemical, durability and mechanical characteristics of cement paste and concrete that may be influenced by admixtures are discussed.

2.0 FORMATION OF PORTLAND CEMENT

According to ASTM C-150, portland cement is a hydraulic cement produced by pulverizing clinker consisting essentially of hydraulic calcium silicates, usually containing one or more types of calcium sulfate as an interground addition.

The raw materials for the manufacture of portland cement contain, in suitable proportions, silica, aluminum oxide, calcium oxide and ferric oxide. The source of lime is calcareous ingredients such as limestone or chalk and the source of silica and aluminum oxide are shales, clays or slates. The iron bearing materials are iron and pyrites. Ferric oxide not only serves as a flux but also forms compounds with lime and alumina. The raw materials also contain small amounts of other compounds such as magnesia, alkalis, phosphates, fluorine compounds, zinc oxide and sulfides. The cement clinker is produced by feeding the crushed, ground and screened raw mix into a rotary kiln and heating to a temperature of about 1300–1450°C. Approximately 1100–1400 kcal/g of energy is consumed in the formation of clinker. The sequence of reactions is as follows. At a temperature of about 100°C (drying zone), free water is expelled. In the preheating zone (100–750°C), firmly bound water from the clay is lost. In the calcining zone (750–1000°C), calcium carbonate is dissociated. In the burning zone (1000–1450°C), partial fusion of the mix occurs, with the formation of C_3S, C_2S and clinker. In the cooling zone (1450–1300°C), crystallization of melt occurs with the formation of calcium aluminate and calcium alumino ferrite. After firing the raw materials for the required period, the resultant clinker is cooled and ground with about 4–5% gypsum to a specified degree of fineness. Grinding aids, generally polar compounds are added to facilitate grinding.

3.0 PORTLAND CEMENT: COMPOSITION

The major phases of portland cement are tricalcium silicate ($3CaO{\bullet}SiO_2$), dicalcium silicate ($2CaO{\bullet}SiO_2$), tricalcium aluminate ($3CaO{\bullet}Al_2O_3$) and a ferrite phase of average composition $4CaO{\bullet}Al_2O_3{\bullet}Fe_2O_3$. In a commercial clinker, they do not exist in a pure form. The $3CaO{\bullet}SiO_2$ phase is a solid solution containing Mg and Al and is called alite. In the clinker it consists of monoclinic or trigonal form, whereas synthesized $3CaO{\bullet}SiO_2$ is triclinic. The $2CaO{\bullet}SiO_2$ phase occurs in the β form termed *belite* and contains, in addition to Al and Mg, some K_2O. Four forms α, α', β and γ of C_2S are known although in clinker only the β form with a monoclinic unit cell exists. The ferrite phase, designated C_4AF, is a solid solution of variable composition from C_2F to C_6A_2F. Potential components of this compound are C_2F, C_6AF_2, C_4AF and C_6A_2F.

In some clinkers, small amounts of calcium aluminate of formula NC_8A_3 may also form.

ASTM C-150 describes five major types of portland cement. They are: Normal Type I (when special properties specified for any other type are not required), Moderate Sulfate Resistant or Moderate Heat of Hydration—Type II, High Early Strength—Type III, Low Heat—Type IV, and Sulfate Resisting—Type V. The general composition, fineness and compressive strength characteristics of these cements are shown in Table 1.[1]

Table 1. Compound Composition, Fineness, and Compressive Strength Characteristics of Some Commercial U.S. Cements

ASTM Type	ASTM Designation	composition				fineness cm^2/g	compressive strength % of type I cement*		
		C_3S	C_2S	C_3A	C_4AF		1 day	2 day	28 days
I	General purpose	50	24	11	8	1800	100	100	100
II	Moderate sulfate resistant-moderate heat of hydration	42	33	5	13	1800	75	85	90
III	High early strength	60	13	9	8	2600	190	120	110
IV	Low heat	26	50	5	12	1900	55	55	75
V	Sulfate resisting	40	40	4	9	1900	65	75	85

* All cements attain almost the same strength at 90 days.

Portland cement may be blended with other ingredients to form blended hydraulic cements. ASTM C-595 covers five kinds of blended hydraulic cements. The portland blast furnace slag cement consists of an intimately ground mixture of portland cement clinker and granulated blast furnace slag or an intimate and uniform blend of portland cement and fine granulated blast furnace slag in which the slag constituent is within specified limits. The portland-pozzolan cement consists of an intimate and uniform blend of portland cement or portland blast furnace slag cement and fine pozzolan. The slag cement consists mostly of granulated blast furnace slag and hydrated lime. The others are pozzolan-modified portland cement (pozzolan $< 15\%$) and slag-modified portland cement (slag $< 25\%$).

4.0 INDIVIDUAL CEMENT COMPOUNDS

4.1 Tricalcium Silicate

Hydration. A knowledge of the hydration behavior of individual cement compounds and their mixtures forms a basis for interpreting the complex reactions that occur when portland cement is hydrated under various conditions.

Tricalcium silicate and dicalcium silicate together make up 75–80% of portland cement (Table 1). In the presence of a limited amount of water, the reaction of C_3S with water is represented as follows:

Eq. (1) $3CaO{\bullet}SiO_2 + xH_2O \rightarrow YCaO{\bullet}SiO_2{\bullet}(x+y\text{-}3)H_2O + (3\text{-}y)Ca(OH)_2$

or typically

Eq. (2) $2[3CaO{\bullet}SiO_2] + 7H_2O \rightarrow 3CaO{\bullet}2SiO_2{\bullet}4H_2O + 3Ca(OH)_2$

The above chemical equation is somewhat approximate because it is not easy to estimate the composition of C-S-H (the C/S and S/H ratio) and there are also problems associated with the determination of $Ca(OH)_2$. In a fully hydrated cement or C_3S paste, about 60–70% of the solid comprises C-S-H. The C-S-H phase is poorly crystallized containing particles of colloidal size and gives only two very weak diffuse peaks in XRD. The degree of hydration of C_3S can be measured by determining C_3S or $Ca(OH)_2$ by XRD, the non-evaporable water by ignition, or $Ca(OH)_2$ by thermal or chemical methods. Each of these methods has limitations. The $Ca(OH)_2$ estimated by XRD differs from that determined by chemical analysis. For example, Pressler et al.[2] found a value of 22% $Ca(OH)_2$ by XRD for portland cement pastes. The chemical extraction method gave values 3–4% higher and this difference was attributed to the presence of amorphous $Ca(OH)_2$. Lehmann et al.,[3] on the other hand, reported that the extraction method yielded 30–90% $Ca(OH)_2$ higher than that by XRD. Thermogravimetric analysis gave identical values to those obtained by x-ray. Recently the technique of differential thermal analysis was applied by Ramachandran[4] and Midgley[5] for estimating $Ca(OH)_2$ in hydrating C_3S.

Figure 1 compares the relative amounts of $Ca(OH)_2$ formed at different periods during the hydration of C_3S using DTA and chemical methods.[4] Although the general trends are similar, the values resulting from the use of chemical analysis are higher than those from the thermal method. This may be explained by the attack of the C-S-H phase by the solvents used in the chemical extraction method. Hence it becomes obvious that the determination of the composition of C-S-H which is based on the estimation of C_3S and $Ca(OH)_2$ has certain limitations. The composition of the C-S-H phase may be modified by admixtures such as calcium chloride and triethanolamine.

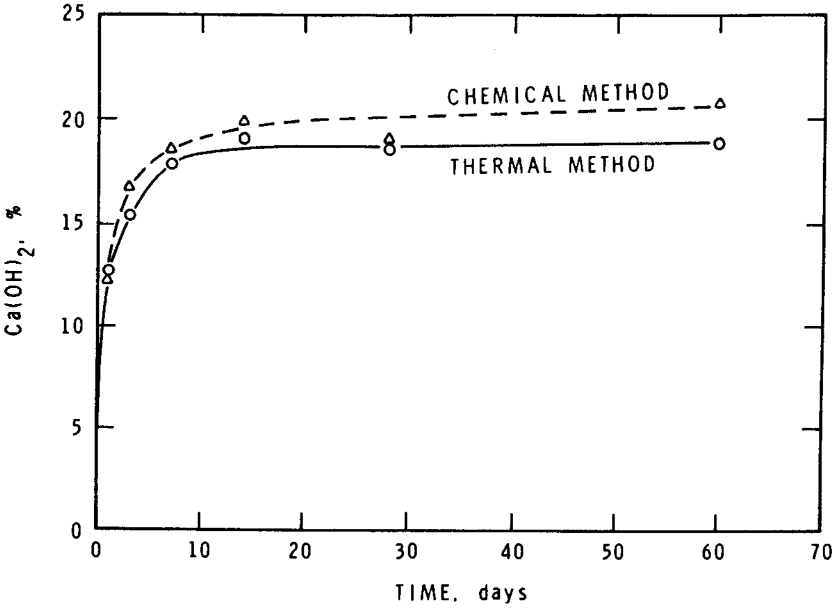


Figure 1. Amounts of $Ca(OH)_2$ formed in the hydration of C_3S.

The direct methods of determining C/S ratios are based on electron optical methods such as electron microprobe or other attachments, or by electron spectroscopy (ESCA). Although several values are reported, the usual value for C/S ratio after a few hours of hydration of C_3S is about 1.4–1.6.[6]

There are problems associated with the determination of H_2O chemically associated with C-S-H. It is difficult to differentiate this water from that present in pores. The stoichiometry of C-S-H is determined by assuming that little or no absorbed water remains in the sample at the d-dry condition (the vapor pressure of water at the sublimation temperature of solid CO_2, i.e., -78°C). In a recent investigation it has been shown that higher hydrates may exist at humidities above the d-dry state.[7] It has been proposed that drying to 11% RH is a good base for studying the stoichiometry of calcium silicate hydrate. At this condition, the estimate of absorbed water can be made with some confidence. This does not mean that higher hydrates do not exist above 11% RH. Feldman and Ramachandran[8] estimated that the bottled hydrated C-S-H equilibrated to 11% RH (approached from 100% RH) had a composition 3.28 CaO:2SiO_2:3.92 H_2O.

Hydration Mechanism. The mechanism of hydration of individual cement components and that of cement itself has been a subject of much discussion and disagreement. In the earliest theory, Le Chatelier explained the cementing action by dissolution of anhydrous compounds followed by the precipitation of interlocking crystalline hydrated compounds. Michaelis considered that cohesion resulted from the formation and subsequent desiccation of the gel.[19] In recent years the topochemical or solid state mechanism has been proposed.

In spite of a large amount of work, even the mechanism of hydration of C_3S, the major phase of cement, is not clear. Any mechanism proposed to explain the hydrating behavior of C_3S should take into account the following steps through which the hydration proceeds. Five steps can be discerned from the isothermal conduction calorimetric studies (Fig. 2). In the first stage, as soon as C_3S comes into contact with water, there is a rapid evolution of heat and this ceases within 15–20 mins. This stage is called pre-induction period. In the second stage, the reaction rate is very slow and is known as dormant or induction period. This may extend for a few hours. At this stage the cement remains plastic and is workable. In the third stage the reaction occurs actively and accelerates with time, reaching a maximum rate at the end of this accelerating period. Initial set occurs at about the time when the rate of reaction becomes vigorous. The final set occurs before the end of the third stage. In the fourth stage there is slow deceleration. An understanding of the first two stages of the reaction has a very important bearing on the subsequent hydration behavior of the sample. The admixtures can influence these steps. The retarders such as sucrose, phosphonic acids, calcium gluconate and sodium heptonate extend the induction period and decrease the amplitude of the acceleration peak.

The processes that occur during the five stages are as follows. In the first stage, as soon as C_3S comes into contact with water it releases calcium and hydroxyl ions into the solution. In the second stage, the dissolution continues and pH reaches a high value of 12.5. Not much silica dissolution occurs at this stage. After a certain critical value of calcium and hydroxide ions is reached, there is a rapid crystallization of CH and C-S-H followed by a rapid reaction. In the fourth stage, there is a continuous formation of hydration products. At the final stage, there is only a slow formation of products and, at this stage, the reaction is diffusion controlled.

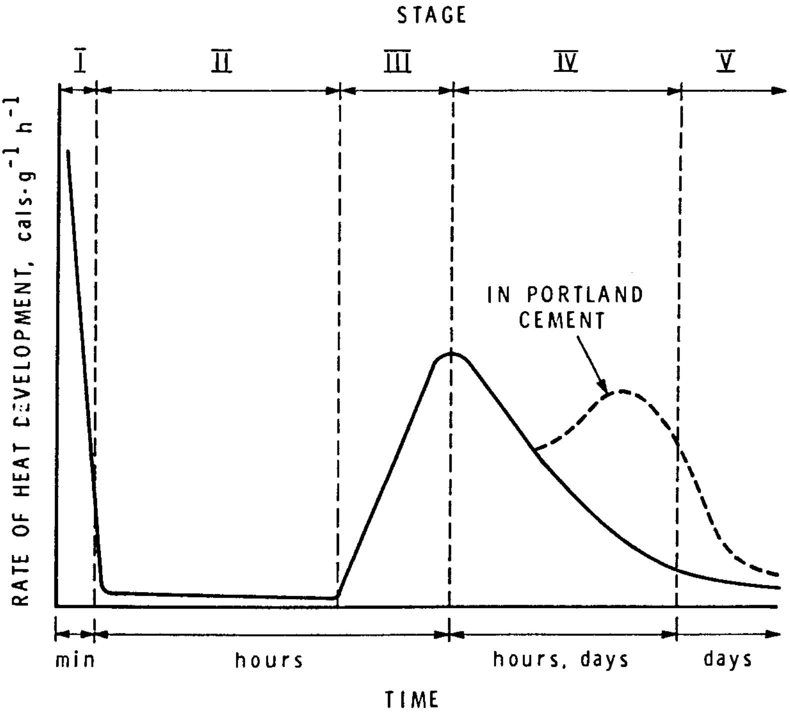


Figure 2. Rate of heat development during the hydration of tricalcium silicate and portland cement.

It is generally thought that initially a reaction product forms on the C_3S surface that slows down the reaction. The renewed reaction is caused by the disruption of the surface layer. According to Stein and Stevels,[20] the first hydrate has a high C/S ratio of about 3, and it transforms into a lower C/S ratio of about 0.8–1.5 through loss of calcium ions into solution.

The second product has the property of allowing ionic species to pass through it, thus enabling a rapid reaction. The conversion of the first to the second hydrate is thought to be a nucleation and growth process. Although this theory is consistent with many observations, there are others which do not conform to this theory. They are: the C/S ratio of the product is lower than what has been reported, the protective layer may not be continuous, the product is a delicate film that easily peels away from the surface and the early dissolution may or may not be congruent.

The end of the induction period has been explained by the delayed nucleation of CH. It is generally observed that the rapid growth of crystalline CH and the fall of calcium ions in solution occur at the end of the induction period. This suggests that the precipitation of CH is related to the start of the acceleration stage. If precipitation of CH triggers the reaction, then additional Ca ions should accelerate the reaction, unless it is poisoned. Addition of saturated lime is known to retard the reaction. Also it does not explain the accelerated formation of C-S-H. Tadros et al.[21] found the zeta potential of the hydrating C_3S to be positive, indicating the possibility of the chemisorption of Ca ions on the surface resulting in a layer that could serve as a barrier between C_3S and water. During the precipitation of $Ca(OH)_2$, it is thought that Ca^{2+} from the solution is removed (which will in turn trigger the removal of Ca^{2+} from the barrier) and the reaction is accelerated.

There are other mechanisms based on the delayed nucleation of C-S-H to explain the end of this induction period. One of them suggests that the stabilization action of C_3S surface by a thin layer of water is removed when a high Ca^{2+} concentration in the solution causes the precipitation of C-S-H nuclei. According to Maycock et al.,[22] the solid state diffusion within the C_3S grain controls the length of the induction period. The defects enhance diffusion and thereby promote the C-S-H nucleation. According to Fierens and Verhaegen,[23] the chemisorption of H_2O and dissolution of some C_3S occur in the induction period. The end of the induction period, according to them, corresponds to the growth of a critical size of C-S-H nuclei.

There are other theories which have been proposed to fit most of the observations. Although they appear to be separate theories, they have many common features. They have been discussed by Pratt and Jennings.[24] A detailed discussion of the mechanisms of hydration of cement and C_3S has been presented by Gartner and Gaidis.[24a]

The hydration of C_2S proceeds in a similar way to that of C_3S but is much slower. As the amount of heat liberated by C_2S is very low compared to that of C_3S, the conduction calorimetric curve will not show the well defined peaks as in Fig. 2. Accelerators will enhance the reaction rate of C_2S. The reaction of C_2S and water has been studied much less than that involving C_3S.

4.2 Dicalcium Silicate

Just as in the hydration process of C_3S, there are uncertainties involved in determining the stoichiometry of the C-S-H phase found in the hydration of C_2S. The hydration of dicalcium silicate phase can be represented by the equation.

Eq. (3) $2\,[2CaO{\bullet}SiO_2] + 5H_2O \rightarrow 3CaO{\bullet}2SiO_2{\bullet}4H_2O + Ca(OH)_2$

The amount of $Ca(OH)_2$ formed in this reaction is less than that produced in the hydration of C_3S. The dicalcium silicate phase hydrates much more slowly than the tricalcium silicate phase.

Figure 3 compares the rates of hydration of C_3S and C_2S. The absolute rates differ from one sample to the other; for example, C_3S is much more reactive than C_2S. Several explanations have been offered to interpret the increased reactivity of C_3S. Proposed explanations include: the coordination number of Ca is higher than 6, coordination of Ca is irregular, holes exist in the crystal lattice and differences occur in the position of the Fermi level. Some preliminary work has been done to test the relative reactivities of Ca^{2+} in CaO, $Ca(OH)_2$, C_3S, C_2S, and by mixing each of them with known amounts of $AgNO_3$.[9] By heating them it was found that the reaction of $AgNO_3$ with CaO, $Ca(OH)_2$ and hydrated C_3S was stoichiometric with respect to Ca. Only 27% Ca present in C_3S and 6% Ca from C_2S reacted with $AgNO_3$. Possibly C_3S and C_2S structures are such that some Ca^{2+} ions are relatively more reactive owing to structural imperfections. There is evidence that if 1 mol of labeled Ca is reacted with C_2S to form C_3S, the hydration of C_3S would show that the initial reaction product contains mainly the labelled Ca ions. Further work is necessary before definite conclusions can be drawn.

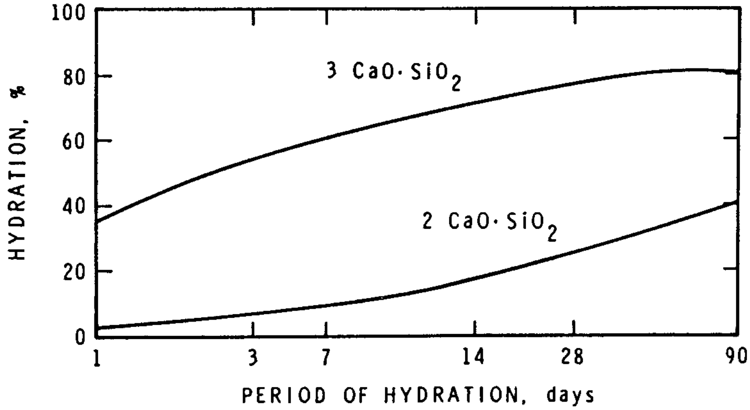


Figure 3. The relative rates of hydration of $3CaO{\bullet}SiO_2$ and $2CaO{\bullet}SiO_2$.

The rate of strength development of individual cement compounds was determined by Bogue and Lerch in 1934.[9a] The comparison of reactivities and strength development of these compounds was not based on adequate control of certain parameters such as particle size distribution, water-solid ratio, specimen geometry, method of estimation of the degree of hydration, etc. Beaudoin and Ramachandran[9b] have reassessed the strength development in cement mineral pastes, both in terms of time and degree of hydration. Figure 4 compares the results of Bogue and Lerch with those of Beaudoin and Ramachandran.[9b] Significant differences in the relative values of strengths developed by various phases were found. At ten days of hydration, the strength values were ranked as follows by Beaudoin and Ramachandran: $C_4AF > C_3S > C_2S > C_3A$. At fourteen days, the relative values were in the order $C_3S > C_4AF > C_2S > C_3A$. The Bogue-Lerch strength values both at ten and fourteen days were: $C_3S > C_2S > C_3A > C_4AF$. At 1 year, the corresponding values were $C_3S > C_2S > C_4AF > C_3A$ (Beaudoin-Ramachandran) and $C_3S = C_2S > C_3A > C_4AF$ (Bogue-Lerch). Beaudoin and Ramachandran found that compressive strength vs porosity curves on a semilog plot showed a linear relationship for all pastes (Fig. 5). The lines seem to merge to the same value of strength of 500 MPa at zero porosity. This would indicate that all the pastes have the same inherent strength. Comparison of strengths as a function of the degree of hydration revealed that, at a hydration degree of 70–100%, the strength was in the decreasing order $C_3S > C_4AF > C_3A$.

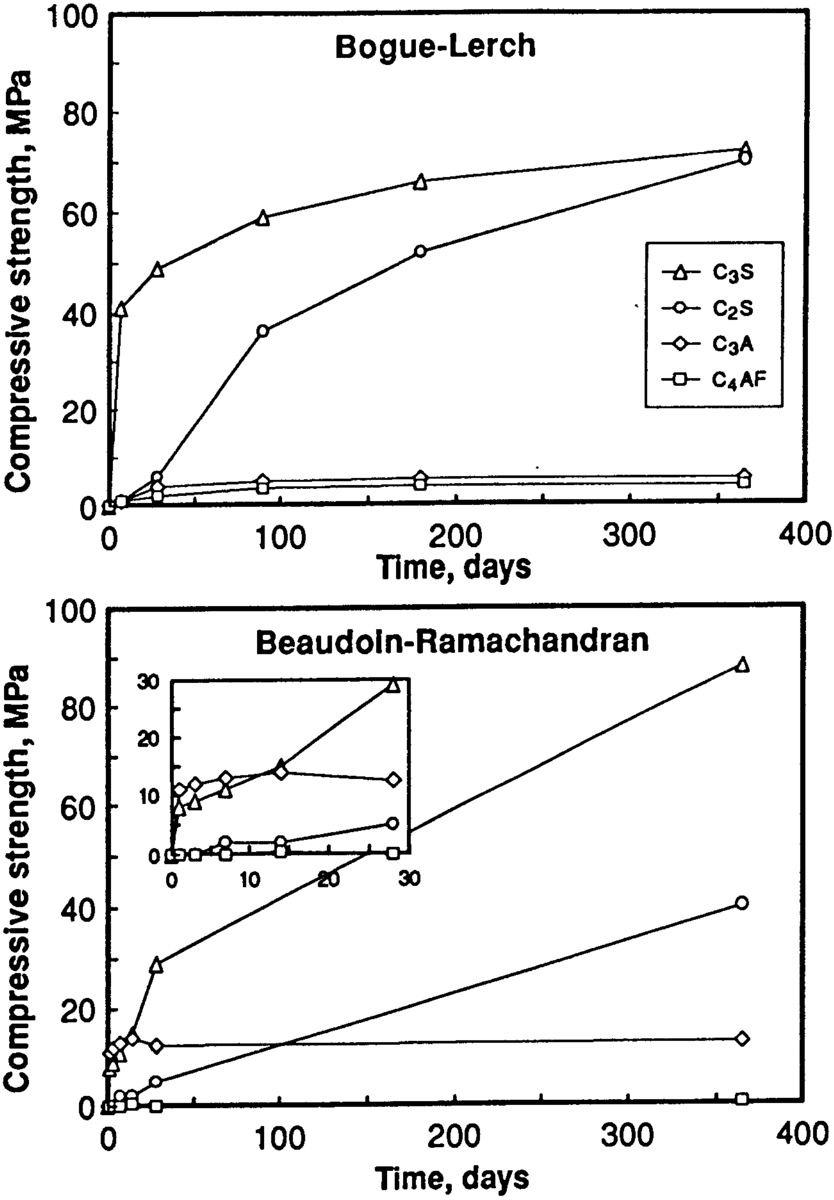


Figure 4. Compressive strength of hydrated cement compounds. *(Reprinted from* Cement Concrete Res., *22:689-694, J. J. Beaudoin and V. S. Ramachandran, © 1992, with kind permission from Elsevier Science Ltd, The Boulevard, Langford Lane, Kidlington 0X51GB.)*

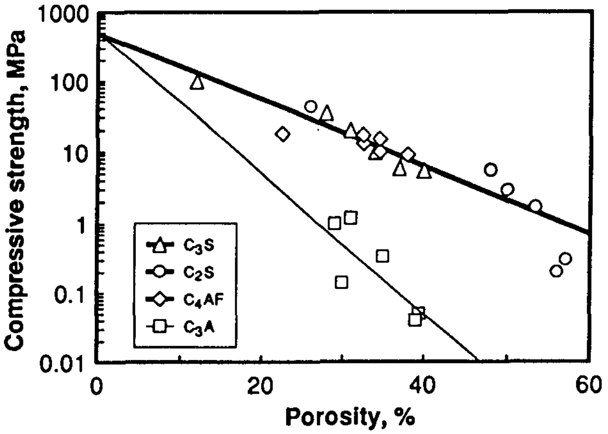


Figure 5. Porosity vs strength relationships for cement compounds. *(Reprinted from* Cement Concrete Res., *22:689-694, J. J. Beaudoin and V. S. Ramachandran, © 1992, with kind permission from Elsevier Science Ltd, The Boulevard, Langford Lane, Kidlington 0X51GB.)*

4.3 Tricalcium Aluminate

The average C_3A content in portland cement is about 4–11% but it influences significantly the early reactions. The phenomenon of *flash set,* the formation of various calcium aluminate hydrates, and calcium carbo- and sulfoaluminates, involves the reactions of C_3A. Higher amounts of C_3A in portland cement may pose durability problems. For example, a cement which is exposed to sulfate solutions should not contain more than 5% C_3A.

Tricalcium aluminate reacts with water to form C_2AH_8 and C_4AH_{13} (hexagonal phases). These products are thermodynamically unstable so that, without stabilizers or admixtures, they convert to the C_3AH_6 phase (cubic phase). The relevant equations for these reactions are:

Eq. (4) $2C_3A + 21H \rightarrow C_4AH_{13} + C_2AH_8$

Eq. (5) $C_4AH_{13} + C_2AH_8 \rightarrow 2C_3AH_6 + 9H$

In saturated $Ca(OH)_2$ solutions, C_2AH_8 reacts with $Ca(OH)_2$ to form C_4AH_{13} or C_3AH_6 depending on the condition of formation. The cubic form (C_3AH_6) can also form directly by hydrating C_3A at temperatures of 80°C or above.[10][11]

Eq. (6) $C_3A + 6H \rightarrow C_3AH_6$

The C_3A pastes exhibit lower strengths than do the silicate phases under normal conditions of hydration. This is attributed to the formation of the cubic phase. Under certain conditions of hydration of C_3A, i.e., at lower water-solid ratios and high temperatures, the direct formation of C_3AH_6 (resulting in the direct bond formation between the particles) can improve the strength of the body substantially.

In portland cement, the hydration of the C_3A phase is controlled by the addition of gypsum. The flash set is thus avoided. The C_3A phase reacts with gypsum in a few minutes to form ettringite as follows:

Eq. (7) $C_3A + 3C\overline{S}H_2 + 26H \rightarrow C_3A{\bullet}3C\overline{S}H_{32}$

After all gypsum is converted to ettringite, the excess C_3A will react with ettringite to form the low sulfoaluminate hydrate.

Eq. (8) $C_3A{\bullet}3C\overline{S}H_{32} + 2C_3A + 4H \rightarrow 3[C_3A{\bullet}C\overline{S}H_{12}]$

Gypsum is a more effective retarder than lime for C_3A hydration and together they are even more effective than either of them. An isothermal conduction calorimetric curve for the hydration of C_3A and gypsum mixture will have a similar shape to that of the C_3S phase (Fig. 2). The time of the appearance of the peaks and their magnitude are, however, not the same. The common explanation of the retardation of C_3A hydration by gypsum is that a fine-grained ettringite forming on C_3A retards the hydration. This layer thickens in the induction period and bursts and reforms during this period. When all sulfate is consumed, the ettringite reacts with C_3A, forming monosulfoaluminate hydrate. This conversion will occur in cements within 12–36 hrs with an exothermic peak. Addition of some admixtures may accelerate or delay this conversion. It has also been suggested that ettringite may not per se influence the induction period[25][26] and that adsorption of sulfate ions on the positively charged C_3A retards the hydration. It has also been suggested that osmotic pressure may be involved in the rupture of ettringite needles. This theory is based on the observation of hollow needles in the C_3A-gypsum-H_2O system. Rupture of ettringite allows transfer of Al ions into the aqueous phase with the quick formation of hollow needles through which more Al^{3+} can travel.[24]

4.4 The Ferrite Phase

The ferrite phase constitutes about 8–13% of an average portland cement. In portland cement, the ferrite phase may have a variable composition that can be expressed as $C_2(A_nF_{1-n})$ where $0 < n < 0.7$.

Of the cement minerals, the ferrite phase has received much less attention than others with regard to its hydration and physico-mechanical characteristics. This may partly be ascribed to the assumption that the ferrite phase and the C_3A phase behave in a similar manner. There is evidence, however, that significant differences exist.

The C_4AF phase is known to yield the same sequence of products as C_3A. The reactions are, however, slower. In the presence of water, C_4AF reacts as follows:

Eq. (9) $$C_4AF + 16H \rightarrow 2C_2(A,F)H_8$$

Eq. (10) $$C_4AF + 16H \rightarrow C_4(A,F)H_{13} + (A,F)H_3$$

Amorphous hydroxides of Fe and Al form in the reaction of C_4AF. The thermodynamically stable product is $C_3(A,F)H_6$ and this is the conversion product of the hexagonal hydrates. Seldom does the formation of these hydrates cause flash set in cements.

Hydration of C_4AF at low water-solid ratios and high temperatures may enhance the direct formation of the cubic phase.[12] Microhardness measurement results show that at a w/s = 0.13, the samples hydrated at 23 and 80°C exhibit microhardness values to 87.4 and 177 kg/mm^2 respectively. The higher strengths at higher temperatures may be attributed to the direct formation of the cubic phase on the original sites of C_4AF. This results in a closely welded, continuous network with enhanced mechanical strength.

In cements, C_4AF reacts much slower than C_3A in the presence of gypsum. In other words, gypsum retards the hydration of C_4AF more efficiently than it does C_3A. The rate of hydration depends on the composition of the ferrite phase: that containing higher amounts of Fe exhibits lower rates of hydration. The reaction of C_4AF with gypsum proceeds as follows:[13]

Eq. (11) $$3C_4AF + 12C\overline{S}H_2 + 110H \rightarrow 4[C_6(A,F)\overline{S}H_{32}] + 2(A,F)H_3$$

The low sulfoaluminate form can form by the reaction of excess C_4AF with the high sulfoaluminate form.

Eq. (12) $3C_4AF + 2[C_6(A,F)\bar{S}H_{32}] \rightarrow 6[C_4A,F)\bar{S}H_{12}] + 2(A,F)H_3$

At low water-solid ratios and high temperatures, the low sulfoaluminate may form directly.[14]

The above equations involve formation of hydroxides of Al and Fe because of insufficient lime in C_4AF. In these products, F can substitute for A. The ratio of A to F need not be the same as in the starting material. Although cements high in C_3A are prone to sulfate attack, those with high C_4AF are not. In high C_4AF cements, ettringite may not form from the low sulfoaluminate, possibly because of the substitution of iron in the monosulfate. It is also possible that amorphous $(A,F)_3$ prevents such a reaction. Another possibility is that the sulfoaluminate phase that forms is produced in such a way that it does not create crystalline growth pressures.

5.0 PORTLAND CEMENT

Although hydration studies of the pure cement compounds are very useful in following the hydration processes of portland cement itself, they cannot be directly applied to cements because of complex interactions. In portland cement, the compounds do not exist in a pure form but are solid solutions containing Al, Mg, Na, etc. The rate of hydration of alites containing different amounts of Al, Mg, or Fe has shown that, at the same degree of hydration, Fe-alite shows the greatest strength. There is evidence the C-S-H formed in different alites is not the same.[15] The hydration of C_3A, C_4AF and C_2S in cement are affected because of changes in the amounts of Ca^{2+} and OH^- in the hydrating solution. The reactivity of C_4AF can be influenced by the amount of SO_4^{2-} ions consumed by C_3A. Some SO_4^{2-} ions may be depleted by being absorbed by the C-S-H phase. Gypsum is also known to affect the rate of hydration of calcium silicates. Significant amounts of Al and Fe are incorporated into C-S-H structure. The presence of alkalis in portland cement also has an influence on the hydration of the individual phases.

As a general rule, the rate of hydration in the first few days of cement compounds in cements proceeds in the order $C_3A > C_3S > C_4AF > C_2S$. The rate of hydration of the compounds depends on the crystal size, imperfections, particle size, particle size distribution, the rate of cooling, surface area, the presence of admixtures, the temperature, etc.

In a mature hydrated portland cement, the products formed are C-S-H gel, $Ca(OH)_2$, ettringite (AFt phases), monosulfate (Afm phases), hydrogarnet phases and possibly amorphous phases high in Al^{3+} and SO_4 ions.[6]

The C-S-H phase in cement paste is amorphous or semicrystalline calcium silicate hydrate and the hyphens denote that the gel does not necessarily consist of 1:1 molar $CaO:SiO_2$. The C-S-H of cement pastes gives powder patterns very similar to that of C_3S pastes. The composition of C-S-H (in terms of C/S ratio) is variable depending on the time of hydration. At one day the C/S ratio is about 2.0 and becomes 1.4–1.6 after several years. The C-S-H can take up substantial amounts of Al^{3+}, Fe^{3+} and SO_4^{2-} ions.

Recent investigations have shown that both in C_3S and portland cement pastes, the monomer that is present in the C_3S and C_2S compounds (SiO_4^{4-} tetrahedra) polymerizes to form dimers, and larger silicate ions as hydration progresses. The gas liquid chromatographic analysis of the trimethyl silylation derivatives has shown that anions with 3 or 4 Si atoms are absent. The polymer content with 5 or more Si atoms increases as the hydration proceeds and the amount of dimer decreases. In C_3S pastes, the disappearance of monomer results in the formation of polymers. In cement pastes, even after the disappearance of all C_3S and C_2S some monomer is detected possibly because of the modification of the anion structure of C-S-H through replacement of some Si atoms by Al, Fe, or S.[6] Admixtures can influence the rate at which the polymerization proceeds in portland cement and C_3S pastes.

The minimum water-cement ratio for attaining complete hydration of cement has been variously given from 0.35 to 0.40, although complete hydration has been reported to have been achieved at a water-cement ratio of 0.22.[15a]

In a fully hydrated portland cement, $Ca(OH)_2$ constitutes about 20–25% of the solid content. The crystals are platy or prismatic and cleave readily. They may be intimately intergrown with C-S-H. The density of $Ca(OH)_2$ is 2.24 g/cm^3. The crystalline $Ca(OH)_2$ gives sharp XRD patterns, shows endothermal peaks in DTA and weight losses in TGA. The morphology of $Ca(OH)_2$ may vary and form as equidimensional crystals, large flat platy crystals, large thin elongated crystals, or a combination of them. Some admixtures and temperature of hydration can modify the morphology of $Ca(OH)_2$. According to some investigators both crystalline and amorphous $Ca(OH)_2$ are formed in portland cement pastes.

The ettringite group, also called AFt phase in cement paste, stands for Al-Fe-tri (tri = three moles of CS) of the formula $C_3A{\bullet}3CS{\bullet}H_{32}$ in which Al can be replaced by Fe to some extent. The AFt phase forms in the first few hours (from C_3A and C_4AF) and plays a role in setting. After a few days of hydration only a little amount of it may remain in cement pastes. It appears as stumpy rods in SEMs and the length does not normally exceed a few micrometers. The principle substitutions that exist in AFt phase are Fe^{3+} and Si^{4+} for Al^{3+} and various anions such as OH-, CO_3^{2-} and silicates for SO_4^{2-}.

The monosulfate group also known as the AFm phase is represented by the formula $C_4A\overline{S}H_{12}$ or $C_3A{\bullet}C\overline{S}{\bullet}H_{12}$. AFm stands for Al-Fe-mono, in which one mole of $C\overline{S}$ is present. In portland cement, this phase forms after the AFt phase disappears. This phase may constitute about 10% of the solid phase in a mature cement paste. In SEMs this phase has a hexagonal morphology resembling that of $Ca(OH)_2$ and the crystals are of sub-micrometer thickness. The principle ionic substitutions in the AFm phase are Fe^{3+} for Al^{3+}, and OH^-, CO_3^{2-}, Cl^-, etc., for SO_4^{2-}. The density of this phase is 2.02 g/ml. The amount of crystalline hydrogarnet present in cement paste is less than 3%.[16] It is of type $Ca_3Al_2(OH)_{12}$ in which part of Al^{3+} is replaced by Fe^{3+} and $4OH^-$ by SiO_4^{4-} [e.g., $C_3(A_{0.5}F_{0.5})SH_4$]. It may be present in small amounts in mature cement pastes and is also formed at higher temperatures. The crystal structure of this phase is related to C_3AS_3 (garnet). The density of $C_6AFS_2H_8$ is 3.042g/ml. Hydrogarnet is decomposed by CO_2 forming $CaCO_3$ as a product.[17]

It is the opinion of some workers that the lowest sulfate form of calcium sulfohydroxy aluminate hydrate, a crystalline solid solution phase in the system $CaO\text{-}Al_2O_3\text{-}CaSO_4\text{-}H_2O$ is also formed in cement pastes.[18]

Table 2 shows a list of some important compounds of interest in cement science.

The mechanisms that have already been described for pure cement compounds form a basis for a study of the hydration mechanism of portland cement. The conduction calorimetric curves of C_3S and portland cement are similar except portland cement may yield a third peak for the formation of monosulfate hydrate (Fig. 2). The detailed influence of C_3A and C_4AF on the hydration of C_3S and C_2S in cement is yet to be worked out. The delayed nucleation models and the protective layer models, taking into account the possible interactions, have been reviewed.[24] Although the initial process is not clear for C_3S (in cements), it appears that C_3A hydration products form through solution and topochemical processes.

Table 2. Some Compounds Present in Cement and Hydrated Cement

No	Compound	Formula	Cement Nomenclature	Remarks
1	Calcium oxide	CaO	C	Present in clinker in small amounts.
2	Periclase	MgO	M	Present in clinker. In excessive amounts causes unsoundness.
3	Gypsum (calcium sulfate dihydrate)	$CaSO_4 \cdot 2H_2O$	$C\bar{S}_2$	Interground with cement clinker. Retards set by reacting with C_3A and prevents flash set.
4	Bassanite (calcium sulfate hemihydrate)	$CaSO_4 \cdot 1/2H_2O$	$C\bar{S}H_{0.5}$	This may form as a dehydration product from gypsum during grinding of gypsum-clinker mixtures. Causes false set.
5	Arcanite (potassium sulfate)	K_2SO_4	$K\bar{S}$	May be present in some clinkers.
6	Aphthiotolite (sodium potassium sulfate)	$(NaK)_2SO_4$	$(NK\bar{S}$	May be present in flue dust and kiln deposits
7	Potassium Calcium sulfate	$K_2Ca_2(SO_4)_3$	$(NK)\bar{S}_3$	Present in clinker and flue deposits.
8	Tricalcium Silicate	Ca_3SiO_5	C_3S	Is a synthesized compound
9	Alite	Substituted Ca_3SiO_5	C_3S (substituted)	Important constituent in portland cement. Contains Fe, Al, Mg, Cr and Zn solid solution. Hydrates to give a strong body in cements.
10	Larnite (beta dicalcium silicate)	β Ca_2SiO_4	β C_2S	Unless stabilized transforms to γ C_2S causing dusting.
11	Belite (substituted dicalcium silicate)	Ca_2SiO_4 (substituted)	C_2S (substituted)	Present in clinker. Ca is substituted by Mg, Na, K, Cr and Mn. The SiO_4 may be substituted by PO_4 or SO_4.

Cont'd

Table 2. (Cont'd)

12	Tricalcium aluminate	$Ca_3Al_2O_6$	C_3A	A constituent in portland cement. Hydrates faster than C_3S, C_2S or C_4AF.
13	Tricalcium (sodium aluminate)	$NaCa_4Al_3O_9$	NC_8A_3	Present in small amounts in some clinkers.
14	Calcium alumino-ferrite solid solution series	$Ca_4Fe_4O_{10}$ to $Ca_4FeAl_3O_{10}$	$Ca_2(F_{1-p}Al_p)_2$ $(0<p<0.7)$	A phase in portland cement composition from $p \approx 0.33$ to $p \approx 0.67$.
15	Portlandite or calcium hydroxide	$Ca(OH)_2$	CH	Is a hydrated product of cement, C_3S and C_2S. Small amounts formed by hydration of free CaO in the clinker
16	Brucite (magnesium hydroxide)	$Mg(OH)_2$	MH	Free MgO in clinker when autoclaved is hydrated to $Mg(OH)_2$. It may take years for hydration under normal exposure conditions.
17	Calcite (calcium carbonate)	$CaCO_3$	$C\bar{C}$	Raw material in the manufacture of portland cement . Carbonation of $Ca(OH)_2$ and C-S-H also produces this compound.
18	Calcium Silicate Hydrate Gel	$XCaO \cdot SiO_2 \cdot YH_2O$	CSH	Is present in a substituted form in hydrated portland cement. X and Y vary depending on the conditions of hydration
19	Tricalcium aluminate 6-hydrate	$Ca_3Al_2(OH)_{12}$	C_3AH_6	Stable hydration product of C_3A.
20	Tetracalcium aluminate 19-hydrate	$4CaO \cdot Al_2O_3 \cdot 19 H_2O$	C_4AH_{19}	Metastable product of hydration of C_3A occasionally found in cement. The lower hydrate product is C_4AH_{13}oC_4FH_{13}, an iron analog.

Cont'd

Table 2. (Cont'd)

21	Dicalcium aluminate 8-hydrate	$2CaO \cdot Al_2O_3 \cdot 8H_2O$	C_2AH_8	Hexagonal hydrate (metastable) formed in the hydration of C_3A.
22	Ettringite	$[Ca_6\{AlOH)_6\}_2 \cdot 24H_2O](SO_4)_3 \cdot 2H_2O$	$C_6A\bar{S}H_{32}$	The reaction product of C_3A with gypsum formed initially. Iron analog is also known.
23	Tetracalcium aluminate monosulfate 12 hydrate	$[Ca_2Al(OH)_6]_2(SO_4) \cdot 6H_2O$	C_4ASH_{12}	Present in hydrated cement. Also forms a solid solution with C_4AH_{13}. Iron analogue is known.

6.0 CEMENT PASTE

6.1 Setting

The stiffening times of cement paste or mortar fraction are determined by setting times. The setting characteristics are assessed by *initial set* and *final set*. When the concrete attains the stage of initial set it can no longer be properly handled and placed. The final set corresponds to the stage at which hardening begins. At the time of the initial set the concrete will have exhibited a measurable loss of slump. Admixtures may influence the setting times. The *retarders* increase the setting times and *accelerators* decrease them.

At the time of initial set of cement paste, the hydration of C_3S will have just started. According to some investigators, the recrystallization of ettringite is the major contributing factor to the initial set. The final set generally occurs before the paste shows the maximum rate of heat development, i.e., before the end of the third stage in conduction calorimetry.

Concrete also exhibits false or flash set. When stiffening occurs due to the presence of partially dehydrated gypsum, false set is noticed. *Workability* is restored by remixing. False set may also be caused by excessive formation of ettringite, especially in the presence of some retarders and an admixture such as triethanolamine. The formation of syngenite (KCS_2H) is reported to cause false set in come instances.

The setting time of cement can be determined by Gillmore (ASTM C 266) or the Vicat apparatus (ASTM 191). In the Gillmore method, a pat of cement paste 3 inches diameter and 1/2 inch thickness is formed on a glass plate and is subjected to indentation by the needle. For the initial set, a needle weighing 1/4 lb with 1/12 inch diameter is used while for the final set the corresponding figures are 1 lb. and 1/24 inch. The initial set occurs when the pat will bear without appreciable indentation, the initial Gillmore needle. Similarly the final set is determined by the final Gillmore needle. All standard ASTM cements should conform to an initial setting time not less than 60 mins and final setting time of not more than 10 hrs. The corresponding times using the Vicat needle are 45 mins and 8 hrs.

The Vicat apparatus is similar to the test method described above except that there are slight differences in the needle weight and diameter, and the dimensions of the cement paste. In this method, the initial setting time occurs when a penetration of 25 mm is obtained. At the time of final set the needle should not sink visibly into the paste. The Canadian Standard method CSA CAN 3-A5 specifies only the initial setting times. The Vicat apparatus is also specified by British Standard BB12.

6.2 Microstructure

Many of the properties of the cement paste are determined by its chemical nature and microstructure. Microstructure constitutes the nature of the solid body and that of the non-solid portion, that is, porous structure. Microstructural features depend on many factors such as the physical and chemical nature of the cement, type and the amount of admixture added to it, temperature and period of hydration, and the initial w/c ratio. The solid phase study includes examination of the morphology (shape and size), bonding of the surfaces, surface area, and density. Porosity, pore shape, and pore size distribution analysis is necessary for investigating the non-solid phase. Many of the properties are interdependent, and no one property can adequately explain the physico-mechanical characteristics of cement paste.

A study of the morphology of the cement paste involves observation of the form and size of the individual particles, particularly through the high resolution electron-microscopes. The most powerful techniques that have been used for this purpose are Transmission Electron Microscopy, Scanning Electron Microscopy, High Voltage Transmission Electron Microscope using environmental cells, Scanning Transmission Electron Microscope (STEM) of ion-beam thinned sections, and High Resolution SEM using STEM instruments in reflection mode.

Attempts have been made to explain the strengths of pastes by a morphological examination, but several exceptions have been found.[29] It is beginning to be recognized that comparison of micromorphological results by different workers has an inherent limitation because of the small number of micrographs usually published and the correspondingly small area of these micrographs, which might not be representative of the structure. Sometimes, micrographs are selected for inclusion primarily because they show a well-defined morphology. In addition, what may be selected by one researcher as the representative structure may differ from that selected by another. Even the description of the apparently similar features becomes subjective. Another problem is the misinterpretation of a particular morphology. This could sometimes be obviated by microanalysis, such as energy-dispersive x-rays. Sometimes misinterpretation of morphology may be due to the sample geometry and its relationship to incidental angle of the electron beam and take-off angle of the detector. The hexagonal etch pits, for example, may appear to be cubic.[30]

Some attempts have been made to estimate the phases quantitatively. There are inherent limitations in these estimates because the fracture passes preferentially through the weaker phase and thus this phase may be overestimated. The visual estimate tends to be unreliable compared to point count estimates. In view of the above, it has been recognized that speculations on the origin of strength and other properties, when based on these observations, have limited validity, especially since many properties of cement paste are influenced at a much lower microlevel than can be observed by an ordinary Scanning Electron Microscope.

The Calcium Silicate Hydrate Phase. The C-S-H phase is a major phase present both in the hydrated portland cement and tricalcium silicate. The principal products of hydration in portland cement or C_3S (other than CH) may be described as follows.[24] The early products in the hydration of C_3S consist of foils and flakes, whereas in portland cement a gelatinous coating or membrane of AFt composition is often observed. The products of C_3S, a few days old, will consist of C-S-H fibers and partly crumpled sheets, whereas in portland cement partly crumpled sheets, reticular network, rods and tubes of AFt are seen. At later stages of hydration, a dense, mottled C-S-H structure (inner product) is observed in hydrated C_3S, and in portland cement, a compact structure of equant grains and some plates of AFm phase.

The morphology of C-S-H gel particles has been divided into four types and described by Diamond.[31] Type I C-S-H, forming elongated or fibrous particles, occurs at early ages. It is also described as spines, acicular, aciculae, prismatic, rod-shaped, rolled sheet, or by other descriptions. These are a few micrometers long. Type II C-S-H is described as reticular or honey-combed structure and forms in conjunction with Type I. It does not normally occur in a C_3S or C_2S paste, unless it is formed in the presence of admixtures. In addition, in hardened cement pastes the microstructure can be nondescript and consist of equant or flattened particles (under 1000 Å in largest dimension) and such a morphological feature is described as Type III. Type IV, a late hydration product, is compact and has a dimpled appearance and it is believed to form in spaces originally occupied by cement grains. This feature is also found in C_3S pastes. The above list is not exclusive because other forms have also been described.

The morphological features in the cement paste hydrated to different periods are shown in Fig. 6. The unhydrated particles are shown in plate A. Within a few minutes of hydration the surface of the particles contains a non crystalline deposit (B). After three days of hydration, the features show a combination of Types I and II morphology (C and D). After seven days of hydration, a more compact structure consisting of massive plates of calcium hydroxide can be seen (E). At twenty-eight days, equant grains representing Type III morphology are discerned (F).

The morphology of C_3S hydrated for different periods is shown in plates F to K. The unhydrated particles have relatively smooth features (G). On some of the particles, elongated rolled sheets may be seen (H). These may have formed during the exposure of portland cement to moisture conditions during storage. At three days, the C_3S particles are covered with the hydration product (I). The enlarged plate (J) shows that fibers protrude from each of the particles. At twenty-eight days of hydration, longer rods of C-S-H are formed and they intermesh with each other (K). At some locations, tabular formation of $Ca(OH)_2$ is evident.

Non C-S-H Phases. Calcium hydroxide appears as thin hexagonal plates of size tens of μm across. At later stages of hydration, CH grows into a massive structure, losing its hexagonal outline. It may also engulf other products of hydration.

Ettringite occurs as relatively long rods with parallel sides with no branching.

The monosulfate hydrate and the hexagonal calcium aluminate hydrate form a thin hexagonal, platy structure.

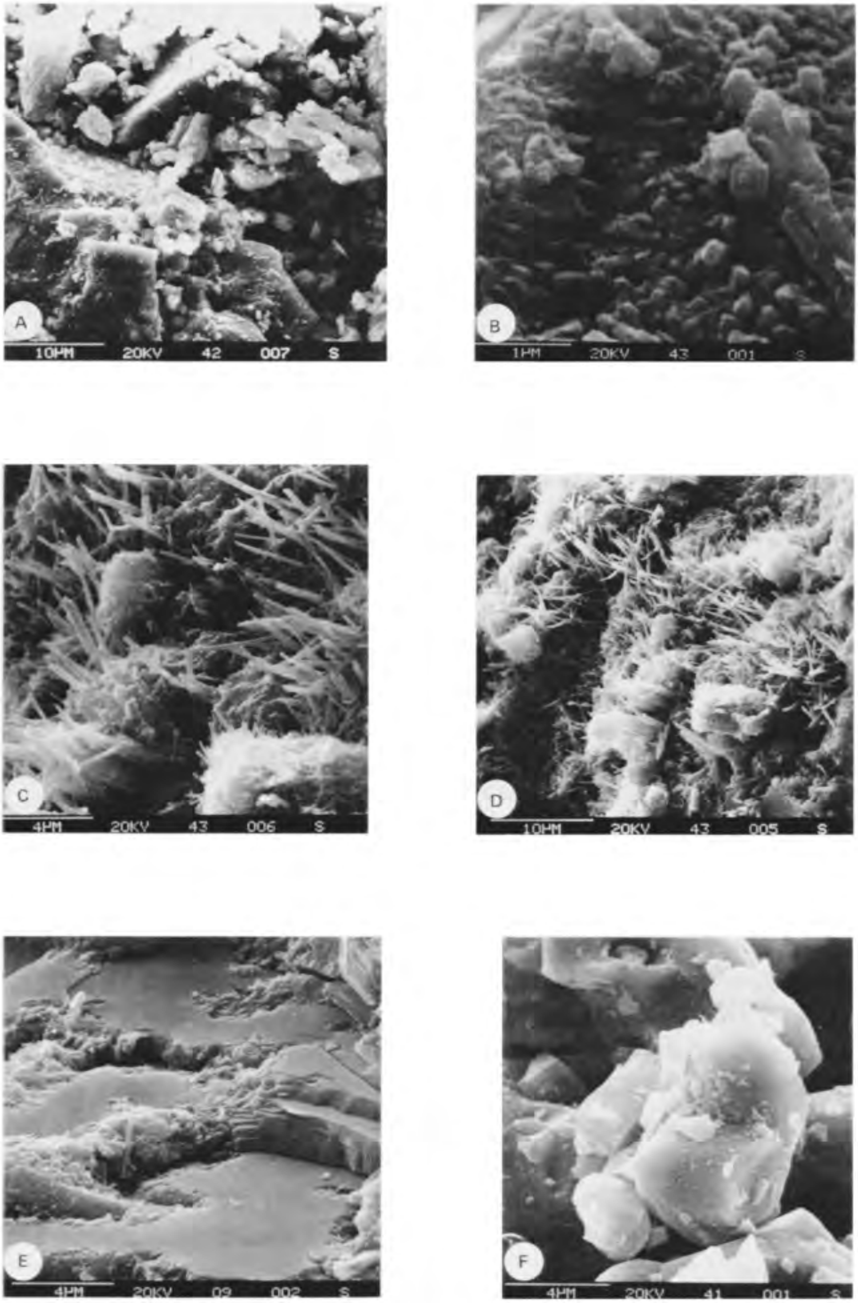


Figure 6. Microstructure of cement and C_3S pastes.

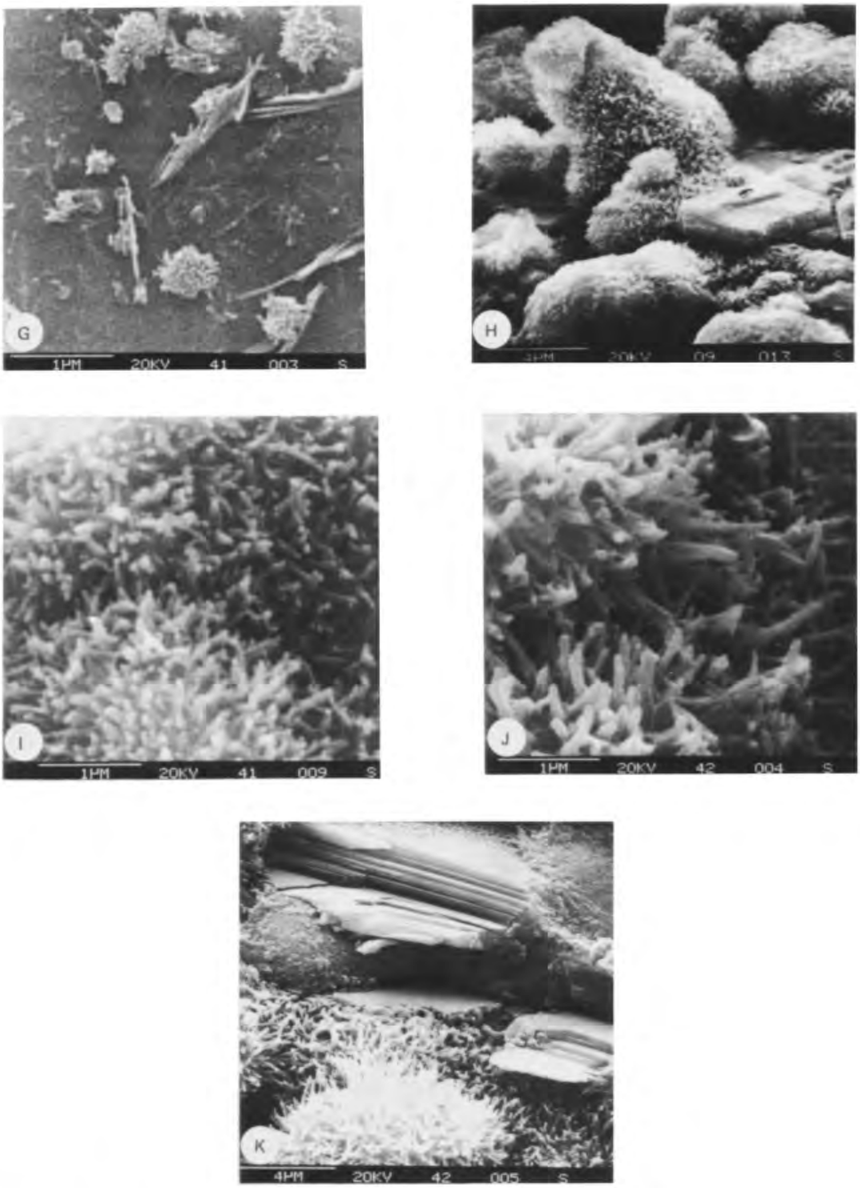


Figure 6. (Cont'd)

6.3 Bond Formation

Cementitious materials, such as gypsum, portland cement, magnesium oxychloride, and alumina cement, form porous bodies, and explanation for their mechanical properties should take into account the nature of the void spaces and the solid portion. If the solid part determines strength, then several factors should be considered including the rate of dissolution and solubility of the cement, the role of nuclei and their growth, chemical and physical nature of the products, energetics of the surface and interfacial bonds.

The C-S-H phase is the main binding agent in portland cement pastes. The exact structure of C-S-H is not easily determined. Considering the several possibilities by which the atoms and ions are bonded to each other in this phase, a model may be constructed. Figure 7 shows a number of possible ways in which siloxane groups, water molecules and calcium ions may contribute to bonds across surfaces or in the interlayer position of poorly crystallized C-S-H material.[29] In this structure, vacant corners of silica tetrahedra will be associated with cations, such as Ca^{++}.

The technique of cold compaction and recompaction of hydrated cement at several hundred MPa pressure has shown that bonds can be formed in this process which are similar to those formed by the normal hydration process.[32] In certain instances, wetting seems to enhance the modulus of elasticity of the body. This is explained by water entering the interlayer position and compensating for any decrease in Young's modulus when layers of C-S-H move apart. This emphasizes the bridging role of water. This type of bond implies that bonds between particles originating from separate nuclei during hydration can be similar to bonds within the particles.[33] The cement paste, made at lower w/c ratios, can be considered as a continuous mass around pores. Thus, the area of contact may be the critical factor determining mechanical properties.

6.4 Density

The density value quoted in the literature for a given material is accepted without much question because it depends simply on mass and volume at a given temperature; that for hydrated portland cement is no exception. An accurate assessment of density however, is one of the most important factors in determining porosity, assessing durability and strength, and estimating lattice constants for the C-S-H phase in hydrated portland cement.

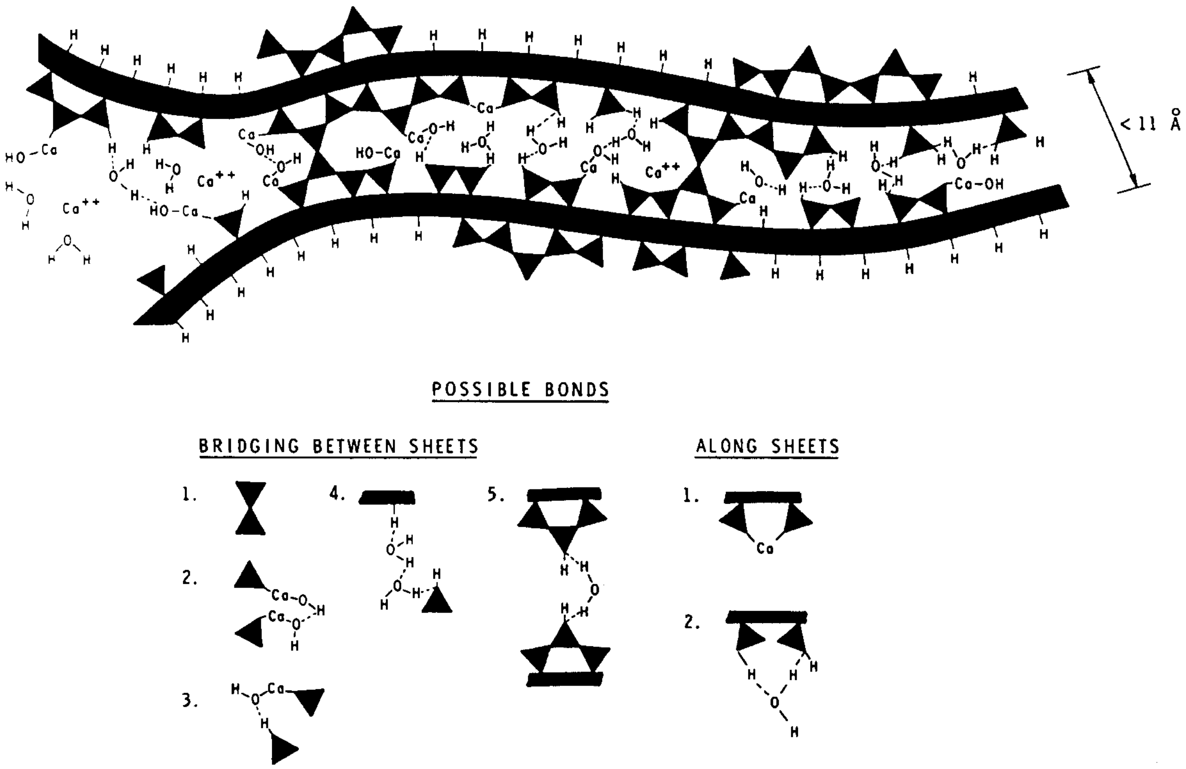


Figure 7. Suggested C-S-H structure illustrating bonds between and along sheets and polymerization of silicate chains.

Traditionally, density of hydrated portland cement was measured in the d-dried state by pycnometric methods, using a saturated solution of calcium hydroxide as a fluid. Since the d-dried hydrated portland cement rehydrates on exposure to water, this method is of questionable value. More realistic values can be obtained by proper conditioning of the sample and using fluids that do not affect the structure of the paste.

Table 3 shows the density values obtained using three methods: helium pycnometry, dried methanol, and saturated aqueous $Ca(OH)_2$ solution.[34] The density values were obtained for the bottle-hydrated cement, dried to 11% RH or at the d-dried state. Values are given for each fluid and four different sets of values are shown for the 11% RH condition. These values are different because of different types of corrections needed. It may be observed that drying to 11% RH and measuring with a saturated solution of $Ca(OH)_2$ gives an uncorrected value of 2.38 g/cc, as compared to a corrected value (type d) of 2.35 g/cc and 2.34 g/cc by helium. At the d-dried state, the exceptionally high value obtained by the $Ca(OH)_2$ solution technique is due to the penetration of water into the interlayer positions of the layered structure of the crystallite.

Table 3. Density of Bottle-Hydrated Portland Cement

Condition, 11% RH	Helium (g/cm^3)	Methanol (g/cm^3)	Saturated aqueous $Ca(OH)_2$ solution (g/cm^3)
(a) No correction	2.30 ± 0.015	2.25 ± 0.02	2.38 ± 0.01
(b) Monolayer adsorbed water correction	2.31 ± 0.015	2.26 ± 0.02	2.39 ± 0.01
(c) Helium flow taken into account	2.37 ± 0.015	2.32 ± 0.02	2.38 ± 0.01
(d) The interlayer space completely filled with water	2.34 ± 0.015	2.29 ± 0.02	2.35 ± 0.01
d-dry state			
(a) d-dry	2.28 ± 0.01	2.285 ± 0.02	2.61 ± 0.01
(b) -d-dry Calculation for layers themselves (uncorrected for free $(Ca(OH)_2)$	2.51 ± 0.01 of paste (w/c ratio 0.8)		2.51 ± 0.01

6.5 Pore Structure

Porosity and pore size distribution are usually determined using mercury porosimetry and nitrogen or water adsorption isotherms. Total porosity may be obtained by using organic fluids or water as a medium. Water cannot be used as it may interact with the body. The d-dried hydrated portland cement, on exposure to water, rehydrates. This is illustrated in Table 4, in which pore volume and density of d-dried hydrated cement are determined with helium, $Ca(OH)_2$ solution, or methanol.[34] The difference in porosity values obtained with $Ca(OH)_2$ solution or methanol at a w/c ratio of 0.4 on a volume/weight basis is equivalent to 8.6 cm^2/100 g of d-dried cement. Methanol has been used with the water-saturated hydrated cement by continually maintaining the methanol in the anhydrous state. Under this condition, methanol replaces all the water, including some bound water.[35] There is also evidence that under these conditions some chemical interaction occurs between methanol and cement.[36]

Table 4. Pore Volume and Density of D-Dried Hydrated Cement Pastes Determined with Different Fluids

	Pore volume percentage (by volume)			Density (g/ml)			
w/c ratio	Helium	$Ca(OH)_2$ solution	Methanol	Helium	$Ca(OH)_2$ solution	Methanol	Surface area (N_2)
0.4	23.3	37.8	19.8	(i) 2.19±0.015 (ii) 2.19±0.015			30 m^2/g
0.5	34.5	44.8	36.6		2.64±0.06	2.27±0.06	55 m^2/g
0.6	42.1	51.0		(i) 2.28±0.015 (ii) 2.26±0.015			51 m^2/g
0.8	53.4	59.5		(i) 2.30±0.015 (ii) 2.27±0.015	2.66±0.06		57 m^2/g
0.8	51.4	58.7	51.6		2.61±0.06	2.27	
1.0				(i) 2.29 (ii) 2.26			57 m^2/g

The quasi-elastic neutron scattering technique has the ability to distinguish between free and bound water.[37] Using this technique, the volume fraction free water in saturated pastes is found to be approximately equal to the porosity determined for pre-dried pastes by fluids such as methanol, helium, and nitrogen.

Pore-Size Distribution. *Mercury Porosimetry.* Mercury porosimetry involves forcing mercury into the vacated pores of a body by the application of pressure. The technique measures a range of pore diameters down to 30 Å. Auskern and Horn[38] used 117° as the value of contact angle. It has also been reported that the porosity measured by carbon tetrachloride saturation is slightly higher than the porosity measured by Hg porosimetry. Beaudoin[39] measured total porosity by Hg porosimetry using pressures up to 408 MPa and concluded that the porosimetry and He pycnometry methods could be used interchangeably to determine porosity of cement paste formed at a w/c ratio equal to or greater than 0.40. These results are shown in Fig. 8.

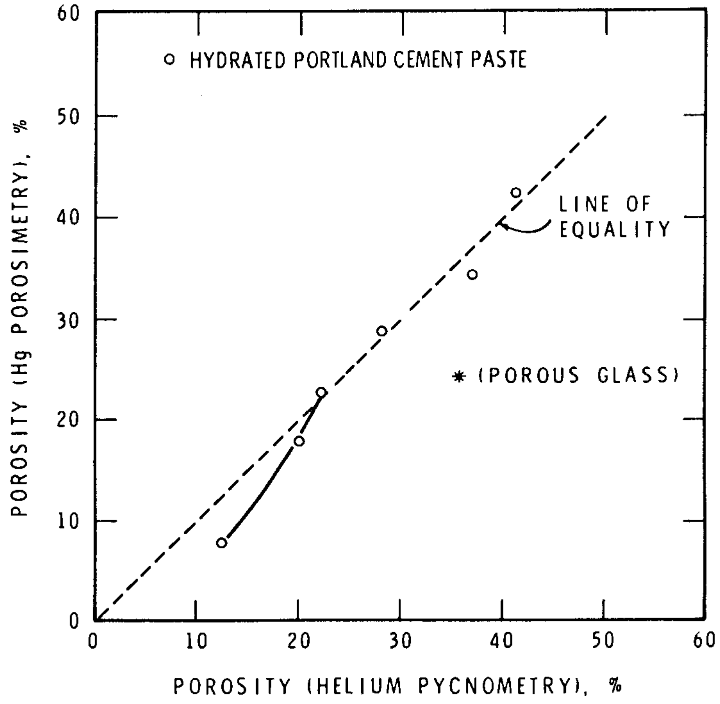


Figure 8. Mercury porosimetry vs helium porosity for hydrated portland cement paste.

In a study of the development of pore structure during the hydration of C_3S, Young[40] found that, on measuring the Hg intrusion, the pastes showed a threshold diameter that decreased with the amount of hydration (Fig. 9). It was suggested that the large intrusion immediately below the threshold diameter of 1000 Å results from the filling of void spaces between C-S-H gel needles and the filling of larger pores accessible only through intergrowth of needles.

Nitrogen Adsorption and Capillary Condensation Methods. Adsorption of a vapor on a surface is considered to take place progressively with the thickness of the adsorbed film increasing with the vapor pressure. At some stage, the thickness of the films on both sides of a pore approximates the size of the pore and *capillary* condensation takes place; from these measurements pore structure analysis can be made. Pore-size distribution can be determined by applying the Kelvin equation to either the adsorption or desorption isotherm. A number of assumptions on pore shape and thickness of the adsorbed film at each relative pressure have been used, leading to some variations in method of calculation.[41][42] In contrast to the Hg porosimetry, capillary condensation methods are limited to pore diameters of about 30–500 Å. Kadle and Dubinin[43] have suggested that Kelvin equation does not apply for pore diameters less than about 35 Å.

Collepardi[44] has determined the pore size distribution by N_2 capillary condensation for room temperature cured pastes.

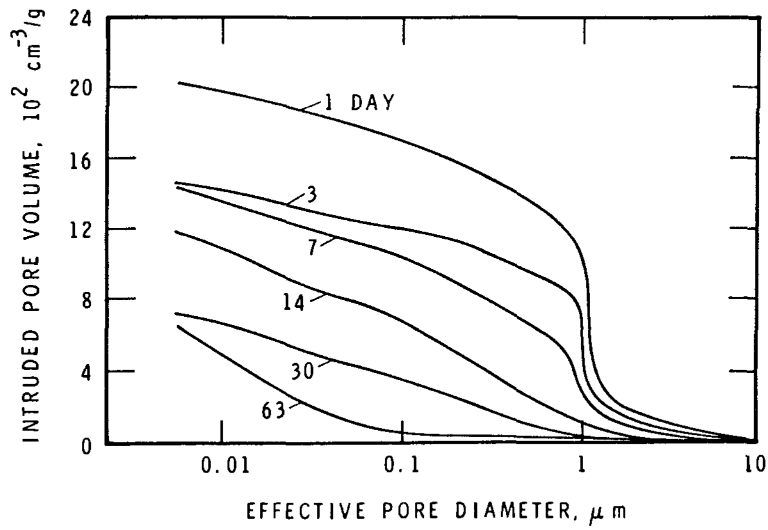


Figure 9. Hg intrusion curves for a series of hydrating C_3S pastes.

6.6 Surface Area and Hydraulic Radius

Surface Area. This is the area available to gases or liquids by way of pores and the external area. Hydrated portland cement is very complex and there is controversy over the significance of H_2O as an adsorbate in determining surface area. With water as adsorbate, the surface area is about 200 m^2/g and remains constant for different w/c ratio pastes. The surface area varies with w/c ratio when using nitrogen, methanol, isopropanol and cyclohexane as adsorbates.[45] With nitrogen, it varies from 3 to 147 m^2/g. Solvent replacement techniques, used in place of d-drying technique, yield different surface areas. Using a solvent technique, Litvan found that one of the samples registered a surface area of 249 m^2/g with nitrogen as an adsorbate.[46] There is evidence to show that during the extended methanol soaking, interaction with the cement may occur.[36][47] This may be responsible for the increased surface area. Drying to various humidities, followed by solvent replacement, shows that the exposure to capillary tension between 80 and 40% RH results in large decreases in surface area.[35] High surface areas have been found with fast drying.[48]

The method of drying seems to determine the extent to which further layering and agglomeration of C-S-H sheets occurs during the removal of water, and this manifests itself in surface area decreases and shrinkage. Subsequent treatment, such as wetting and drying and application of stress, also affects these properties. The low angle x-ray scattering data of Winslow et al. have provided a value at 670 m^2/g for the hydrated cement in a wet state.[49]

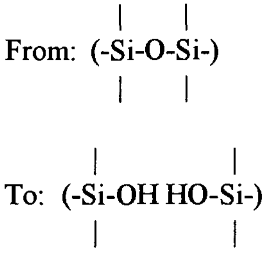
Hydraulic Radius. The average characteristic of a pore structure can be represented by the *hydraulic radius* which is obtained by dividing the total pore volume by the total surface area. The pore volume of d-dried paste determined by nitrogen, helium, or methanol is due to capillary porosity, and hydraulic radius is known to vary from 30 to 107 Å for w/c ratios from 0.4 to 0.8. Calculation of the hydraulic radius of the interlayer space can be done by knowing the surface area of the interlayer space (total surface area less surface area of capillary space) and the volume of the interlayer space. This varies with the degree of penetration of water molecules, but can be computed from pore volumes obtained by comparing values for water and nitrogen. An average value of 1.23 Å is obtained. A value for the hydraulic radius of partially water-occupied interlayer space is found to be 1.0 Å. For a w/c ratio paste of 0.2, the value is about 1.5 Å. These results are consistent with the idea that most of the water in the interlayer space is held as a single layer.[50]

6.7 Mechanical Properties

Hydrated portland cement contains several types of solid phases and the theoretical treatment of such a material is complex.

Many observations have led to the conclusion that the strength development of hydrated portland cement depends on the total porosity. Most data can be fitted to an exponential dependence term, e^{-bp}, with b values associated with different types of pores. Porosity and grain size effects on strength become clearly separable as pores approach or become smaller than the grain size. Uniform distributions of different types of pores will have similar exponential strength-porosity trends but the "b" values will change. They will depend on the pore location, size and shape. The latter two are important only when the pore causing failure is large in comparison with the grain size or with the specimen size. For small pores, its location is important. Pores at grain boundaries are more critical than pores within grains.

The fracture mechanism at a region of stress concentration is often affected by the environment. Measurements of strength of hydrated cement paste in flexure as a function of relative humidity[51] have shown significant decreases in strength as the humidity is increased from 0 to 20%. Under high stress conditions as at a tip of crack, the presence of H_2O vapor promotes rupture of the siloxane groups in the cement paste to form silanol groups as follows:



From: (-Si-O-Si-)

To: (-Si-OH HO-Si-)

Correlation of porosity with mechanical property has led to several types of semi-empirical equations, the most common being that due to Ryshkewitch,[52]

Eq. (13) $$M = M_o \exp(-bP)$$

where M is the mechanical strength property at porosity P, M_o the value at zero porosity, and b is a constant. As stated previously, b is related to pore shape and orientation. This equation shows good agreement with experimental values at lower porosities. Another equation, due to Schiller,[53]

$$\text{Eq. (14)} \qquad M = D \ln \frac{P_{CR}}{P}$$

where D is a constant and P_{CR} is the porosity at zero strength, shows good agreement at high porosities.

Feldman and Beaudoin[54] correlated strength and modulus of elasticity for several systems over a wide range of porosities. The systems included pastes hydrated at room temperature, autoclaved cement paste with and without additions of fly-ash, and those obtained by other workers. Porosity was obtained by measurement of solid volume by a helium pycnometric technique, and apparent volume through the application of Archimedes' principle. Correlation based on Eq. (1) is shown in Fig. 10.

There are essentially three lines of different slopes: line AB represents the pastes cured at room temperature, covering porosities from 1.4 to 41.5% and having a value of about 290 MPa at zero porosity. The second line, CD, represents the best fit for most of the autoclaved specimens, excluding those made with fly-ash. This line intersects AB at 27% porosity (corresponding w/c ratio = 0.45). On the basis of the same porosity at porosities about 27%, the room temperature pastes are stronger than those made by autoclaving. When the line CD is extrapolated towards low porosities, it meets the point for hot-pressed cement paste.[55] At zero porosity, a strength of over 800 MPa would be obtained for this series. The third line, EF, for the autoclaved fly-ash-cement mixtures [containing 11 Å tobermorite, C-S-H (I) and C-S-H (II)] is parallel to the room-temperature paste line, shows higher strengths, and is composed of higher density material. Further work by Beaudoin and Feldman[56] on autoclaved ground silica-normal Type I cement showed that the results conformed to Eq. (13). It was also found that the greater the density of the product, the greater was M_o and the slope b of the log M-porosity plot. Examination revealed that autoclaved mixtures made with low silica content contain largely well-crystallized, high density α-C_2S-hydrate, while those with 20–40% silica contain predominately C-S-H (I), CSH (II), and tobermorite. The mixtures with higher silica (50–65%) contain unreacted silica, tobermorite, C-S-H (I) and C-S-H (II).

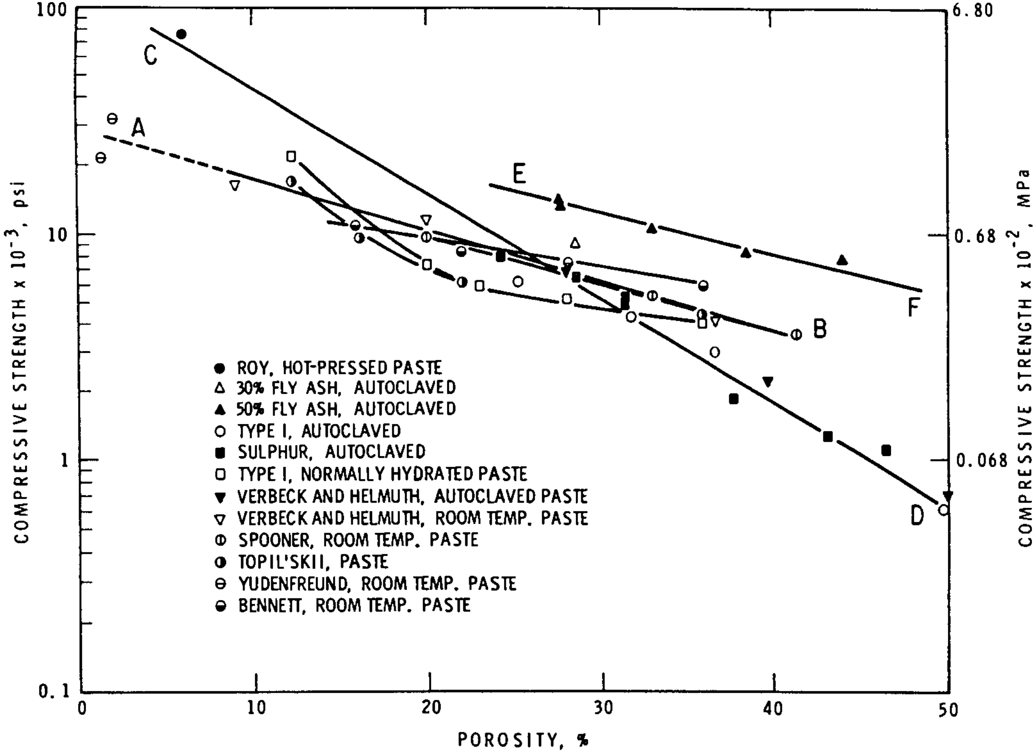


Figure 10. Strength vs porosity for autoclaved and room temperature cured preparations.

These results indicated that an optimum amount of poorly crystallized hydrosilicate and well-crystallized dense material provides maximum values of strength and modulus of elasticity at a particular porosity. At higher porosity, not only porosity but also bonding of individual crystallites plays a role in controlling strengths.

It is apparent that disorganized, poorly crystallized units tend to form bonds of higher contact area, resulting in smaller pores. As porosity decreases, better bonding will develop between high density, well-crystallized and poorly crystallized material and consequently, higher strengths will result. The potential strength of the high density and high strength material is thus manifested. This explains how very high strengths are obtained by the hot-pressing technique. In this method, a small, but an adequate quantity, of poorly crystallized material at low porosities provides the bonding for the high-density clinker material. Work by Ramachandran and Feldman with C_3A and CA systems has shown that at low porosities, high strength could be obtained from the C_3AH_6 product because a greater area of contact forms between crystallites than is possible at higher porosities.[11]

6.8 Permeability of Cement Paste

The rate of movement of water through concrete under a pressure gradient, termed *permeability*, has an important bearing upon the durability of concrete. The measure of the rate of fluid flow is sometimes regarded as a direct measure of durability.

It is known that the permeability of hardened cement paste is mainly dependent on the pore volume. However, pore volume, resulting at different water-cement ratios and degrees of hydration, does not uniquely define the pore system and thus is not uniquely related to the permeability.

Nyame and Illston[57] have used mercury intrusion data to define a parameter, termed "the maximum continuous pore size (r_∞)," and related it to the permeability. The relationship was found by linear regression to be

Eq. (15) $$K = 1.684\ r_\alpha\ 3.284 \times 10^{-22}$$

with a correlation coefficient of 0.9576 where K = permeability (m/s) and r_α = maximum continuous pore radius (Å).

It was found that below w/c ratios of 0.7, the values of permeability and the maximum continuous pore radius did not change significantly after twenty-eight days of hydration. Some of these results are shown in Fig. 11.

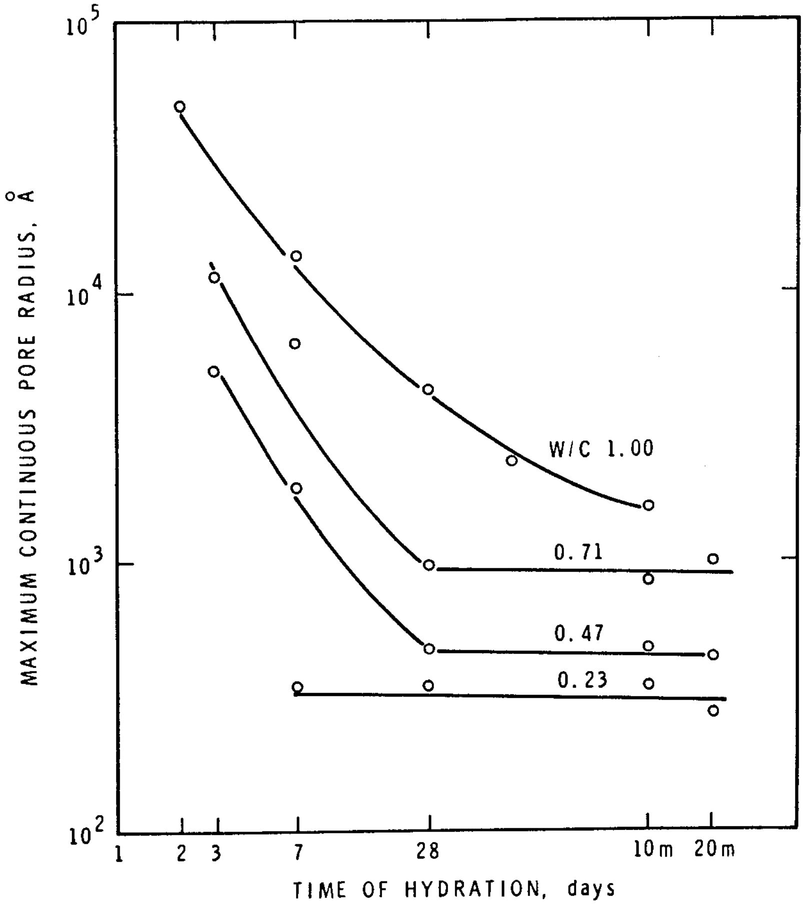


Figure 11. Effect of water-cement ratio and time of hydration on the maximum continuous pore radius of hardened cement paste.

Permeability can be related to pore structure, using the hydraulic radius theory which relates flow rates to the viscous forces opposing flow. Permeability is related to hydraulic radius as follows:

Eq. (16) $\log K = 38.45 + 4.08 \log (\varepsilon r_h^2)$

where r_h is the hydraulic radius and ε is the porosity.

6.9 Aging Phenomena

Aging, within the context of surface chemical considerations, refers to a decrease in surface area with time. For hydrated portland cement this definition can be extended to include changes in solid volume, apparent volume, porosity and some chemical changes (excluding hydration) which occur over extended periods of time.

Shrinkage and Swelling. The volume of cement paste varies with its water content, shrinking when dried and swelling when rewetted. It has been found that the first drying shrinkage (starting from 100% RH) for a paste is unique in that a large portion of it is irreversible. By drying to intermediate relative humidities (47% RH), it has been observed that the irreversible component is strongly dependent on the porosity of the paste, being less at lower porosities and w/c ratios.[58]

The irreversible component of first drying shrinkage is strongly dependent on the time the specimen is held in the 80–40% RH region. It is due to the capillary forces that exist in this humidity region and gradual movement of the surfaces of C-S-H sheets closer to each other; during this process, with time, permanent bonds form. This illustrates the similarity of first drying shrinkage to the creep phenomenon. Also, the shrinkage-water content relationship during first drying and redrying appears to depend significantly upon the length of time the specimen is held in the "dried" condition (47 %RH) (Fig. 12).[58] Each of four specimens shown in Fig. 12 was held at 47 % RH for different periods of time during first drying. Very little irreversible shrinkage or irreversible water loss resulted from drying for 0.1 days; however, with increased drying time, considerable irreversible shrinkage and water loss occurred.

First drying shrinkage can also be affected greatly by incorporation of some admixtures. A large, irreversible shrinkage of paste relative to that without admixture on drying to 47% RH suggests that the admixture promotes dispersion in terms of the alignment of sheets of C-S-H. In addition, drying from 15% RH to the d-dry condition results in the same shrinkage at the same w/c ratio, regardless of the admixture content.[59]

Creep. Concrete exhibits the phenomenon of creep, involving deformation at a constant stress, that increases with time. Creep of concrete (basic creep) may be measured in compression using ASTM C512 method. There are two types of creep: *basic creep* in which the specimen is under constant humidity conditions and *drying creep* when the specimen is dried during the period under load.

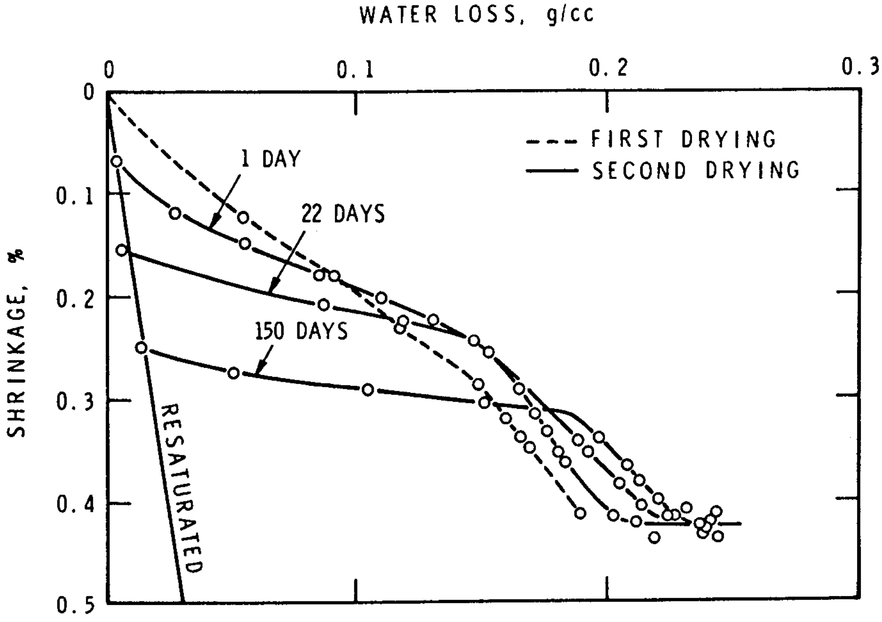


Figure 12. Effect of drying at 47% RH for periods indicated on length recovery, on saturation, and on shrinkage vs water loss relationship of second drying.

Creep of a cement paste increases at a gradually decreasing rate, approaching a value several times larger than the elastic deformation (Fig. 13).

As can be seen, creep is, in part, irrecoverable, as in drying shrinkage. On unloading, deformation decreases immediately due to elastic recovery. This instantaneous recovery is followed by a more gradual decrease in deformation due to creep recovery. The remaining residual deformation, under equilibrium conditions, is called the *irreversible creep.* Creep increases with w/c ratio and is very sensitive to relative humidity and water content. It may also be affected by admixtures.

Many theories have been proposed over the years to account for creep mechanisms in cement paste and each is capable of accounting for some of the observed facts. The descriptions and mechanisms are based on seepage,[61][62] change of solid structure[63]-[65] and interlayer space.[60]-[68]

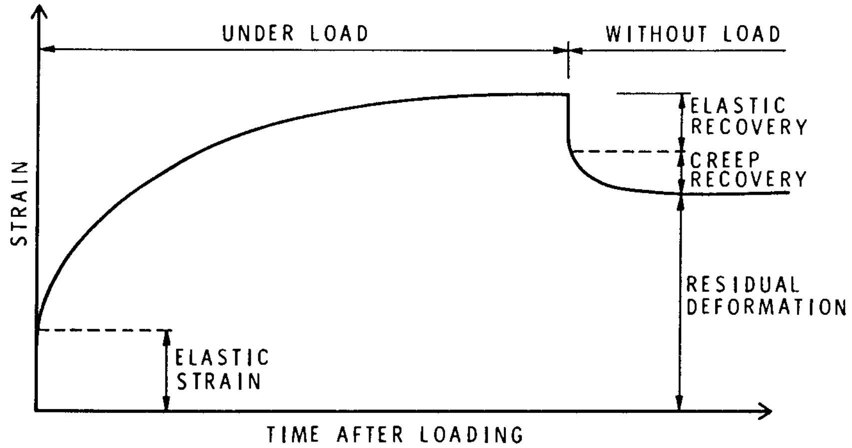


Figure 13. Creep and creep recovery of cement paste in hygral equilibrium with the surrounding medium.

7.0 MODELS OF HYDRATED CEMENT

In order to predict the performance of concrete, it is important to have a model of cement paste that incorporates its important properties and explains its behavior. There are two main models. In the Powers-Brunauer model, the cement paste is a poorly crystalline gel and layered. The gel has a specific surface area of 180 m^2/g with a minimum porosity of 28%. The gel pores are assumed to be accessible only to water molecules because the entrance to these pores is less than 4 Å in diameter. Any space not filled with cement gel is called *capillary* space.

The mechanical properties of the gel are described using this model The particles are held together mainly by van der Waal's forces (Fig. 14a).[69] Swelling on exposure to water is explained by the individual particles separating, due to layers of water molecules existing between them. Creep is the result of water being squeezed out from between the particles during the application of stress (Fig. 14c). This model recognizes the existence of some chemical bonds between the particles (Fig. 14b) and the existence of layers (Fig. 14d).

In the Feldman-Sereda model, the gel is considered as poorly crystallized layered silicate. It proposes, however, that the role of water is much more complex (Fig. 15) than is recognized by the Powers-Brunauer model.[69]

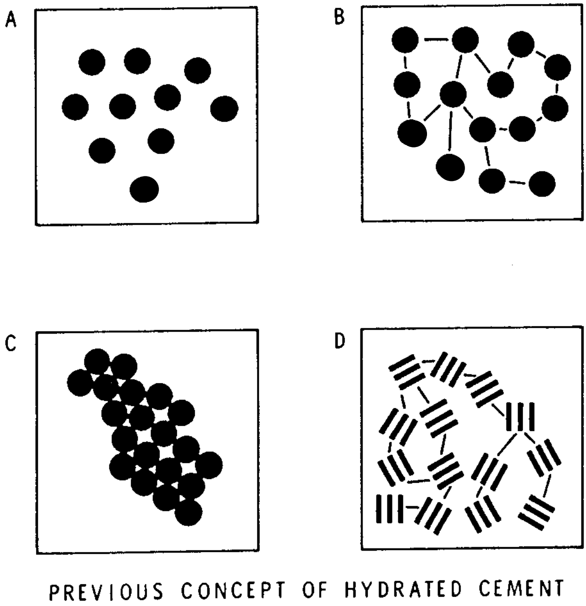


Figure 14. Development of Powers-Brunauer Model.

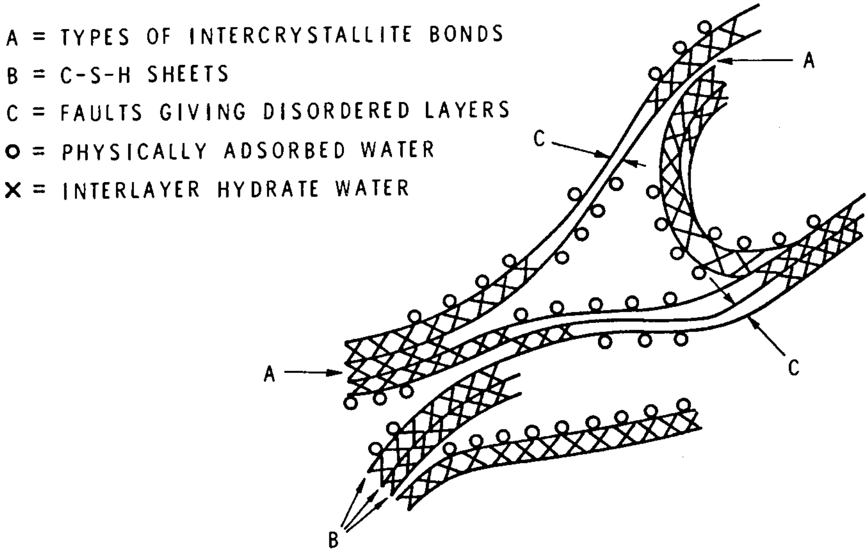


Figure 15. Structure of C-S-H gel according to Feldman-Sereda.

Water in contact with the d-dried gel acts in several ways: *(a)* it interacts with the free surface, forming hydrogen bonds; *(b)* it is physically adsorbed on the surface; *(c)* it enters the collapsed layered structure of the material even at humidities below 10% RH; *(d)* it fills large pores by capillary condensation at higher humidities.

The water that enters the interlayer spaces acts as part of the solid structure and is more organized than normal water; it contributes to the rigidity of the system. Most of the water is removed from the structure below 10% RH but some structural water is removed at higher humidities. Thus, the structural water is not considered as pore water, and gel pores in the Powers-Brunauer model should be considered as a manifestation of interlayer spaces. According to Feldman-Sereda model, gel pores, as such, do not exist. Therefore, the total porosity can only be obtained by fluids that penetrate the interlayer space; if they do, it should be taken into calculation. These fluids include methanol, nitrogen at liquid nitrogen temperatures, or helium gas at room temperature and are used on cement at the d-dried state. Under conditions (saturated state) other than the d-dried state, some fluids, including methanol, do penetrate the interlayer structure. The surface area of the gel measured by nitrogen or methanol varies approximately between 1 and 150 m^2/g, depending on the method of preparation and subsequent drying procedure.

Further modifications have been made to this model to explain the unstable nature of the material and its effect on the mechanical properties. It recognizes that this material derives its strength from a combination of van der Waal's forces, siloxane (-Si-O-Si-), hydrogen and calcium-silica (-Si-O-Ca-O-Si-) bonds. Swelling or wetting is not due just to separation of the primary aggregations or breaking of these bonds but to the net effect of several factors: *(a)* reduction of the solid surface energy due to physical interaction of the surfaces with water molecules, known as Bingham effect; *(b)* penetration of water molecules between the layers, and their limited separation as the H_2O molecules take up a more rigid configuration between the sheets; *(c)* menisci effects due to capillary condensation; *(d)* aging effects, generally considered to be a further agglomeration of sheets forming layers of the malformed crystallites. This last effect should result in decreased surface area, an increase in solid volume, and a net shrinkage.

Interlayer penetration occurs on wetting throughout the 0–100% RH range while the aging effect appears to be more dominant at humidities above 20% RH, especially in the zone where menisci forces exist (between 80 and 35% RH). The loss of compressive strength of the hydrated cement gel exposed to increasing RH is explained by a lowering of the stress of rupture of siloxane bonds in the presence of higher concentrations of water molecules.

Creep is a manifestation of aging, i.e., the material moves towards a lower total energy by aggregation of sheets due to the formation of more layers. Surface area is reduced by this process. Aggregation is accelerated by stress and facilitated by the presence of interlayer water.

8.0 CONCRETE PROPERTIES

8.1 Workability

The quality of fresh concrete is determined by the ease and homogeneity with which it can be mixed, transported, compacted and finished. It has also been defined as the amount of internal work necessary to produce full compaction.[27] The rheological behavior of concrete is related to the rheological terms such as plasticity and visco-elasticity of cement paste. As the workability depends on the conditions of placement, the intended use will determine whether the concrete has the required workability. A good workable concrete should not exhibit excessive bleeding or segregation. Thus workability includes properties such as flowability, moldability, cohesiveness and compactibility. One of the main factors affecting workability is the water content in the concrete mix. A harsh concrete becomes workable by the addition of water. Workability may also be improved by the addition of plasticizers and air entraining agents. The factors that affect workability include quantities of paste and aggregates, plasticity of the cement paste, maximum size and grading of the aggregates, and shape and surface characteristics of the aggregate.

Another term that has been used to describe the state of fresh concrete is consistency of fluidity. It describes the ease with which a substance flows. It is loosely related to, and an important component of, workability. The term *consistency* is sometimes used to describe the degree of wetness of concrete. Wet concrete is more workable than the dry concrete. A concrete having the same consistency may however, have different workability characteristics. The ASTM C-187 and Canadian Standard CSA CAN 3-A5 measure the consistency of cement paste by a Vicat apparatus consisting of a needle of diameter 1 mm with a plunger of diameter 10 mm. The paste is considered to have normal consistency when the rod settles to a point to 10 ± 1 mm below the original surface in 30 secs after release. In the determination of setting and soundness of cement paste, the material should be made to normal consistency requirements.

Although several methods have been suggested to determine workability, none is capable of measuring this property directly. It is therefore usual to measure some type of consistency as an index of workability. The most extensively used test is the slump test. This method is described by ASTM C143. The slump test uses a frustum of cone 30 mm (12 in.) high. Concrete is filled in this cone and the cone is lifted slowly and the decrease in the height of the center of the slumped concrete is measured. For structural concrete, a slump of 75–100 mm (3–4 inches) is sufficient for placement in forms. Another method called the *Compacting Factor Test* is based on the measurement of the density ratio (the ratio of the density actually achieved in the test to the density of the fully compacted concrete). This method is described in the BS1881, and by AC1 211. Another method called the *Ball Penetration Test* is described in ASTM-C360. This method is based on measuring the penetration of 150 mm (6 in.) diameter steel cylinder with a hemispherically shaped bottom weighing 13.6 kg (30 lbs.). The ratio of slump to the penetration of the ball is about 1.5–2. In the *Remolding Test* developed by Powers, workability is assessed on the basis of the effort required in changing the shape of the concrete.[27] The *Vebe Test* is similar to the remolding test except that the inner ring is omitted and compaction is achieved by vibration instead of rolling. In addition to the above, other methods have been used. They include *Vebe Consistometer, German Flow Table, Nasser's K-probe,* and *Tattersall's Two Point Test.* The details of these methods are described in Refs. 27 and 28. All these tests attempt to measure workability and they are not comparable. No ideal test for workability has been developed as yet.

8.2 Setting

The setting of concrete is determined by using the mortar contained in it. A penetrometer is used for determining the initial and final setting times of mortar. A needle of appropriate size has to be used. The force required to penetrate 1 inch depth is noted. The force divided by the area of the bearing surface of the needle yields the penetration resistance. The initial setting time is the elapsed time after the initial contact of cement and water required for the mortar sieved form the concrete to reach a penetration resistance of 500 lbs/sq.in. (3.5 MPa). The corresponding resistance for the final setting time is 4000 lbs/sq.in. (27.6 MPa).

Concrete may exhibit flash set due to the reaction of C_3A, forming calcium aluminate hydrates and monosulfate hydrate. Workability will not be restored by remixing when flash set occurs.

8.3 Bleeding and Segregation

In a freshly placed concrete which is still plastic, settlement of solids is followed by the formation of a layer of water on the surface. This is known as bleeding or water gain. In lean mixes, localized channels develop and the seepage of water transports some particles to the surface. Bleeding may thus give rise to *laitance,* a layer of weak, nondurable material containing diluted cement paste and fines from the aggregate. If bleeding occurs by uniform seepage of water, no undesirable effects result and such a bleeding is known as "normal bleeding." Bleeding is not necessarily harmful. If undisturbed, the water evaporates so that the effective water-cement ratio is lowered with a resultant increase in strength.

The amount of bleeding can be reduced by using proper amounts of fines, high alkali or C_3A contents, increasing cement content and admixtures such as pozzolans, calcium chloride or air entraining admixtures. Bleeding characteristics are measured by bleeding rate or bleeding capacity applying the ASTM C232 standard. In this method, the relative amount of mix water that appears on the surface of concrete placed in a cylindrical container is measured. At specified intervals the water accumulating on the surface is determined until bleeding ceases. The top surface of concrete subsides during bleeding causing what is known as "plastic shrinkage."

During the handling of concrete mixture, there may be some separation of coarse aggregates from the mixture resulting in a nonuniform concrete mass. This is known as segregation. Segregation may lead to flaws in the final product and honeycombing may occur in some instances. Segregation may result during handling, placing, vibrating or finishing operations. The primary cause of segregation is the differences in the size of the particles and specific gravity of the mix. The tendency to segregate increases with slump, reduction in cement content, or increase in the maximum size and amount of aggregate. By proper grading of the constituents and handling, this problem can be controlled.

There is no standard procedure developed for measuring segregation. For over-vibrated concrete, proneness to segregation can be assessed by vibrating a concrete cube for about ten minutes, stripping it, and observing the distribution of coarse aggregate.[27]

8.4 Mechanical Properties

The hardened concrete has to conform to certain requirements for mechanical properties. They include compressive strength, splitting tensile strength, flexural strength, static modulus of elasticity, Poisson's ratio, mechanical properties under triaxial loads, creep under compression, abrasion resistance, bond development with steel, penetration resistance, pull-out strength, etc. These tests are briefly described in Ch. 2. Admixtures influence most of these properties and they are discussed under relevant chapters.

The mechanical behavior of concrete should be viewed from the point of view of a composite material. A composite material is a three dimensional combination of at least two chemically and mechanically distinct materials with a definite interface separating the components. This multiphase material will have different properties from the original components. Concrete qualifies as such a multiphase material.[27a] Concrete is composed of hydrated cement paste (C-S-H, CH, aluminate and ferrite-based compounds), and unhydrated cement, containing a network of a mixture of different materials. In dealing with cement paste behavior, basically it is considered that the paste consists of C-S-H and CH with a capillary system. The model of concrete is simplified by treating it as a matrix containing aggregate embedded in a matrix of cement paste. This model provides information on the mechanical properties of concrete.

The factors that influence the mechanical behavior of concrete are: shape of particles, size and distribution of particles, concentration of particles, the orientation of particles, topology, composition of the disperse and continuous phases, and that between the continuous and disperse phase and the pore structure.

The strength of concrete depends on the strength of the paste, coarse aggregate, and the paste-aggregate interface. This interface is the weakest region of concrete and that is where the failure occurs before its occurrence on the aggregate or the paste. The weakness of this interface is due to weak bonding and the development of cracks. They may develop due to bleeding and segregation and volume changes of the cement paste during setting and hydration. The transition zone extends about 50 microns from the surface of the aggregate, and has a higher porosity and permeability. This space is occupied by oriented, well developed crystals of calcium hydroxide and in some cases, ettringite. The transition zonal effects are particularly significant with pastes or concrete made at w/c ratios greater than 0.4. The presence of silica fume however, may modify or even eliminate the transition zone. This is generally attributed to the changes in the viscosity or cohesiveness imparted by silica fume to concrete. The altered transition zone and improved matrix-aggregate bond in the presence of silica fume result in enhanced strength.

9.0 DURABILITY OF CONCRETE

One of the most important requirements of concrete is that it should be durable under certain conditions of exposure. Deterioration can occur in various forms such as alkali-aggregate expansion reaction, freeze-thaw expansion, salt scaling by de-icing salts, shrinkage and enhanced attack on the reinforcement of steel due to carbonation, sulfate attack on exposure to ground waters containing sulfate ions, sea water attack and corrosion caused by salts. Addition of admixtures may control these deleterious effects. Air entrainment results in increased protection against freeze-thaw action, corrosion inhibiting admixtures increase the resistance to corrosion, inclusion of silica fume in concrete decreases the permeability and consequently the rate of ingress of salts, and the addition of slags in concrete increases the resistance to sulfate attack.

9.1 Alkali-Aggregate Expansion

Although all aggregates can be considered reactive, only those that actually cause damage to concrete are cause for concern. Experience has shown that the presence of excessive amount of alkalis enhances the attack on concrete by an expansion reaction. Use of marginal quality aggregate and the production of high strength concrete may also produce this effect.

The alkali-aggregate reaction in concrete may manifest itself as map cracking on the exposed surface, although other reactions may also produce such failures. The alkali-aggregate reaction, known as alkali-silica type, may promote exudation of a water gel, which dries to a white deposit. These effects may appear after only a few months or even years.

Three types of alkali-aggregate reactions are mentioned in the literature: alkali-silica reaction,[70]-[72] alkali-carbonate reaction, and alkali-silicate reaction. The alkali-silicate reaction has not received general recognition as a separate entity. Alkali-silica reactions are caused by the presence of opal, vitreous volcanic rocks, and those containing more than 90% silica. The alkali-carbonate reaction is different from the alkali-silica reaction in forming different products.[73]-[75] Expansive dolomite contains more calcium carbonate than the ideal 50% (mole) proportion and frequently also contains illite and chlorite clay minerals. The alkali-silicate reaction was proposed by Gillott.[76] The rocks that produced this reaction were graywackes, argillites and phyllites containing vermiculites.

The preventive methods to counteract alkali-aggregate expansion include, replacement of cement with pozzolans or blast-furnace slag and addition of some chemicals such as lithium compounds.[77]-[81] A more detailed treatment of alkali-aggregate reactions can be found in a separate chapter.

9.2 Frost Action

Frost action is defined as the freezing and thawing of the moisture in materials and the resultant effects of these materials. Essentially three kinds of defects are recognized: spalling, scaling, and cracking. Scaling occurs to a depth of an inch from the surface, resulting in local peeling or flaking. Spalling occurs as a definite depression caused by the separation of surface concrete, while cracking occurs as D- or map-cracking and is sometimes related to the aggregate performance. Good resistance to frost expansion can be obtained by proper design and choice of materials, and thus durability to frost action is only partly a material behavior. In addition to w/c ratio, quality of aggregate and proper air entrainment, the frost resistance depends on the exposure conditions. Dry concrete will withstand freezing-thawing, whereas highly saturated concrete may be severely damaged by a few cycles of freezing and thawing.

According to many workers, frost damage is not necessarily connected with the expansion during freezing of water, although it can contribute to damage. Although many organic compounds such as benzene and chloroform contract during freezing they can cause damage during the freezing transition. When a water-saturated porous material freezes, macroscopic ice crystals form in the coarser pores and water, which is unfrozen in the finer pores, migrates to the coarser pores or the surfaces.[82] The large ice crystals can feed on the small ice crystals, even when the larger ones are under constraint.

Length Changes During Freezing of Hydrated Portland Cement. The pore structure of hardened cement paste determines freezing of water contained in the pores. The pore structure depends largely on the initial w/c ratio and the degree of hydration. In general, the pore structure is composed of pores having diameters ranging from 10,000 to 50 Å for non-matured pastes and 1000 to 50 Å for mature pastes. The higher the w/c ratio, the greater will be the volume fraction of larger pores. When these pores are saturated with water, a large amount of water will be able to freeze during cooling. A saturated concrete, prepared at a higher w/c ratio and with a lower degree of hydration, contains a greater amount of water.

Fully saturated samples, on cooling at 0.33°C/min, show dilations during freezing and residual expansion on thawing. These values are increased in samples made at higher w/c ratios. Thicker samples also exhibit larger expansions. Cooling rates also influence length change values. It was also found that, during slow cooling, 30–40% of the evaporable water was lost from the samples. These results are similar to those obtained for other porous materials.[84] It is apparent that the large dilation is not only due to water freezing in larger pores but also to water migrating from smaller pores, freezing in limited spaces and generating stresses. When the rate of cooling is slow, there is enough time for water to vacate the small pores of the sample, causing contraction due to drying shrinkage. Powers and Helmuth[85] added an air-entraining admixture to the paste, producing various amounts of air bubbles of uniform size. With a knowledge of the total volume and average size of the bubbles, the average distance between them (air-void spacing) was calculated. Length change measurements, on cooling (0.25°C/min) relatively thick specimens of different air-void spacings but having similar porosity, are shown in Fig. 16. Shrinkage occurred in specimens with bubble spacings of 0.30 mm or lower. These specimens were saturated (except for the entrained space) and, therefore, the existence of closely-spaced air bubbles provided sites for water to migrate and for ice crystals to grow, without the imposition of stress.

De-Icing Salts. Deterioration of plain concrete, due to de-icing agents, may generally be termed *salt scaling;* it is similar in appearance to frost action but more severe. Any theory on salt scaling should account for this increased damage.

Length change measurements on freezing and thawing specimens saturated with different concentrations of brine solutions have been conducted by Litvan.[86] Typical results are shown in Fig. 17. The curves are qualitatively similar to those samples containing NaCl, but the magnitude of length changes is different. Maximum dilation effects are observed in solutions containing 5–9% NaCl. The explanation is that the vapor pressure of the saline solution is decreased (with respect to water) and the tendency for the water to migrate from the smaller pores will be lower for the saline solution in comparison with that for pure water. Consequently, on freezing, greater dilation will occur in the salt-containing specimen than in the salt-free specimen. At high salt concentrations, other phenomena, such as a change in the range of freezing temperatures or the effect of high viscosity of the saline solution on the mechanical properties of the body, have to be considered.

In concrete, the pores of the aggregate may be such that the pore water may readily freeze. Larger pores, equivalent to air-entrained bubbles (diameter > 100 Å), may not exist in the aggregates. Thus, the tendency to expand due to freezing of water will either be taken up by elastic expansion of the aggregate or by water flowing out from the aggregate under pressure. For saturated aggregates, there may be a critical size below which no frost action occurs because during freezing, water will flow out of the specimen.[87]

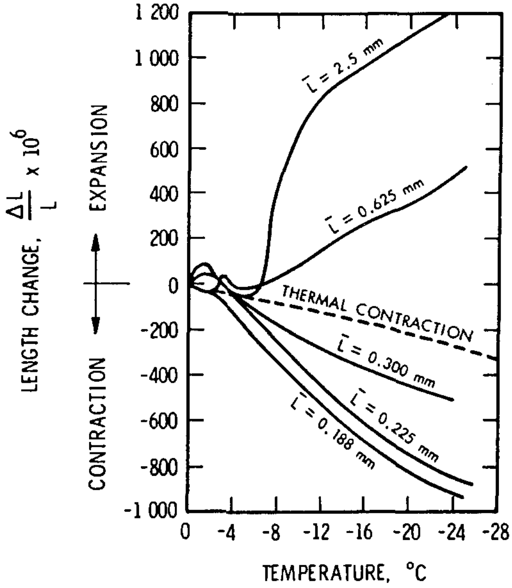


Figure 16. Length changes due to freezing of cement pastes of different air contents. $\bar{L}$ is the spacing factor.

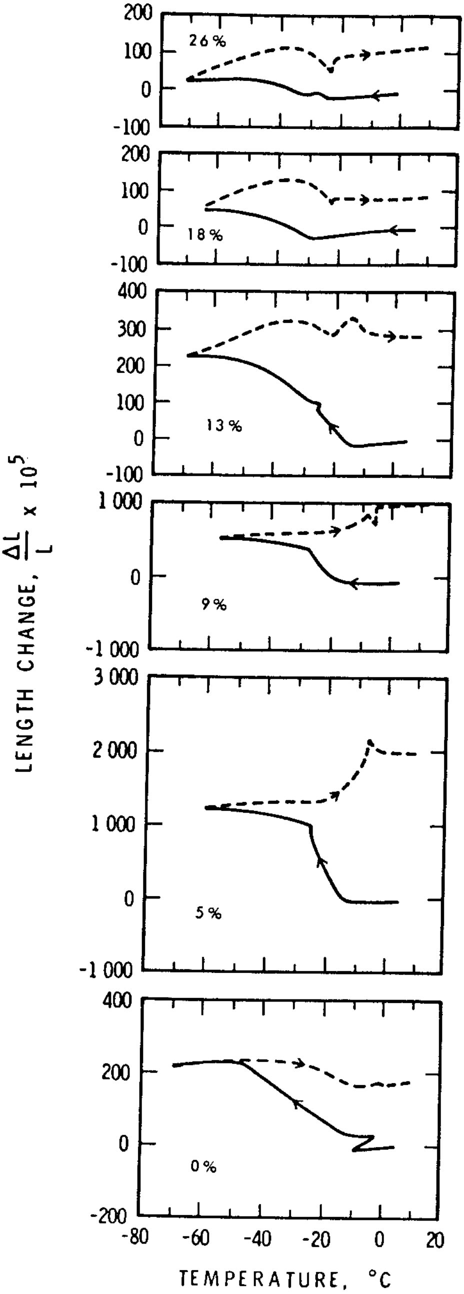


Figure 17. Length changes for air-entrained 0.5 w/c cement paste saturated with brine of various concentrations.

Tests for Frost Resistance. The most widely used test for assessing the resistance of concrete to freezing and thawing is the ASTM test entitled "Resistance of Concrete to Rapid Freezing and Thawing" (ASTM C 666). In Procedure A, both freezing and thawing occur with the specimens surrounded by water and in the Procedure B, the specimens are frozen in air and thawed in water. Procedure A is somewhat more reproducible than Procedure B. Durability as such is not measurable, although expansion during a slow cycle of freezing is possible and relevant.[88] It has been proposed that specimens be prepared and conditioned so as to simulate field conditions and then be subjected alternately to slow freezing and thawing and to storage in water. Several variations of this procedure are reflected in ASTM C 671 for air-entrained concrete. This test is not used extensively because it is more elaborate and time consuming. In a work[89] on outdoor exposed precast concrete, it was found that the moisture content of the exposed slabs was at the level equivalent to exposure at 87 % RH. This indicated all but one of the commercial products was durable, contrary to the results that can be obtained from ASTM C 666. RILEM Committee 4-CDC has made a similar approach to that found in ASTM C 671.[90]

Control of Frost Resistance. The general approach to preventing frost attack in concrete is to use an air-entraining agent. Tiny bubbles of air are entrapped in concrete due to the foaming action developed by the admixture during mixing. Many factors, such as the variability in the materials, impurities, mixing, and placing methods, make it difficult to adjust the required amount of air containing the right bubble spacing and size. Trial mixes are often carried out for this purpose.

These problems could largely be avoided if the preformed bubble reservoirs could be added in the form of particles. Two inventions have used this principle. The plastic microspheres[91] and porous particles[92] which have the required air are added to concrete. It has been shown that addition of particles, which correspond to less than 2% equivalent air, is similar to conventional air-entrained concrete containing 5% air. Control of the right size and spacing of air pockets in these particles can add to the effectiveness to frost action.

9.3 Sea Water Attack

Construction activity has been extending into the oceans and coastal areas because of the increasing number of oil and seabed mining operations. A large portion of these installations will be made from portland cement concrete and great demands will be made on it for increased safety and long term durability.

The deterioration of concrete due to sea water attack is the result of several simultaneous reactions. However, sea water is less severe on concrete than can be predicted from the possible reactions associated with the salts contained in it. Sea water contains 3.5% salts by weight. They include NaCl, $MgCl_2$, $MgSO_4$, $CaSO_4$, and possibly $KHCO_3$.

The deterioration of concrete depends on the exposure conditions. Concrete not immersed but exposed to marine atmosphere will be subjected to corrosion of reinforcement and frost action. Concrete in the tidal zone, however, will be exposed to the additional problems of chemical decomposition of hydrated products, mechanical erosion, and wetting and drying. Parts of the structure permanently immersed are less vulnerable to frost action and corrosion of the reinforcing steel.

The aggressive components of sea water are CO_2, $MgCl_2$ and $MgSO_4$. Carbon dioxide reacts with $Ca(OH)_2$, finally producing calcium bicarbonate, that leads to the removal of $Ca(OH)_2$. Carbon dioxide may also react with calcium aluminate monosulfate and break down the main strength-giving C-S-H component to form aragonite and silica. Even though $MgCl_2$ and sulfate are present only in small amounts, they can cause deleterious reactions. These compounds react with $Ca(OH)_2$ to form soluble $CaCl_2$ or gypsum. Sodium chloride in sea water has a strong influence on the solubility of several compounds. Leaching of them makes the concrete weak. Magnesium sulfate may also react with calcium monosulfate aluminate in the presence of $Ca(OH)_2$ to form ettringite; this reaction is slowed down in the presence of NaCl[93] and may not occur if $Ca(OH)_2$ is converted by CO_2 to carbonate.

Calcium chloroaluminate seldom forms in sea water because in the presence of sulfate, ettringite is the preferred phase. Ettringite formation affects the durability of concrete in seawater in the presence of cements containing $C_3A > 13\%$.[94] Tricalcium aluminate, in combination with high C_3S content, shows an even lower resistance to seawater than C_3A alone (Fig. 18). This is probably also due to the large amount of $Ca(OH)_2$ liberated by the hydration of C_3S. This explains why the addition of blast furnace slag or fly ash to cement improves the performance in sea water. This is due to the reaction of $Ca(OH)_2$ with the reactive SiO_2 and Al_2O_3 from the fly ash and the low level of $Ca(OH)_2$ that is generally present in good blast furnace slags after the hydration reaction.

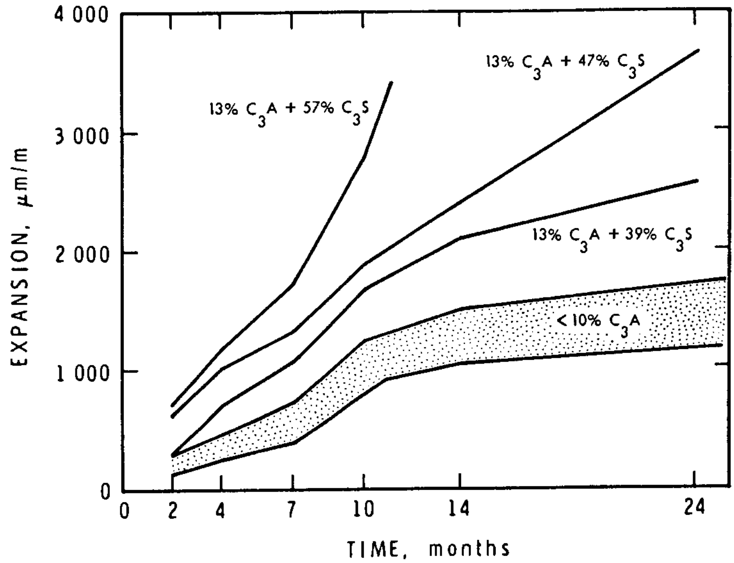


Figure 18. Linear expansion of mortar samples stored in sea water.

Some standards allow the inclusion of $CaCO_3$ as an additive to cement. For example, the Canadian Standards allow the addition of up to 5% carbonate. Ramachandran et al. examined the durability of mortars containing different amounts of $CaCO_3$ in mortars.[95] Mortar mixes were prepared at a w/c ratio of 0.42 and 0.60 and different amounts of calcium carbonate (0–15%) in ground or precipitated form were added. The mortars were exposed to sea water for up to one year. Modulus of elasticity and length changes were monitored. Most mortars had higher expansion values than the reference specimen. Those containing coarse carbonate showed relatively lower expansions than those with fine carbonate. The samples prepared at a w/c ratio of 0.42 and containing up to 2.5–5.0% ground carbonate showed smaller expansions. It was also found that the compressive strengths of the specimens were not indicative of the durability behavior of the specimens. Figure 19 shows the effect of precipitated $CaCO_3$ on the expansion of mortar exposed to the sea water.

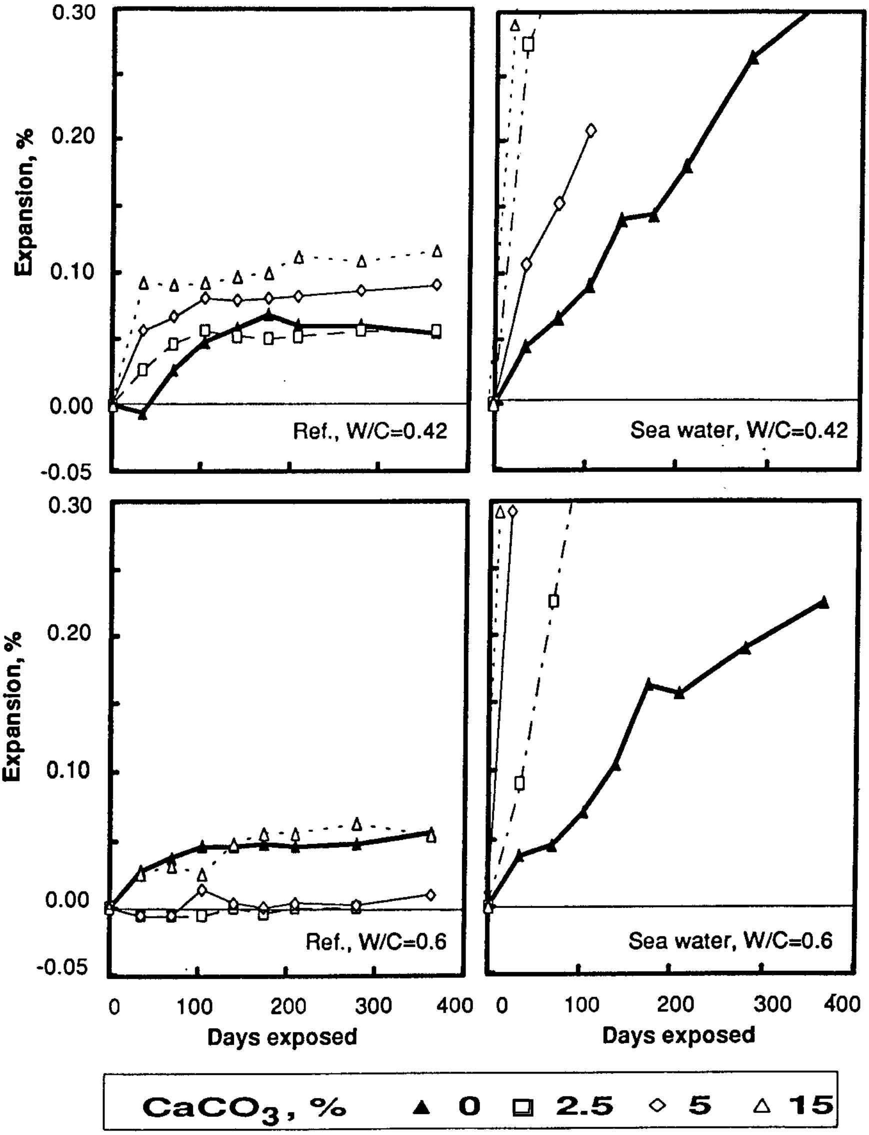


Figure 19. Effect of precipitated calcium carbonate on expansion of mortars exposed to sea water.

9.4 Corrosion of Reinforcement

Corrosion of steel in concrete is probably the most serious durability problem of reinforced concrete in modern times, and therefore a clear understanding of the phenomenon is of crucial importance. The phenomenon itself is an electrochemical reaction. In its simplest form, corrosion may be described as current flow from anodic to cathodic sites in the presence of oxygen and water. This is represented by the following equations:

Eq. (17) ANODE $Fe \rightarrow Fe^{2+} + 2e^-$

Eq. (18) CATHODE $\frac{1}{2}O_2 + H_2O + 2e- \rightarrow 2(OH)^-$

These reactions would result in the formation of oxide at cathodic sites. The high alkalinity of cement paste, however, provides protection for the steel reinforcement. Although it is understandable that the likelihood of corrosion depends on the pH of the solution and the electrical redox potential of the metal, initial observations of diagrams, known as *Pourbaix plots* (showing equilibrium regions where the metal is in a state of immunity or passivity, or where corrosion will occur) for carbon steel or iron show that the redox potential for the hydrogen electrode lies above the region of immunity for iron in both acid and alkaline solutions, suggesting that iron will dissolve with evolution of hydrogen in solutions of all pH values. However, in the pH interval 9.5 to 12.5, a layer of ferrous oxide or hydroxide forms on the metal surface thus conferring immunity from corrosion in these solutions in this range. Some authors[96] refer to this layer, or film, as γ-Fe_2O_3. This protective film is believed to form quite rapidly[96] during the early stages of cement hydration and may grow to a thickness of the order of 10^{-3} to 10^{-1} µm. Only indirect evidence of an oxide film exists and is mainly based on anodic polarization measurements. Much is not known about the conditions of formation, or chemical or mineralogical composition of these passivating layers and it is feasible that the film may consist of several phases.[97]

Chloride depassivation of steel is perhaps better understood than the passivation process and there are several mechanisms proposed.[98][99] One of the mechanisms frequently put forth involves the formation of a complex ion between chloride ion and the ferrous ion, in the passive film. It is possible that low Cl ion concentrations enhance Fe solubility[100] even at pH's as high as 12–13, as a result of a chloride complex containing both Fe^{2+} and Fe^{3+}. Migration of this complex destabilizes the passive layer, and by this mechanism, chloride can rejuvenate the corrosion process. The chloride ion is also responsible for other deleterious effects. It contributes, together with CO_2 ingress, to the depression of the pH of the pore fluid and increases the electrical conductance of the concrete, allowing the corrosion current to increase.

Currently a limit of 0.2 percent of chloride ion concentration by weight of cement in the concrete is proposed. However, there is no theoretical basis to this value, and it appears possible that the amount of hydroxyl ion in the cement paste modifies this value. Thus some researchers have placed a limit on the ratio of chloride to hydroxyl ion[100][101] such that corrosion will occur if the ratios of Cl^- to OH^- is as follows:

$$\frac{Cl-}{OH^-} > 0.6$$

Consequently the chloride ion threshold must also depend upon the alkalis in the cement. The effect of alkalis in aggregates and the removal of chloride ions by aluminate phases, further complicate this picture, and it has been pointed out[99] that the fixation of chloride by the latter should not be considered permanent as the chloroaluminate may be unstable in the presence of sulfate or carbon dioxide.

Although the corrosion of the reinforcing steel in concrete is detrimental for the simple fact that the composite will lose strength, the main cause for concern is that this phenomenon causes cracking of the surrounding concrete. Estimates are that as little as 0.1 mil of rust thickness can cause cracking.

Early detection of the corrosion can allow remedial action to be made successfully. One of the more widely used tests is the measurement of the half-cell potential of the reinforcing steel embedded in the concrete (ASTM C876). It is usually understood that corrosion is taking place when half-cell potential values more negative than -0.35 volts are obtained. However, frequently, this rule does not strictly apply, and it is recommended that corrosion rate values be obtained in questionable areas by measuring polarization resistance.

Generally, it is felt that the rate of corrosion of steel is primarily controlled by the diffusion of oxygen through the concrete cover followed by the cathodic reaction involving oxygen reduction.[102] However, there are situations where chloride contents are high and corrosion rates are much higher than would be expected from possible diffusion rates of oxygen. It has been postulated[102] that in these cases, there are strong localized reductions in pH in crevices, where iron is converted to $Fe(OH)_2$, through the prior conversion to chloride. These reactions involve hydrogen evolution.

Several methods of corrosion prevention have been tried over the years. These include protective coatings, placement of impermeable concrete overlays, cathodic protection or the use of corrosion resistant steels and galvanized or epoxy coated bars. In the later category, recent work has shown[103] that galvanized steel may be of benefit if used in low chloride bearing concrete (0.3 percent by weight of cement). Epoxy-coated bars have performed well where the concrete contained up to 1.2 percent chloride, but a breakdown of the coating was detected in chlorides at 4.8 percent, indicating finite tolerance limit for chloride. The best durability was exhibited by the stainless clad reinforcing bars.

9.5 Carbonation of Concrete

The corrosion of depassivated steel in reinforced concrete has focused attention to the reactions of acidic gases such as carbon dioxide with hydrated cement and concrete. As a result of the reaction of carbon dioxide, the alkalinity of concrete can be progressively reduced, resulting in a pH value below 10.

The process of carbonation of concrete may be considered to take place in stages. Initially, CO_2 diffusion into the pores takes place, followed by dissolution in the pore solution. Reaction with the very soluble alkali metal hydroxide probably takes place first, reducing the pH and allowing more $Ca(OH)_2$ into the solution. The reaction of $Ca(OH)_2$ with CO_2 takes place by first forming $Ca(HCO_3)_2$ and finally $CaCO_3$, the product precipitates on the walls and in crevices of the pores. This reduction in pH also leads to the eventual breakdown of the other hydration products, such as the aluminates, C-S-H gel and sulfoaluminates.

The relative humidity with which the pore solution is in equilibrium greatly affects the rate of carbonation. The relative humidity controls the shape and area of the menisci at the air-water interfaces of the pores; at relative humidities greater than 80 percent, the area of the menisci contacting the air becomes quite small, resulting in a low rate of absorption of CO_2. At relative humidities below 40 percent, no menisci exist and the pore water is predominantly adsorbed water and does not effectively dissolve the CO_2. Consequently carbonation occurs at a maximum rate between 50 and 70 percent relative humidity. In addition to atmospheric conditions, carbonation rate is also influenced by the permeability of the concrete, and the cement content of the concrete. Cement content of approximately 15 percent produces a concrete relatively resistant to carbonation. An increase over this level produces marginal increases, while below this, results in a precipitous drop in resistance. Generally, it is found that good compaction and curing cause larger improvements in concrete permeability and resistance to carbonation than minor alterations in mix design.

Several workers[104]-[107] have concluded that carbonation depth is proportional to the square root of time. The proportionality constant is a coefficient related to the permeability of the concrete. Factors, such as cement content in concrete, CO_2 concentration in the atmosphere, and the relative humidity, in addition to normal factors such as concrete density, affect the value of this coefficient. If the depth of carbonation is measured in mm and the time in years, the average coefficient for precast prestressed quality concrete is < 1; for high strength concrete used in bridges an average value of 1 is found, while normal in situ reinforced concrete, an average value of 4–5 has been recorded. If the value of 1 is used and reinforced concrete is designed with a cover of 25 mm, predicted time for the carbonated layer to reach the steel would be 625 years. Some doubt may exist with regard to this prediction, since some authors[107] have stated that the actual relationship between depth of carbonation and time may be between linear and square root of the time making the above prediction optimistic. In addition, higher levels of carbonation can lead to densification and blocking of pores, which is beneficial, but carbonation can also lead to carbonation shrinkage and cracking, especially when carbonation occurs at relative humidities between 50 and 75 percent.

It has been clearly shown[105] that concretes with higher levels of fly ash ($\cong$50 percent) have increased carbonation, especially when poorly cured. However, the carbonation of concretes containing lower levels of fly ash (15–30 percent) is generally similar to or slightly higher than that of the control concretes. This increased carbonation observed for the 50 percent fly ash concrete cannot be explained by increased permeability since it has been shown[105] that the permeabilities of these concretes are lower than those of the control. However, the lower permeabilities of these blended cement concretes is due to a discontinuous pore structure. Carbonation and shrinkage cracking may lead to an opening up of the structure, yielding continuous pores and an increase in permeability.

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2

Research Techniques, Standards and Specifications

V. S. Ramachandran

1.0 RESEARCH TECHNIQUES

Advancements in the science and technology of cements and admixtures are related to the utilization of different techniques and proper interpretation of the data derived from them. This chapter contains a brief description of some of the tools that have been commonly employed in cement science and also of those that may have potentiality in cement investigations. Examples of the application of these techniques for investigating the effect of admixtures on cement and concrete are provided in other chapters in the book. A brief discussion of the standards and specifications on cement and concrete with reference to North American, Canadian and RILEM standards and specifications is also included.

1.1 X-ray Diffraction

X-ray diffraction is one of the established techniques used in cement science. It is capable of identifying, estimating and elucidating the structure of many unhydrated and hydrated phases of portland cement. It cannot, however, be efficiently used for C-S-H and other phases which are extremely fine-grained and nearly amorphous. In such investigations other techniques may be usefully employed. X-ray diffraction is used to follow the kinetics of hydration of cement both in the presence and absence of admixtures. Various hydration products that are formed at higher temperatures may be identified by x-rays. Automatic/manual search and match programs are available for looking through operator-created subdirectories for compounds in concrete. This alleviates the painstaking, physical comparison. Another possible application of x-rays is for the determination of the specific surface area of hydrated portland cement by low angle x-ray scattering. The correct determination of the specific surface area of cement pastes for different conditions of exposure to H_2O is important for a correct interpretation of the model of hydrated cement. One of the advantages of this method is that the surface area can be determined without degassing. Initial results suggest that a completely saturated cement paste has a specific surface area of about 700 m^2/g, which when d-dried shows a value of about 220 m^2/g. Oven drying decreases the area further to 180 m^2/g.[1] In concrete quartz, feldspar minerals, ettringite, monosulfoaluminate, chloroaluminate, carboaluminate, portlandite, calcite, dolomite, etc., can be identified by using this technique.

1.2 Differential Thermal Analysis

In the DTA technique, the heat effects associated with physical or chemical changes are recorded as a function of temperature or time, as the substance is heated at a uniform rate. Exothermic or endothermic reactions caused by reactions such as crystal inversion, dehydration, decomposition, oxidation, reduction, chemical reactions, and destruction of lattice are detected by DTA. In the DTA technique, the temperature difference (termed *differential temperature)* between the sample and a reference material is continuously recorded as a function of temperature of the furnace, reference material or time. The method has been used for both qualitative and quantitative work in cement chemistry. Identification, kinetics, and a study of the mechanism of reactions are some of the applications of this technique in cement science. In many instances this technique detects a substance that may not be observed using x-ray diffraction.

DTA has also been used to study the mechanism of the clinkering reaction and the burnability of the raw mix to form cement clinker.[2] The kinetics of hydration of cement minerals and cement has been extensively studied by DTA.[3] The DTA technique has been used to identify chemical admixtures such as salts of hydroxy-carboxylic acids.[4] The application of DTA in cement chemistry has been reviewed in a book by Ramachandran.[5]

Differential Scanning Calorimeter (DSC) has also been applied successfully in cement science for qualitative and quantitative evaluation of various hydration products. In this technique, the sample is maintained isothermally with respect to an inert material by supplying heat to the sample or inert material. The heat energy required to maintain isothermal conditions is recorded as a function of time or temperature.

1.3 Thermogravimetry

Thermogravimetric analysis (TG) permits determination of weight changes that occur when a sample is continuously heated at a uniform rate. It differs from the static or semi-static method in which the sample is held at a constant temperature for a desired length of time. The TG technique provides information on the thermal stability of a particular sample, composition of the intermediate and of the residue.[6] In cement chemistry it has been applied in conjunction with differential thermal analysis to follow hydration reactions. The first derivation of change in mass (DTG) can also be used for identification purposes. A modified TG unit for use under controlled humidity conditions has been developed and used for plotting the adsorption-desorption isotherms of the hydrated C_3S and cement.[7] The TG method may be used to estimate free lime in hydrated portland cement. The method shows, for example, that compared to C_3S + 0% $CaCl_2$, hydration in the presence of excess of $CaCl_2$ results in lower amounts of calcium hydroxide, though the degree of hydration is greater in terms of the disappearance of C_3S. Thus it could be concluded that, in the presence of excess $CaCl_2$, the C-S-H product has a higher than normal C/S ratio. The TG method cannot be applied to detect phase transformations in which no loss in weight occurs.

Evolved Gas Analysis measures the quantity of water liberated and the water vapor pressure as a function of temperature. Water produced by dissociation is passed through P_2O_5. Current passes through the P_2O_5 layer and the adsorbed water is electrolyzed and measured coulometrically. Characteristic peaks are obtained for calcium aluminum monosulfate hydrate, ettringite, gypsum, $Ca(OH)_2$, etc.[8]

1.4 Atomic Absorption Spectroscopy

The atomic absorption technique has found applications in various fields including cement chemistry. In this method a solution containing the compound of interest is sprayed into the flame to produce atoms and the absorption of radiation by the atoms in the flame is determined. The basic instrument consists of a source which is a hollow cathode lamp that emits the resonance spectrum of a particular element. The radiation passes through the flame containing atoms and to the monochromator where the absorption line is isolated. The intensity of the radiation is measured by the photomultiplier and then amplified. The read-out systems consist of meters and strip charts. Digital read-out systems are also available. The atomic absorption method may be used to determine elements such as Al, Ca, Si, Sr, Na, K, Fe, Mg and Mn in cements. Interference and matrix effects are minimized using the standard solutions of standard cements. Sulfates and chlorides in cements may be determined indirectly. For the estimation of sulfate, an accurately measured excess of $BaCl_2$ solution is added to the sulfate solution and the unreacted excess Ba is determined. Similarly, chloride can be determined using $AgNO_3$ solution. Atomic absorption is useful for the determination of various elements in the clinker and can also be applied to follow the amount of free chloride available in the hydrating cements or cement minerals containing $CaCl_2$.

1.5 Conduction Calorimetry (Isothermal)

The reaction of portland cement and its components with water is an exothermal process. Depending on the temperature, water-solid ratio, particle size and composition, the intensity of heat liberated varies with time. Much of the heat in the hydration of cement is given off in the first few days. Measurement of the rate of heat evolution provides information on the rate of hydration in the presence of admixtures. In conduction calorimetry the rate of heat liberation is recorded as a function of time. In one type of conduction calorimeter there is a watertight block containing six chambers. Each chamber contains a teflon-coated sample cup into which a known amount of sample and water are mixed. Six samples may be analyzed simultaneously. The block is placed in a constant temperature bath. The heats given off by the reactions at different times are carried by thermopiles and the signals are amplified and registered in a computer system. The rate of heat conduction is plotted as a function of time. Portland cement gives an initial peak immediately after contact with water, a second peak in a few hours for C_3S hydration, and sometimes it is followed by a hump for C_3A reaction. Accelerators not only increase the peak intensity of the C_3S exotherm but also decrease the time at which it appears. The conduction calorimetric curves also provide a relatively quick estimate of the time of setting times of cement containing admixtures. The area under the curve can be used to calculate the total heat developed within a particular time interval.

1.6 Potentiometric Methods

A quantitative analysis of calcium chloride is often needed whether it is to be added to cement or is present as a component of the de-icer salt or is in different forms in a hydrated cement paste or hardened concrete. Several methods have been suggested for this purpose. The Volhard method based on titration is commonly used. The potentiometric titration has also been successfully employed for the quantitative estimation of chloride in cements, mortars and concrete. In this technique, glass electrode-Ag•AgCl electrode combination may be used. The sample is treated with HNO_3, filtered, and titrated with 0.1 M $AgNO_3$ solution. The potential after each 0–10-ml addition is recorded. By determining the potential break, a corresponding volume of the titrant is obtained from which the percentage chloride in the sample is calculated.

1.7 X-Ray Fluorescence Analysis

If a sample is irradiated by an intense x-ray beam, the elements in the specimen emit their characteristic x-ray spectra. The wavelengths of the spectral lines may be used to identify an element, and the intensity of the line determines the concentration of the element. This technique is different from the x-ray diffraction method in that the elements rather than the compounds are identified and estimated. Noncrystalline substances are also amenable to this analysis. The method is commonly used for elements present in concentration >0.1% but lower concentrations can also be determined. Analysis of elements above about atomic no. 12 is accomplished within a fraction of the time needed for the usual wet chemical analysis. In many cement production operations, the x-ray fluorescence technique has replaced the chemical methods of analysis. It has also been used for chloride estimation in cements and concretes.[9][10] The typical diameter of analysis area is 20–30 mm, the depth of analysis being tens of μm and the detection limit is 10^{-9} g.

1.8 Neutron Activation Analysis

In this method, the sample is irradiated by thermal neutrons from a nuclear reactor. The interaction of neutrons with the nucleus in the sample produces radioactivity. The emission of both beta and gamma radiation is measured by detecting devices. Trace quantities of elements such as Mn, Na, Cu, Cl, Si, K, Ca, S and Fe can be determined by neutron activation analysis. If an element produces a radioisotope with sufficient yield, even extremely small quantities (millimicrograms) can be determined. In most determinations, standardization is accomplished by irradiating known concentrations of the desired material and measuring this standard under identical conditions with the unknown.

1.9 Mossbauer Spectrometry

This method is based on the Mossbauer effect in which the recoil free emission and resonant reabsorption of nuclear gamma rays in solids occur. The method enables detection of differences in chemical bonding, structure and nuclear electron density. Mossbauer effect is particularly useful in studying the iron-containing compounds in cement clinker. Color in cement may be related to an isomer shift in the iron.[11] This technique has also revealed that, in the hydration of C_4AF, the hexagonal phase is essentially iron-free whereas iron atoms preferentially occupy the lattice sites of the cubic phase.[12]

1.10 Nuclear Magnetic Resonance Spectroscopy

The energies of the nuclei of certain elements, in the presence of a strong magnetic field, may be split into two or more quantized levels. By the absorption of electromagnetic radiation, transitions among the magnetically induced levels can be achieved. The study of the absorption of radiofrequency radiation by nuclei constitutes nuclear magnetic resonance. This method has been used in the determination of the structure of many organic and inorganic substances. Recently its application has been extended to a study of the states of water in cementitious systems.

1.11 Infrared/UV Absorption Spectroscopy

Infrared spectroscopy has been extensively used for organic compounds and only recently has it been suggested as a useful tool in cement chemistry. For a majority of applications, this method has been confined to the region of wavelength in the range 2.5 to 15 nm. The technique has been used with some success in the detection of organic admixtures present in cement.[13] It can also be used for differentiating the principal components of portland cement and for investigating the structural changes occurring during hydration.[14]-[16] UV absorption spectroscopy has been used to quantitatively estimate the amount of admixtures in solutions. Such studies are useful to assess the amount of absorbed admixtures during the hydration of cement and cement minerals. Absorption-desorption of sulfonated melamine superplasticizer on cement may be studied by estimating the unadsorbed admixture in solution with UV at a wavelength of 219 nm.[17] Halstead and Chaiken[18] examined 15 commercial admixtures by various methods. They concluded that UV was useful for identifying lignosulfonate but IR proved to be of greater value in identification, classification and establishment of uniformity of all types of retarders studied.

Khorami and Aitcin[19] applied Fourier Infrared Spectroscopy in diffusion reflectance mode to characterize superplasticizers. Laser Raman Spectroscopy may possibly be used as a complementary technique to infrared spectroscopy.

1.12 Electron Microscopy

Optical microscopy has been used extensively for the examination of cement clinkers and aggregates used in concrete. However, many materials of interest in cement chemistry are too small for resolution in the optical microscope and in such cases the electron microscope is very useful. The electron microscope has some features common to those of the optical microscope. The sample is placed in a high vacuum system and the cathode at 50–100 kV emits and accelerates a stream of electrons regulated by electromagnetic condenser lenses. In the transmission electron microscope, thin surface replicas are prepared and examined. The resolution of this microscope may be in the order 8–25 Å. Electron diffraction of the sample may also be obtained with this instrument. Radczewski et al.[20] appear to have been the first to apply this technique to the study of cements. The transmission electron microscope has revealed that C-S-H (I) phase is made of crumpled foils and C-S-H (II), made by bottle hydration of beta-C_2S, is cigar-shaped. In the hydration of C_3S and beta-C_2S, the calcium hydroxide phase appears as large thin plates and the CSH phase may appear as aggregated masses or flocks of small irregular elements or long rod-like particles having a tubular or reed-like internal structure, probably formed by rolling of sheet elements. In some samples, laths or needles have also been reported. The presence of $CaCl_2$ in the hydration of C_3S modifies the morphology of the hydrated product.

The scanning electron microscope (SEM) has recently played a significant role in our understanding of the microstructure of hydrated cementitious systems. The technique consists of a narrow electron beam scanning the surface of a specimen. The scattered electrons are collected by a detector and the amplified signal controls the brightness of a spot on the cathode ray tube. The SEM has a large depth of focus but its resolution is only about 200 Å. The depth of focus enables examination of a sample in a three-dimensional arrangement. Clear indications have been obtained of the presence of hexagonal crystals of $Ca(OH)_2$ and calcium monosulfate aluminate hydrate in the hydrated cement systems. Needles of ettringite and calcium silicate hydrate have also been reported, the former being larger than the latter. The general morphology of C-S-H is dependent on various factors such as the hydration period, water-solid ratio, temperature, presence of admixture, etc. It may be present as a mass of irregular small plates.

In addition to a study of the morphology of the material, some elements such as Ca, Si and Al present in the hydrated cement may be estimated using some attachments to the SEM. In the energy-dispersive spectrometer attachment, the electron beam is focused on a point of interest. X-ray photons generated by the sample are converted to electrical impulses and the chemical elements present in an area are examined. This method may be applied to determine the ratio of Ca to Si, S and Al in a cement paste.[21] It may also be used to detect the distribution of Cl ions in the cement paste formed with $CaCl_2$ as an admixture.[22] An environmental chamber can be attached to the SEM to study the sequence of products formed as the hydration of the sample proceeds within the chamber.

1.13 Surface Area

The specific surface area of unhydrated portland cement is usually determined by the Blaine air permeability method. The values obtained using the air permeability method are different from those derived from Wagner, Andreasen, and nitrogen adsorption methods. The determination of surface area using N_2 or A as an adsorbate is perhaps the closest approach to an absolute surface area measurement.

The determination of specific surface area of hydrated portland cement is much more involved. One of the methods suggested is based on the adsorption of H_2O vapor. The method uses the well-known BET (Brunauer-Emmett-Teller) equation for the determination of the amount of adsorbed water required to form a monomolecular layer over the solid. The following equation is used:

$$\text{Eq. (1)} \qquad S = a_1 \frac{VmN}{M}$$

where S = specific surface area in cm^2/g; a_1 = area covered by the single adsorbed H_2O molecule. The surface area value of hydrated cement is estimated at about 200 m^2/g. This includes the area of 20–30% $Ca(OH)_2$ contained in the hydrated product. The validity of this method using H_2O as adsorbate has been questioned because the adsorption-desorption isotherms for water vapor are not reversible at low relative pressures. Presumably part of the water is taken up by the interlayer spaces in the hydrated cement. It appears that this limitation does not apply if N_2 is used as the adsorbate. A study of the effect of $CaCl_2$ on the surface area values of hydrating C_3S and portland cement has provided important information regarding hydration mechanism and strength developments in these systems.

1.14 Helium Pycnometry

This technique has been applied with some success for the determination of the true density and porosity of hydrated cement and tricalcium silicate. A study of the flow of He into the hydrated cement subjected to different treatments has yielded important information on its structure.[23] Essentially the pycnometer consists of two cylinders with pistons (one is a reference and the other contains the sample) which are filled with He to a pressure of about 1 atm. After isolating the pistons the gas is compressed to 2 atm by moving the reference piston. This results in a decrease of volume by 50% and pressure is doubled. The sample piston and the reference piston are moved with respect to the differential pressure indicator by keeping the pressure in the two cylinders the same. Using the gas laws and assuming an ideal gas, absolute volume of a solid can be determined. If the apparent volume is known, the total porosity of the solid can be calculated. This method should be particularly useful in finding out if an admixture changes the true density of cements during hydration. For example, in the hydration of cement the absolute density decreases with the progress of hydration. It is also found that with the addition of 3.5% $CaCl_2$ consistently higher density products are formed.[24]

1.15 Microhardness

Microhardness measurement is a nondestructive method and is a measure of strength of metals and nonporous materials. The test method employs the Vicker's pyramid indentor placed in a conditioned box. Hardness is calculated by the formula:

Eq. (2) $$H_v(\text{Kg mm}^{-2}) = \frac{1854.4 \text{ X } P}{d^2}$$

where P = load (g); d = mean value of the indentation diagonals; and H_v = microhardness. Microhardness can be useful as a measure of strength development in cements and cement minerals hydrated for different lengths of time. The compressive strength bears a linear relationship with microhardness. It is a particularly valuable method for investigating the hydration of cement minerals containing admixtures because the method needs only a small amount of sample. Measurements can be obtained at different relative humidities in the absence of carbon dioxide by placing the equipment in a conditioned glove box. The following relationship holds good for cements and other materials.[25]

Eq. (3) $$H = H_o e^{-bp}$$

where H and H_o are microhardness values for the porous and nonporous sample of a given material respectively, b = empirical constant and p = sample porosity. The method yields data on the relative strength development of cements treated with various admixtures.

1.16 Mercury Porosimetry

The properties of cement and concrete not only depend on the solid phase but also on the nature of the void or pore space. In many cementitious systems, porosity can be correlated with strength on a semilog plot. In concrete, the porosity of an aggregate may indicate the strength of the aggregate-cement bond and the resistance of concrete to freezing and thawing.

Porosity and pore-size distribution of materials may be determined by adsorption techniques. A mercury porosimeter is also used to determine pore sizes in the range 25 Å to 1000 µm. The principle of the mercury porosimeter consists of determining the quantity of mercury that is forced into the pores of the material at different pressures. The minimum pore diameter penetrated by the mercury depends on the applied pressure. For example, at 5 psi, pores of 35 µm diameter are penetrated whereas at 60,000 psi, pores down to 30 Å diameter are intruded. The porosity characteristics of the cement paste may be influenced by admixtures.

At a given w/c ratio, water-reducing admixtures influence porosity and pore size distribution. For example, the total porosity is increased slightly in the presence of lignosulfonate. There is evidence that the total pore volume of pores of radius >100 Å is higher by 8% in mortar and by 30% in cement paste containing lignosulfonate.[26]

1.17 Rheology

Rheological studies of cement paste comprise a study of the deformation behavior under stress. Such studies are useful in explaining one of the roles of admixtures in cement. The rheological properties depend on water-cement ratio, type of cement, specific surface area of cement, mixing procedure, time after mixing and temperature of hydration.

A viscometer is used to measure yield stress and viscosity. In this method, the shear stress is plotted against the shear rate. If the relationship is a straight line passing through the origin the body it is known as a Newtonian liquid. Non-Newtonian fluids are not characterized by a constant value for the shear stress to shear rate. Cement paste is considered to exhibit approximately the Bingham plastic behavior according to the equation: $\tau = \tau_y + \mu_p \nu$ where τ = shear stress, τ_y = yield value, μ_p = plastic viscosity and ν = shear rate.

The coefficient of viscosity is related to the reciprocal value of the line in the plot of shear stress and shear rate and this value is related to the consistency of the material. Systems which exhibit an intercept on the shear stress axis show plastic flow behavior. The value of the intercept is called yield stress and is related to cohesion.

Superplasticizers may significantly influence the rheological behavior of cement paste. These admixtures reduce both the yield value and plastic viscosity. In an investigation of the yield value in cement paste containing SNF, Banfill[27] found that the yield value decreased as the concentration of SNF increased, and at 0.8% the value was nearly equivalent to zero.

1.18 Zeta Potential

The stability of colloidal particles is usually due to the development of charge as a result of adsorption of ions. These particles, developing the same charge, repel each other and prevent agglomeration or precipitation. Hydrated cement, especially the calcium silicate hydrates are in the form of extremely small interlocking particles and in the presence of some admixtures are dispersed. Hence colloidal chemical principles have been applied to cement-water-admixture systems.

The difference in potential between the outer fixed layer of adsorbate and the bulk of the dispersing medium constitutes the electrokinetic potential or zeta potential. The zeta potential measurements are based on the following techniques. The electro-osmosis method is based on the application of a potential to two locations in a liquid separated by a porous membrane or set of capillaries. The streaming potential method is a reverse of electro-osmosis. The sedimentation potential method is based on the sedimentary particles in a liquid acquiring a potential different from that of the surrounding liquid (Dorn effect).

Attractive forces exist in cement particles suspended in water and in time, the particles form a rigid body. Admixtures such as lignosulfonates are adsorbed on the cement particles and exert an electrostatic repulsion and thus decrease the viscosity of the system. Petrie's work[28] has shown that attractive forces existing between the surfaces of the cement particles can be neutralized by the adsorption of anionic surfactants such as naphthalene sulfonic acid condensates.

The zeta potential development in suspension of cement, alite, C_3A and $Ca(OH)_2$ containing superplasticizers has been studied. Addition of the superplasticizer results in large -ve potentials. Although with time this potential decreases, the value is still high, even at 1200 mins.

Similarly high -ve zeta potentials occur in alite and C_3A suspensions containing the superplasticizers. Large negative potentials have also been determined in suspensions containing C_3A + gypsum.

1.19 Minislump

When investigating the effect of a large number of admixtures on the workability of cement, mortar or individual cement mineral pastes, it is very quick and economical to use the minislump method. The cone used for this purpose is smaller than the regular slump line. For investigating workability of mortar, the minislump cone with a top diameter 37.5 mm, bottom diameter 75.0 mm and a height of 112.5 mm is used. The area of the pat rather than the height is determined. Ramachandran et al.[29] have investigated the effect of admixtures on the minislump of mortar and found the results could be correlated with the regular slump values. Very good correlation was obtained between the pat area (minislump) and the increased area in the regular slump cone rather the conventional height.

1.20 Trimethyl Silylation

During the hydration of cement, polymerization of the silicates occurs. The degree of polymerization is studied by using trimethyl silane (TMS) or molybdate. In this method the hydrate is treated with TMS. The silicate skeleton released after dissolving the Ca ions reacts with TMS to give a liquid which is analyzed by high pressure liquid chromatography, thin layer chromatography, IR or mass spectroscopy. The hydration kinetics, polymerization, C/S ratio, etc., are studied by this technique. It has been found that the anions in the C-S-H of C_3S pastes are chains with 2, 5, 8, (3n-1) tetrahedra. The onset of polymerization of silicate has been studied with sucrose. The onset of polymerization occurred at 8, 6, 24 and 170 hr with sucrose concentrations of 0, 1, 5, at 30 millimole/l respectively.[30]

1.21 Other Techniques

Despite the large amount of work carried out on many aspects of the science of cements utilizing different techniques, there are still many unresolved problems. Introduction of new techniques has assisted in a better interpretation of certain phenomena. Below are mentioned a few techniques which have been used to some extent in cement investigation.

The thermoluminescence technique has been used for studying the mechanism of hydration of silicates in portland cement. This technique studies the excited centers in solids, especially the structural defects.[31]

The hydration of cement and cement minerals may be followed by Emanation Thermal Analysis. It is based on the measurement of radioactive inert gas released from the sample. In cement studies the sample is labelled with Th-228 and Ra-224. At the beginning of the hydration the radon release is directly proportional to the velocity of the interaction between cement and water.[32]

Elemental analysis of portland cement is important for control purposes. One of the techniques suggested for this purpose involves a laser for vaporization of the sample and analysis of the emitted radiation.[33]

Occasionally the setting and hardening behavior of cement is modified due to the presence of small amounts of organic matter. These can be detected by thin layer chromatographic analysis.[33a] Another technique which combines the gas chromatograph with the mass spectrometer can be used for identifying admixtures, grinding aids and trace organic matter present in cements. In this method, advantage is taken of the identifying capability of the mass spectrometer and the separation capability of the gas chromatograph.

One of the problems encountered in cement chemistry concerns distinguishing free from combined water in a cement paste. Quasi-elastic neutron scattering has been used for obtaining this information. The results indicated that the capillary volume is approximately equal to the total pore volume available to liquid N_2 in pre-dried cement pastes.[34]

The electron spectroscopy for chemical analysis (ESCA) is a surface analytical technique for measuring the kinetic energy of electron photoejected from a solid surface using soft x-rays. It has been used in the study of cement hydrate. The depth of investigation is between 50–100 Å. The ESCA scans of calcium silicate gives peaks for O_2, Ca and Si.

The interaction of portland cement and its constituents with water can be followed by determination of the length change with time, using a compacted unhydrated material. A modified Tuckerman gauge extensometer has been developed for this purpose.[35]

Other specialized techniques include secondary ion mass spectrometry, ultrasonic pulse velocity measurements, photoacoustic spectroscopy, floatation studies, radio tracer technique, positron annihilation, NQR spectroscopy, and electrical measurements (based on conductivity, dielectric constants, radio frequency, dielcometry, polarization, and electrochemical potential). The microstructure of the transition zone between aggregate and cement paste and the effect of silica fume, slag, fly ash and latex has been investigated by ac impedance techniques.[36] There are excellent references which describe the application of various techniques in concrete science.[37]-[46]

1.22 Recent Conferences

Many national and international conferences on cement and concrete have been held in which papers pertaining to the application various specialized techniques for the studies of cement paste and cement components have appeared. In early 1994, two international conferences dealt with concrete admixtures. One was specific to the quantitative determination of admixtures in hardened concrete.

At the fourth International Conference on Superplasticizers and Other Admixtures held in Montreal, Canada, Oct. 11-13, 1994, several papers were related to the rheological aspects of cement, mortar and concrete. Examples are: the rheological peculiarities in cement pastes in the presence of superplasticizer and silica fume; influence of acrylic polymers on the rheology of mortars; slump loss and rheology of superplasticized mortar and concrete containing polysaccharide groups; rheological behavior of antiwashout underwater concrete; rheological modifiers for superplasticized cementitious systems; degree of flocculation in cement pastes; and plasticizing characteristics of polymers containing methacrylic acid derivatives.

Another symposium entitled "Symposium on Determination of the Chemical and Mineral Admixture Content of Hardened Concrete," sponsored by ASTM Committee C-9 on Concrete and Aggregates, was also held in Montreal, June 20, 1994. Several useful papers were presented related to the application of various techniques for estimating admixture contents. Examples are: quantitative analyses of water reducing admixtures in concrete; carbonate extraction method for determining lignosulfonate-based admixtures; estimation of nitrite-based corrosion inhibitor in plastic and hardened concrete; determination of slag content; determination of silica fume in dry cement matrix and hydrated mortar; and determination of fly ash content and slag content.

The third CANMET/ACI International Conference on the Durability of Concrete, was held in Nice, France, May 22-28, 1994. There were many papers that dealt with the application of various techniques to assess the corrosion potential, abrasion potential, chloride diffusion, alkali-aggregate expansion, de-icing salt attack, permeability, microstructure, chemical/sea water attack, freeze-thaw resistance, etc., of concrete containing admixtures.

The conference on "Concrete Technology, Past, Present and Future," held in San Francisco, March 20-25, 1994, contained overview articles on the important test methods used for the assessment of the durability of normal and reinforced concrete containing admixtures

2.0 STANDARDS AND SPECIFICATIONS

The standards and specifications pertaining to each of the admixtures are described under relevant chapters. This section contains a general review of the classification and specifications of admixtures with reference to North American and RILEM (Reunion Internationale des laboratoires d'Essais et de Recherches sur les Materiaux et lea Constructions) recommendations. The North American sources include American Concrete Institute (ACI), American Society for Testing and Materials (ASTM), and Canadian Standards (CSA).

Admixtures are used to modify the properties of mortar or concrete to make them more suitable for a particular work or for economy or for saving energy. Some of the properties modified are: increased workability without a change in the water:cement ratio; decreased water requirements without a change in the workability, retardation or acceleration of setting; creation of slight expansion; modifications of the bleeding, segregation and pumpability characteristics; reduction in heat evolution; increased rate of strength development; durability enhancement; decreased permeability; reduction in alkali-aggregate expansion; increased bonding of concrete to steel or new to old concrete; corrosion inhibition of steel; and production of colored concrete.

2.1 American Concrete Institute: Manual of Practice

Part 1 of the ACI Manual of Practice contains reports on standards related to materials and general properties of concrete. Section 212 deals with chemical admixtures. The chemical admixtures are divided into five categories: air-entraining admixtures, accelerating admixtures, water-reducing and set controlling admixtures, admixtures for flowing concrete, and miscellaneous admixtures. The pozzolans are not considered in this group. ACI committee 226 deals with ground blast furnace slag and pozzolans.

Admixtures are defined by ACI 116R and ASTM C 125 as a material other than water, aggregate, hydraulic cement, and fiber reinforcement used as an ingredient of concrete or mortar which is added to the batch immediately before or during its mixing.

The air-entraining (AE) admixture increases workability and frost resistance of concrete. Air-entrained concrete is also required for concrete which will be exposed to de-icing salts such as sodium and calcium chlorides. The addition of AE in superplasticized concrete may increase the spacing factor and decrease the surface area of the air void system. However, the resistance to freezing-thawing is not affected. In hardened concrete, AE reduces strength with moderate or high cement contents. The AE's are composed of salts of wood resins, synthetic detergents, salts of sulfonated lignin, salts of petroleum acids, and their salts and organic salts of sulfonated hydrocarbons. Some porous particles have also been used to increase the frost resistance of concrete.

Accelerators are used to reduce setting times and accelerate early strength development. They are not to be construed as antifreezing admixtures. The best known accelerator is calcium chloride but it is not recommended in prestressed concrete or in concrete exposed to a moist environment. The well known chloride-free accelerators are nitrates, nitrites and formates. Others are fluorides, carbonates, silicates and thiocyanates. Some solid materials such as calcium aluminate cement, seeds of cement, silicate minerals and magnesium carbonate may be used for quick setting purposes.

Water-reducing or set-controlling admixtures are used in air-entrained and non-air entrained concrete to reduce the water requirements for a given slump or modify the time of setting or both. They increase the strength of concrete at a given slump by reducing water requirements. High range water-reducing admixtures (superplasticizers) are similar to conventional water reducers except that they increase the fluidity to a much greater extent without affecting the surface tension of water significantly. They can be used at higher dosages without excessive air-entrainment. Water-reducing and set-controlling admixtures are subdivided into the following categories: *(1)* water reducing, *(2)* retarding, *(3)* accelerating, *(4)* water-reducing retarding, *(5)* water-reducing accelerating, *(6)* water-reducing (high range), *(7)* water reducing (high range, retarding). Many types of materials are used for achieving the above functions. They are: lignosulfonic acids and their salts, hydroxycarboxylic acids and their salts, modifications and derivatives of hydroxylated carboxylic acids and their salts, salts of melamine condensation products, salts of sulfonated naphthalene sulfonic acid, and blends of the above. Many other materials are also used and some examples are: zinc salts, borates, phosphates, chlorides, amines, carbohydrates, polysaccharides or sugar acids, certain polymeric compounds such as cellulose ethers, melamine derivatives, naphthalene derivatives, silicones and sulfonated hydrocarbons.

Admixtures for flowing concrete in which the slump is greater than 7½" with cohesive properties consist of sulfonated melamine or naphthalene condensates, or modified lignosulfonates. They are used in areas requiring maximum volume placements in congested locations. Flowing concrete is also useful for pumping purposes.

Several types of admixtures are described in Ch. 15, "Miscellaneous Admixtures." Some of them are described below.

The gas forming admixtures are added to counteract settlement and bleeding, and enable concrete to retain nearly the same volume as it was cast. Some added materials produce hydrogen peroxide and oxygen, metallic aluminum generates hydrogen, and activated carbon liberates adsorbed air.

Grouting admixtures are used in oil well operations in which concrete encounters high temperatures or pressures. They are also used in preplaced aggregate concrete and in operations in which no reduction in volume at placement is permitted. For oil well cement grouts, retarders are used. Others are bentonite, barites, gels, starch and methyl cellulose.

Expansion-producing admixtures are used to minimize the effects of drying shrinkage. The most common admixture used for this purpose is finely divided granulated iron and chemicals to promote oxidation of iron.

The bonding admixtures are formulated to enhance bonding properties of concrete. Latex is commonly used. A wide variety of latexes are formulated for this purpose.

Pumping aids have the sole function of improving concrete pumpability. The admixtures that are recommended include water soluble synthetic and natural organic polymers, organic flocculants, emulsions of various organic materials, high surface area inorganic materials and finely divided inorganic materials.

Flocculating admixtures increase the bleeding rate and decrease the bleeding capacity, reduce flow, increase cohesiveness and early strength. Synthetic polyelectrolytes such as vinyl acetate-maleic anhydride are used as flocculating admixtures.

Fungicidal, germicidal and insecticidal admixtures are used on concrete surfaces. The materials used for this purpose include polyhalogenated phenols, dieldrin emulsion and copper compounds.

Dampproofing admixtures reduce the rate of penetration of water into dry concrete. Soaps, butyl stearate and petroleum products are some of the products that belong to this category.

Permeability-reducing admixtures are formulated to reduce the permeability of saturated concrete under externally maintained hydraulic gradient. Mineral powders comprising fly ash, pozzolans and silica fume are known to reduce permeability of concrete in which the amount of cement paste is low.

Admixtures other than pozzolans have been suggested for reducing the expansion due to alkali-aggregate reaction. Soluble salts of Li, Ba and certain air-entraining admixtures have been shown to reduce the expansion to a significant extent.

The major contributor to corrosion of steel in concrete is chlorides. Some chemicals have been used to counteract corrosion. They include sodium benzoate, Ca lignosulfonate, sodium nitrite and calcium nitrite. The ACI 318/318R specifies maximum levels of chloride contents for corrosion protection.

2.2 Canadian Standards Association

The Canadian Standards Association (CSA) has several standards pertaining to admixtures. The A 266.2 M78 deals with chemical admixtures, A266.6 M85, and A 266.5 M 1981 give information on superplasticizing admixtures. A 266.5 refers to the guidelines for the use of superplasticizers whereas A 266.6 M85 deals with the requirements of superplasticizers. A 266.4 M78, provides guidelines for the use of admixtures. The air-entraining admixtures are separately treated under A 266.1. The pozzolanic mineral admixtures are dealt under A 266.3. The supplementary cementing materials such as blast-furnace slag, fly ash and silica fume come under the purview of standard A 23.5. Hydraulic slags are described in CSA A 363.

The chemical admixtures are divided into four categories. The water-reducing strength-increasing (maximum water content being 95% with respect to the reference) admixtures are of two types: the normal setting type increases strength as a result of reduction in water requirement, and the set-retarding type which also decreases water requirement but retards the set (minimum setting time, +1 hr and maximum setting time, +3 hrs). With these admixtures the minimum compressive strength increase at 3, 7 and 28 days is 115% with respect to the reference concrete. There are two types of set-retarding admixtures. The type R moderately retards the setting (initial set: min 1 hr and max 3 hrs) and type RX that produces extended set times (initial set: min 5 hrs and no limit on the max). Accelerating admixtures, mainly based on chloride, accelerate the set time (min 1 hr and max 3 hrs) and early strengths (125, 110 and 105% of the reference concrete at 3, 7 and 28 days). There are two types of strength-increasing admixtures designated SN and SR. Both do not affect the water requirements. The SN produces normal setting. The stipulated strength increase is 120% of the reference concrete at 3, 7, and 28 days. The SR (set retarding) type also increases the strength but retards the initial set (min 1 hr and max 3 hrs). The minimum strength requirement is 120% of the reference at 3, 7, and 28 days. The concretes containing these admixtures also have to pass length change, air-void spacing and relative durability requirements.

Two categories of superplasticizers are described by CSA, the non-flowing water-reducing type and another, the flowing type. The details of their requirements are described in a table. The maximum water content for non-flowing SPN type is 88% and compressive strength (T/Rx100x1.05) at 1, 3, 7, and 28 days, 6 months, and 1 year is 150, 130, 125, 120, 100, and 100 % respectively. The corresponding values for the flowing type is 100% at all times. There is no requirement for water reduction for the flowing type. The SPR type has similar requirements to those of SPN expect that the set time requirements are different. The minimum and maximum set times with respect to the reference for the SPN type are -1:20 and +1:20 (hrs:mins) whereas for the type SPR it is +1:00 and +3:00 (hrs:mins) respectively.

The air-entraining admixtures have to meet requirements with respect to setting, compressive strength, length change, air-void spacing factor and relative durability factor. The setting times should be a minimum of -1 hr and a maximum of +1 hr. The compressive strength defined as T/Rx100x1.05 (T = test and R = reference concrete) should be a minimum of 100% at 3 days to 1 year with respect to the reference. The length change requirements are: if R exceeds 0.03%, T/R shall not exceed 1.20%; if R is not more than 0.03%, T-R shall not exceed 0.006%. The air void spacing factor (maximum) is 200 mm and the minimum durability factor is 100 using the equation T/Rx100x1.10.

The A 266.3 dealing with the pozzolanic admixture describes the requirements for type N which is a raw or calcined natural pozzolan and type F fly ash. Both physical and chemical requirements are given. Values for pozzolanic activity index, water, drying shrinkage, autoclave expansion, reactivity with cement alkalis, requirements of air-entraining admixtures, etc., are given.

2.3 ASTM (American Society for Testing and Materials)

Most standards related to concrete and admixtures are described in ASTM volume 4.02. In order to assess the role of admixtures, many tests of concrete in the fresh and hardened state have to be carried out. Some tests relevant to the durability of concrete are also to be found in ASTM. Some of the more important tests that are applied to assess concrete containing admixtures are give below.

Standards exist for chemical admixtures (C 494), shotcrete (C 1141), air-entraining agents (C 226, C 260 and C 233), fly ash or calcined pozzolans (C 618 and C 311), ground blast furnace slag (C 618), foaming agents (C 796 and C 869), latex agents for bonding fresh concrete to hardened concrete (C 1059, C 1042), chemical admixtures for corrosion (G 109) and pigments for integrally colored concrete (C 979).

Standards related to the properties of the fresh cement paste, mortar and concrete include water soluble chloride determination in aggregates (D 1411), slump of concrete (C 143), flow table for hydraulic cement (C 230), normal consistency of hydraulic cement (C 187), time of setting by Vicat or Gillmore needles for cements (C 191 and C 266), time of setting for mortars (C 807), time of setting of portland cement pastes containing accelerating admixtures for shotcrete (C 1102), time of setting for concrete mixtures (C 403), time of setting for grouts (C 953), early stiffening for mortar or paste (C 359 and C 415 respectively), bleeding of cement paste and concrete (C 243 and C 232), heat of hydration for cement (C 186), expansion and bleeding of freshly mixed grouts (C 940), and air content and air void parameters (C 231, 173).

Some of the standards pertaining to the hardened paste or concrete include drying shrinkage (C 490), air content parameters (C 457 and C 138), effective shrinkage of epoxy resin systems in concrete (C 883), compressive strength of hydraulic cement with 2 inch cubes (C109), compressive strength of cylindrical specimens of concrete (C 39), abrasion resistance of concrete (C 779 and C 1138), compressive strength of cement mortars (C 109, C 349), shrinkage of mortars (C 596), air content of mortar (C 185), dynamic and modulus of elasticity (C 125 and C 469), flexural strengths (C 78, C 293, C 876 and C 1018), flexural strength of mortars (C 348), splitting-tensile strength (C 496) and bond strength of latex systems used with concrete (C 1042).

Tests are specified for the assessment of durability. Some of them are: determination of half potential for corrosion (C 876), potential sulfate expansion of mortars (C 452), mineral admixtures for preventing alkali-silica expansion reaction (C 441), petrographic examination of hardened concrete (C 856), chloride determination in hardened concrete (C 1152), freezing-thawing test (C 666), salt scaling test (C 672) potential volume change of cement-aggregate combinations (C 342) length changes of hydraulic cement mortars exposed to sulfate solution (C 1012), frost resistance of coarse aggregates in air-entrained concrete (C 682), potential reactivity of aggregates by chemical method (C 289), and potential alkali reactivity of mortar bars (C 227).

Standards for chemical admixtures are covered in ASTM C 494. This standard recognizes seven types of chemical admixtures. There is no clear definition of chemical admixtures. Mineral admixtures and air-entraining admixtures are not included in this standard. Type A, D , E, F and G are all water-reducing admixtures. Type A is water-reducing and should reduce water requirements by at least 5%, whereas Type F should reduce water by 12%. The setting requirements for these two admixtures are similar, i.e., the initial setting time should be earlier than 1 hr but not 3:30 hrs later; the final setting times not more than 1 hr earlier nor 1:30 hrs later. Whereas Type F should have a minimum strength of 140% of the control at 1 day, no figures are given for Type A. Strength requirements for Type F are 125% at 3 days, 115% at 7 days, 110% at 28 days and 100% at 6 months and 1 year. Corresponding figures for Type A are 110%, 110%, 110%, 100% and 100% of the control. The main differences between the requirements of Type D and Type G are water reductions of 5 and 12% respectively. The strength requirements for Type G at 1, 3, 7 and 28 days are 125, 125, 115 and 110% of the control whereas for Type D the figures are 110, 110, and 110% at 3, 7 and 28 days respectively. The Type B, being a retarder, should exhibit at least a set retardation 1 hr later than the reference but not more than 3:30 hrs later. The strengths could be 10% lower than the reference at 3, 7, and 28 days and also up to 1 year. Type C, an accelerating admixture should show early set at least 1 hr earlier but not more than 3:30 earlier. The 3 day strength should be 25% more than the control, although at 28 days it could be equal to that of the control and at 6 months and 1 year it could be 10% lower than that of the reference. Type E should reduce water requirements by at least 5% and setting properties are similar to those required for Type C. But the strength at 3, 7, and 28 days should be a minimum of 125, 110 and 110% of the control. These and other requirements are discussed in relevant chapters.

A separate standard exists for admixtures used in flowing concrete (C 1017-92). Two types, Type I (plasticizing) and Type II (plasticizing and retarding), are dealt in this standard. The minimum slump values using these admixtures should be 3.5". Compressive and flexural strengths should be at least 90% of the control, at 3 days to 1 year. The main difference is in the setting requirements. For Type I, the initial and final setting times should not be more than 1 hr earlier nor 1½ hrs later. For Type II, the initial set should not be more than 1 hr earlier and 3½ hrs later and the final set should not be more than 3½ hrs later. The strengths should be a minimum of 90% of the control at all times of testing from 3 days to 1 year. The minimum relative durability value is specified at 80.

2.4 RILEM (Reunion Internationale des Laboratoires d'Essais et de Recherches sur les Materiaux et les Constructions)

The RILEM has published a useful guide for use of admixtures in concrete.[47] In this guide, admixtures are defined as inorganic (including minerals) or organic materials in solid or liquid state, added to the normal components of the mix, in most cases up to a maximum of 5% by weight of the cement or cementitious materials. Materials such as fly ash, slag, pozzolans or silica fume which can be constituents of cement or concrete, and also products acting as reinforcement, are not classified as admixtures.

The guidelines contain information on the relative effects of the admixtures on concrete in the fresh and hardened state. The relative effects of admixtures such as water reducers and high range water reducers, setting and hardening accelerators, superplasticizers, setting retarders and air-entrainers are described in tables.

Information is given on the main and secondary effects of admixtures. For example, the main effect of superplasticizer is the increase in workability and the side effects are water reduction, change in setting times and strengths. The main effect of air entrainer is air entrainment and increased durability of concrete and the side effects are water reduction and increased workability.

A table is provided in the guide to describe the effects admixtures on the properties of concrete. The dosages are specified but other effects are described in relative terms of decrease, increase or without effect. A typical example with respect to retarders is given below. Retarders are used in dosages less than 0.5%. They are introduced with the mixing water. Air content, unit mass, consistency, segregation, final setting time, bleeding, 91 day compressive and flexural strengths, freeze-thaw resistance, shrinkage, and corrosion either remain unaffected or are increased. Initial set time and plastic shrinkage are increased. No changes result in the 28 day compressive or flexural strength , thermal expansion and modulus of elasticity.

More detailed description, in qualitative terms are provided on the main and secondary effects in a separate table in the guide. Also described are the durability aspects of concrete containing water reducers or high range water reducers. Effects on freeze thaw resistance, resistance to carbon dioxide, sea water, chemical agents such as sulfates and water penetration have been described.

2.5 British Standards (BS)

The technical barriers to trade are disappearing in Europe and this has resulted in the development of common standards. The European standards limit the upper dosage of admixtures to 5% by mass of cement.[48] Table 1 provides a list standards according to BS and EN standards. The BS standard limits the chloride content in admixtures to 0.1% when used in concrete containing embedded metals. Alkali content in admixtures is included for the calculation of total alkali content in cement.

Table 1: British and European Standards Pertaining to Admixtures

Admixture	BS No.	EN No.
Accelerator	BS 5075: Part 1	EN 934-2
Accelerating/Water -Reducing (without Chloride)	BS 5075: Part 1	----
Accelerating/Water -Reducing (with chloride)	BS 5075: Part 1	----
Retarder	BS 5075: Part 1	EN 934-2
Retarder (Mortar)	BS BS 4887: Part 2	EN 934-3
Retarding/Water-Reducing	----	----
Retarding/Superplasticizing	BS 5075: Part 3	
Superplasticizer	BS 5075: Part 3	EN 934-2
Water reducers (normal)	BS 5075: Part 1	----
Air-Entraining Agent	BS 5075: Part 2	EN 934-2
Air-Entraining (plasticizing, mortar)	BS 4887: Part 1	EN 934-3
Integral Permeability Reducer	----	EN 934-2
Pigments	BS 1014	----

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3

Admixture Interactions in Concrete

V. S. Ramachandran

1.0 INTRODUCTION

Admixtures confer several beneficial effects on concrete including reduction in water requirements, increased workability, controlled setting, accelerated hardening, improved strength, better durability, desired coloration and volume changes. The use of admixtures is generally based on trial-and-error because of an incomplete understanding of their mechanism of action. One approach is to study the interactions that occur between the admixtures and the hydrating cement components. The admixtures may remain in a free state as a solid or solution, may interact at the surface or chemically combine with the constituents of cement or cement paste. The type and extent of interaction may influence the physico-chemical and mechanical properties of concrete such as water demand, hydration kinetics, composition of the products, setting times, microstructure, strength, and durability. The practical consequences of an understanding of the cement-admixture interactions include: development of methods to estimate admixtures in fresh and hardened concrete; understanding of the compatibility between two or more admixtures in concrete; predictability of properties of concrete; troubleshooting; production of better concrete; development of new types of admixtures; standards development; and better utilization of waste and marginal materials in concrete. Two publications have described the consequences of the interaction of cement with admixtures.[1][2]

2.0 CHEMICAL ADMIXTURES

2.1 Accelerators

Accelerators are used to reduce the setting times and accelerate the hardening of concrete. Many inorganic compounds play this role, including chlorides, fluorides, carbonates, silicates, aluminates, borates, nitrites, thiosulfates, etc. Organic compounds such as triethanolamine, diethanolamine, propionate, urea, glyoxal, and formate have also been advocated for use as accelerators.

Calcium chloride is perhaps the most efficient and economical accelerator for use in concrete. Several theories have been suggested on its accelerating action.[3] Calcium chloride accelerates the hydration of tricalcium silicate. There is evidence that calcium chloride exists in different states in the C_3S paste. Based on thermal analysis and leaching studies, Ramachandran[4] has concluded that depending on the time of hydration, the chloride may exist in the free form (extractable by ethyl alcohol), incorporated strongly into the C-S-H phase (unleachable with water), chemisorbed or in interlayer position (leachable with water). Figure 1 gives an estimate of the relative amounts of chloride existing in different states in the C_3S paste to which 5% $CaCl_2$ was added originally.[5] These results may be used to explain the accelerating action, microstructural development, CaO/SiO_2 ratio of C-S-H product, corrosion potential of chlorides used in different types of cements, and intrinsic properties of portland cement. The properties of portland cement paste containing calcium chloride are not the same as those without the chloride, when compared at the same degree of hydration. Figure 2 indicates that at the same degree of hydration (as a function of the non-evaporable water content), the paste with calcium chloride has a larger porosity than the reference paste containing 0% chloride.[5a]

Calcium chloride accelerates the reaction between C_3A and gypsum. Monochloroaluminate forms after all the gypsum is consumed.[5b] Conversion of ettringite to monosulfoaluminate occurs after all $CaCl_2$ is reacted. It appears that chloride bound as chloroaluminate may not release chloride ions into the solution to promote corrosion of reinforcement. Leaching and pressure extraction experiments have shown that more chloride is immobilized by the C_3A+gypsum mixture than by C_3S or portland cement (Fig. 3).[6] It has been suggested that there is a possibility of the formation of a metastable calcium oxychloride and the precipitation of $Ca(OH)_2$ during the acceleration of cement.[6a]

Triethanolamine is used to counteract the excessive retardation caused by some water-reducing admixtures. At early stages triethanolamine acts as a retarder.[7] An examination of the thermal behavior of C_3S hydrated for different periods in the presence of 0.5% triethanolamine reveals the development of exothermal peaks that could be attributed to the decomposition of a complex of the amine with the hydrated products of C_3S (Fig. 4). This exothermic peak is not caused by the free triethanolamine. Triethanolamine is soluble in ethyl alcohol. Extraction of the paste with alcohol does not affect the exothermic peak, suggesting that the amine is not in a free state. This complex may be responsible for early retardation and possibly for the higher C/S ratio of the C-S-H product.

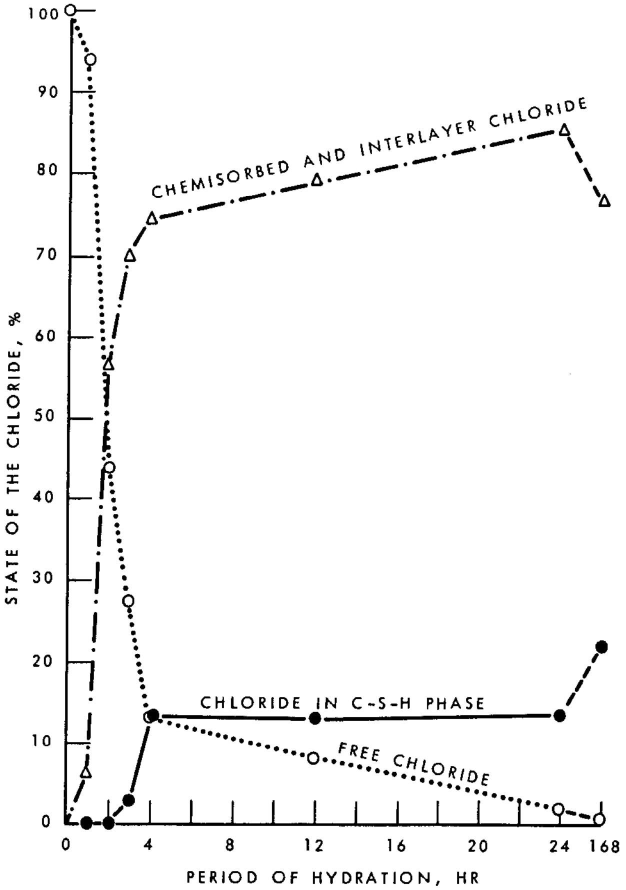

Figure 1. State of chloride in the hydrating tricalcium silicate.

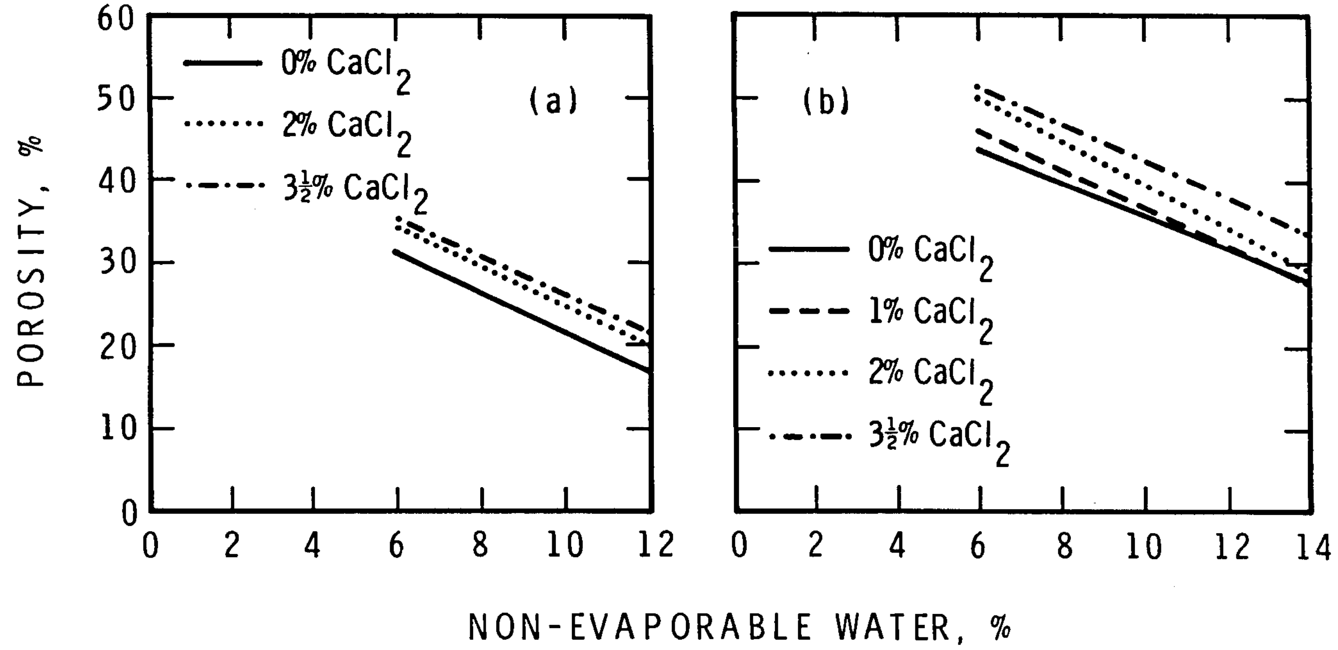

Figure 7 The effect of porosity on non-evaporable water content (a: W/C = 0.25; b: W/C = 0.4).

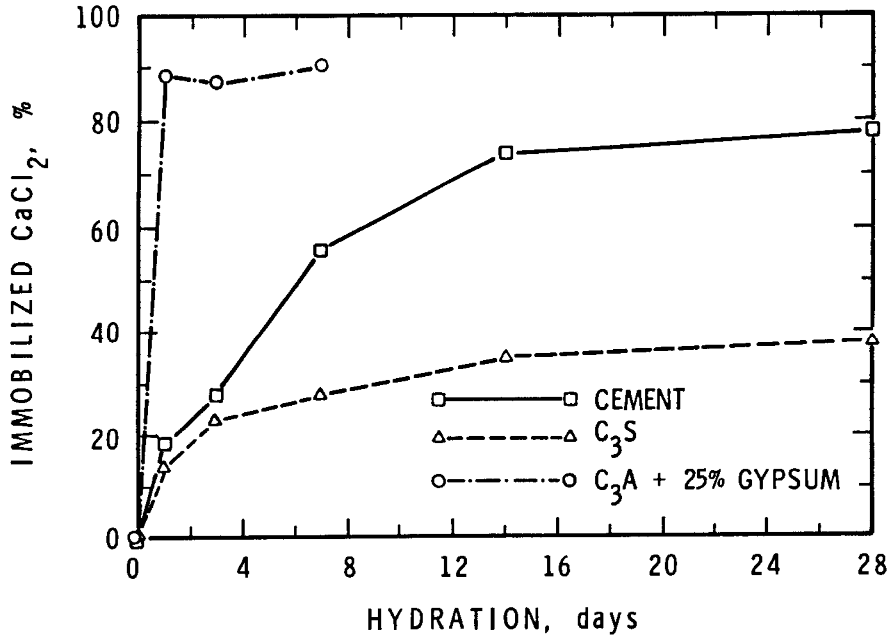

Figure 3. Amount of immobilized chloride in various pastes.

Triethanolamine accelerates the reaction between C_3A and gypsum.[8] The cation-active amine may replace Al and Ca ions on the surface of C_3A and form less crystalline ettringite.[9] In cements at a dosage of 0.1 or 0.5% triethanolamine setting occurs rapidly within 2–6 mins.[8] This can be attributed to the accelerated formation of ettringite and C_3A hydration products.

Because of the corrosion potential of the chloride admixture, alternatives to chloride have been advocated. Many formulations contain calcium formate as an accelerating agent. At equal concentrations of calcium chloride and calcium formate in cement, more ettringite is formed in the presence of formate (Table 1).[10] This may result in higher early strengths.[10a]

The increased formation of ettringite in the presence of Ca-formate is attributed to the formation of a complex $C_3A{\bullet}3Ca(HCO_2)_2{\bullet}30H_2O$ at ordinary temperatures, analogous to ettringite. Thus formate ions are more likely than chloride ions to enter the ettringite phase in solid solution and could augment the development of this phase. The effect of Ca-formate as an accelerator is influenced by the C_3A/SO_3 ratio in cement; the ratio should be higher for accelerated development of strength. The rate of formation of ettringite and formate analogue may dictate the optimum C_3A/SO_3 ratio in cements. Enhanced formation of ettringite in the presence of Ca-acetate and Ca-propionate is also explained by their ability to form hexagonal prism-type phases with C_3A.[11]

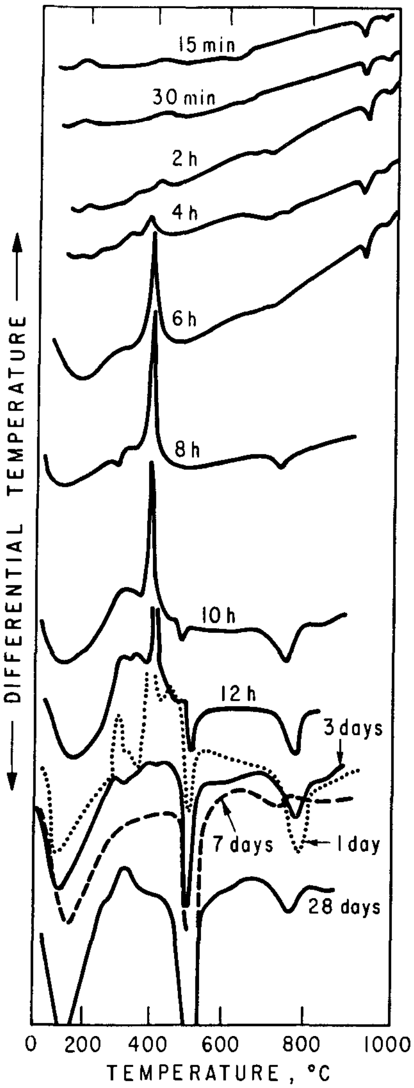

Figure 4. Thermograms of tricalcium silicate hydrated in the presence of triethanolamine.

Table 1. Amount of Ettringite Formed in the Presence of Calcium Chloride and Calcium Formate

Hydration time(min)	Water/Cement	$CaCl_2$	$Ca(HCOO)_2$
	Percent Ettringite		
10	1.39	2.09	3.49
15	1.76	2.44	3.79
30	2.02	3.21	4.36
90	2.35	4.58	6.80
120	2.41	4.80	7.72

Calcium formate is reported to accelerate the hydration of C_3S. An explanation is that formate ions interfere with the protective layer normally formed on the surface, and this implies the formation of a surface complex.[12]

Sodium carbonate decreases the setting time of cement by 2–4 hrs. X-ray studies have shown that early hydration of the constituents of cement is accelerated by sodium carbonate. After 10–12 hrs the hydration is retarded. This retardation is explained by the precipitation of calcium carbonate in the pores as a consequence of the reaction between the carbonate and lime. The carbonate in the pores decreases the permeability of water causing retardation, although at earlier ages there is an acceleratory effect.[13] In the hydration of dicalcium silicate it is believed that, in the presence of alkali sulfates and carbonates, the formation of calcium carbonate accelerates the formation of C-S-H gel.[14]

Oxalic acid may also act as an accelerator by decreasing the setting time of cement by 43% at a dosage of 2%.[14a] Compressive strength of cement is increased by 12, 10 and 9% at 5,15 and 28 days respectively. In the paste, the existence of Ca-oxalate was ascribed to the reaction between calcium hydroxide and oxalic acid. Strength development was explained by the formation of Ca-oxalate.

The addition of Na-gluconate may cause early setting consequent on the formation of a complex between gluconic acid and calcium ions in the liquid phase.[14b]

Sodium hydroxide accelerates the hydration of C_3S and early strengths but the later strengths are decreased (Fig. 5). Evidence has been obtained for the incorporation of NaOH in the hydrated phases. The accelerating effect of NaOH is explained by the formation of a metastable C-S-H containing Na and forming on the silicate surface, with a lower adhesive strength compared to the fibrous hydrate that is normally formed in the absence of the additive.[14c]

One of the mechanisms of acceleration of the silicate phase may involve precipitation. Magnesium and lanthanum salts precipitate insoluble and unreactive hydroxides very rapidly and increase the calcium ion concentration and the dissolution rate. This effect is similar to the addition of Ca salts that accelerate hydration.[5a]

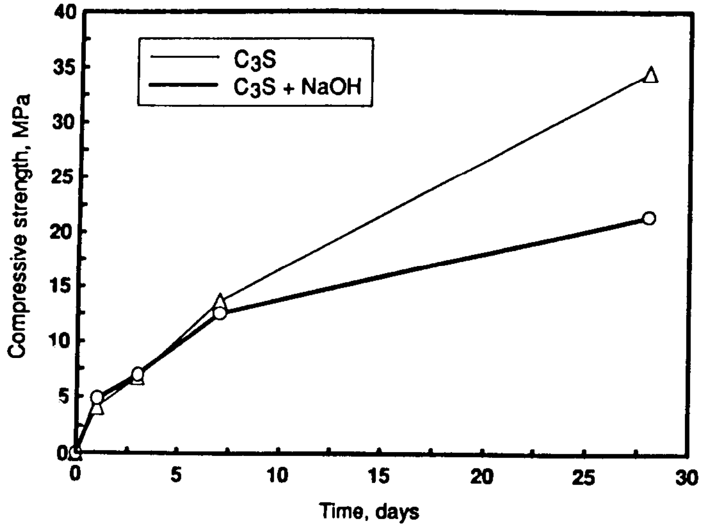

Figure 5. Strength development in tricalcium silicate hydrated in the presence of NaOH.

2.2 Retarders

Many organic and inorganic compounds have been used as retarders. The organic compounds include unrefined Na, Ca, or NH_4 salts of lignosulfonic acids, hydroxycarboxylic acids (Na, Ca or triethanolamine salts of adipic, gluconic, tartaric, succinic, citric, and heptonic acids), and carbohydrates. Inorganic compounds such as oxides of Pb and Zn, phosphates, Mg salts, fluorates and borates also act as retarders.

A considerable amount of work has been carried out to explain the retarding action of various sugars and there is divergence of opinion as to what causes the retardation effect. Theories are based on adsorption, precipitation, complexation and nucleation. In all these theories some sort of interactions are involved.[14d] Nearly all monosaccharides and disaccharides contain HO - C - C = O groups, or are converted by dilute alkalis to acids containing this group and these are adsorbed strongly by the cement particles.[15] According to Milestone, sugar and sugar acids adsorb on to Ca^+ ions on the hydrating C_3S surface and poison the C-S-H nucleating sites.[16][16a] Adsorption of glucose, for example, results in the zeta potential becoming -ve from the +ve values. Poisoning of CH nuclei by adsorption of sugars is also envisaged.[17] According to the precipitation theory, addition of mono or polysaccharides increases the concentration of Ca, Al and Fe. Sugars combine with them to form insoluble metal organic complexes, which coat the cement grains and retard hydration.[18]

Not all sugars retard cement hydration to the same extent. Non-reducing sugars (trehalose) are non-retarding, and the non-reducing sugars containing five-membered rings (sucrose, raffinose) are the best retarders. The reducing sugars (glucose, maltose and lactose) are moderate retarders.[19] The best retarders seem to increase the amount of silica in solution. No sucrose-silicate or Ca-complex has been detected. It is suggested that a half salt formed by the attachment of Ca and OH groups to the five-membered ring may poison CH and C-S-H nuclei.

In a study of various monosaccharides and polysaccharides on the hydration of C_3A, Young found that the sugars retarded hydration to different extents.[20][21] Retardation was explained by the formation of an interlayer complex of the hexagonal aluminate hydrate with the organic compounds.

A review of these theories suggests that one or more mechanisms may be operating. No one theory can be applied to explain the behavior of all sugars under all conditions of hydration. It cannot be said unequivocally that adsorption occurs only on hydrated surfaces. The formation of ettringite and its conversion to the monosulfate are affected by sugars. Some sugars accelerate the initial formation of ettringite in the C_3A-gypsum-water system and others retard it. Sucrose is an accelerator, whereas raffinose and trehalose are retarders. When sucrose is used, it is assumed that adsorption occurs on the anhydrous surface, preventing the formation of an impermeable layer of ettringite.[22]

The precipitation theory may not be valid in all cases. For example, the stability constants of Ca-complexes of various compounds do not bear correlation with their potency as retarders. A study of many complexes has shown that some are retarders and others are not. The poisoning of $Ca(OH)_2$ nuclei by itself may not always cause retardation. Although $Ca(OH)_2$ can be modified by incorporation of dyes, it does not show any retarding characteristics.[23] A nucleation effect of C-S-H cannot be ruled out. A combination of two mechanisms may occur. For example, EDTA retards the hydration of C_3S. The retarding action is explained by the precipitated gel coating of C-S-H on the hydrating C_3S, consequent on the formation of a complex between EDTA and $Ca(OH)_2$ in the solution phase.[23] The idea that retarding agents should contain the α-hydroxy carbonyl group has been questioned. According to Daugherty and Kowalewski,[24] organic compounds with two or more (OH) groups are necessary for the retardation of C_3A hydration.

Considerable work has been carried out on the hydration of cement containing hydroxycarboxylic acids. Adsorption data have been obtained of salicylic acid on cement compounds.[25]-[27] Only a small amount of adsorption occurs on the unhydrated phases compared to that on the hydrated products of cement minerals. The C_3A phase adsorbs the maximum amount. Some evidence has indicated the formation of a complex of salicylic acid with Al. The complex may be responsible for the retardation of the hydration of C_3A. Similar complexes may form with the C_4AF phase. The hydroxycarboxylic acids act more efficiently on cements containing low alkali and C_3A contents. At lower C_3A contents, smaller amounts of retarder are adsorbed, leaving larger amounts of the admixture to affect the C_3S component. The effect of alkalis may involve dissolution and interaction reactions.

Citric acid is also a retarder for cement. Early hydration of C_3A+gypsum+CH may be accelerated and the later reaction involving the conversion of ettringite to monosulfoaluminate may be retarded.[28] Acceleration in the initial stages may be due to the preferential adsorption of citric acid, which promotes the hydration of C_3A to the hexagonal phases. The later retardation may be due to the formation of a complex between citric acid and monosulfate. Koslowski and Ludwig,[29] investigating the effect of citric acid on the microstructural development of gypsum, concluded that $Ca(OH)_2$ and $CaCO_3$ impurities in the plaster form calcium citrate on the plaster of Paris hindering the development of nuclei. At higher concentrations, this compound also interferes with the morphology of gypsum crystals.

Lignosulfonates retard the hydration of C_3A and C_3S. In the hydration of C_3A, the role of sugars present in lignosulfonate is not resolved. As the hydrating C_3A irreversibly adsorbs substantial amounts of lignosulfonate, it is possible that pure lignosulfonate contributes to the retarding effect. The rate of heat development in C_3A containing commercial lignosulfonate has been compared with that developed in the presence of sugar-free Ca or Na lignosulfonate.[30] Thermograms showed that both commercial and sugar-free lignosulfonates are equally effective in retarding the hydration of cements (Fig. 6). In Table 2, the initial and final setting times of portland cement containing lignosulfonate are compared. Both the commercial and pure lignosulfonates retard setting times. In other investigations it has been reported that either the sugar-free lignosulfonate is a poor retarder or it is inert in its action on cement.[31][32] The disagreement may be due to the difficulty of preparing pure lignosulfonate and the differences in the molecular weights of lignosulfonates used.

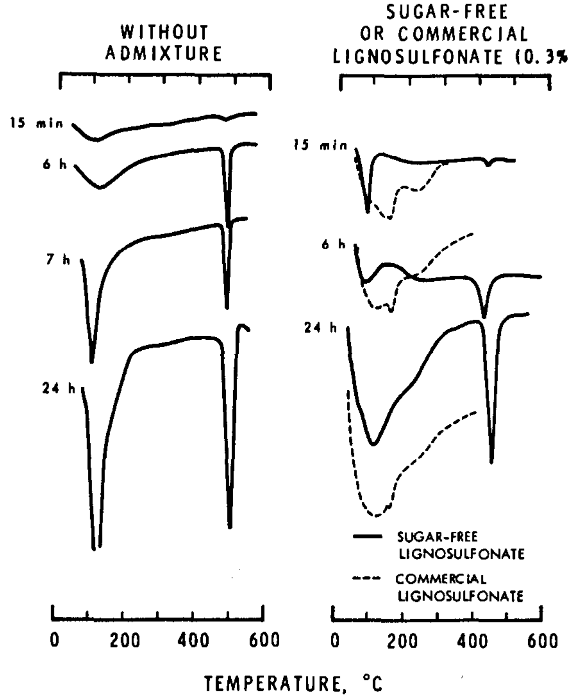

Figure 6. DTA of cement hydrated in the presence of lignosulfonates.

Table 2. Setting Characteristics of Mortars Containing Lignosulfonates

Admixture Type	Amount (%)	Initial Setting Time (Hrs)	Final Setting Time (Hrs)
Nil	——	5	9
Commercial	0.1	7	12
Sugar-Free (Na)	0.1	7	12
Sugar-Free (Ca)	0.1	7	12
Commercial	0.3	Quick Set	13.5
Sugar-Free (Na)	0.3	12	15
Sugar-Free (Ca)	0.3	14	16.5
Commercial	0.5	Quick Set	22
Sugar-Free (Na)	0.5	23	28
Sugar-Free (Ca)	0.5	22	27.5

In undersulfated cement systems, the amount of C_3A hydrate is decreased by the addition of lignosulfonate. However, lignosulfonate may accelerate the hydration of C_4AF, causing the precipitation of gelatinous Fe^+ ion on C_3S hydrate. This would result in the retardation of hydration of C_3S.[32a] Premature stiffening may occur when unrefined lignosulfonate is used. It is possible that unrefined lignosulfonate, contrary to refined sample, prevents the formation of iron hydroxide by forming a complex with iron. This presumes that iron hydroxide formed from C_4AF as well as ettringite is responsible for the setting process.[32b]

Many inorganic salts retard the hydration of cement. Some of the cations of this group have amphoteric properties. These salts form insoluble hydroxides in alkaline solution and may form coating on the cement particles.

Zinc oxide is known to be a retarder of cement hydration. It retards the hydration of C_3S without affecting the hydration of C_3A+gypsum mixture. When it is added to cement, no $Ca(OH)_2$ is detected even at one day. The formation of calcium hydroxyzincate by the reaction of $Ca(OH)_2$ with ZnO has been confirmed.[33] Lieber has examined the amount of Zn that is incorporated into the C-S-H phase when calcium hydroxyzincate is used as a retarder. At an addition of 10% Zn equivalent, 3.3.% Zn was incorporated. The C-S-H product occurred in the form of long fibers.[34]

The retarding effect of $Pb(NO)_2$ is ascribed to the very rapid precipitation of a protective layer of $Pb(OH)_2$ on the cement grain.[35]

The effect of various phosphates on the setting properties of cements has been reported.[36] Most phosphates retard the setting of cement. The adsorption of phosphate ions at the surface of the clinker phase or on the first hydration product is thought to result in the precipitation of Ca-phosphates that retard the hydration.

Although the products were not clearly identified, Tanaka et al. have reported that C_3A and C_3S hydrate slowly in the presence of Na_2SO_3 by interactions resulting in the formation of $CaSO_3$, Na-silicate, etc.[37]

Small amounts of alkali carbonates and bicarbonates retard setting of cement. Retardation is the result of the precipitation of $CaCO_3$ on alite.[37a]

Several other retarders are known to interact with cement. A comprehensive review of the interaction of various polymers and organic compounds with hydrating cement has appeared.[37b] In some instances an additive to cement by itself may not retard, but the product of chemical reaction becomes a good retarder. Tannic acid is hydrolyzed under alkaline conditions to gallic acid which is a better retarder than tannic acid.[37c] The retarding action of 1,4 dioxane was found to be due to its interaction with hydrated cement phases.[37d]

The importance of chelation is recognized in admixture science. Many retarders have α and β hydroxyl groups with respect to the carboxylate or aldehyde groups. These molecular groups are able to form chelates with the metal ions. Retardation is favored by the formation of a chelate with a moderate stability constant and limited solubility. The formation of a surface complex between the retarder and the $Ca(OH)_2$ nuclei may be envisaged. The retarder may also interact with the C_3A phase.

When retarders are ringed organic compounds, the relative positions of the group may be an important factor determining their action in cements. The action of nitrobenzoic acid and aminobenzoic acid on the hydration of C_3S depends on the relative positions of $-NO_2$ and $-NH_2$ groups with respect to the -COOH group. The o-nitrobenzoic acid , *-o*, *-m* and *p*-amino benzoic acids are retarders. The retarding action involves interaction between the surface of the silicate and the retarder.

Phosphonic acid-based chemicals are known to form complexes with inorganic species. The role of phosphonates on the hydration of cement has been investigated by Ramachandran et al.[37f] The phosphonic acids and their salts are good retarders of hydration of cement. The induction period may be increased to more than 20 hrs from 3 hrs in the presence of only 0.05% phosphonic acid (Fig. 7).

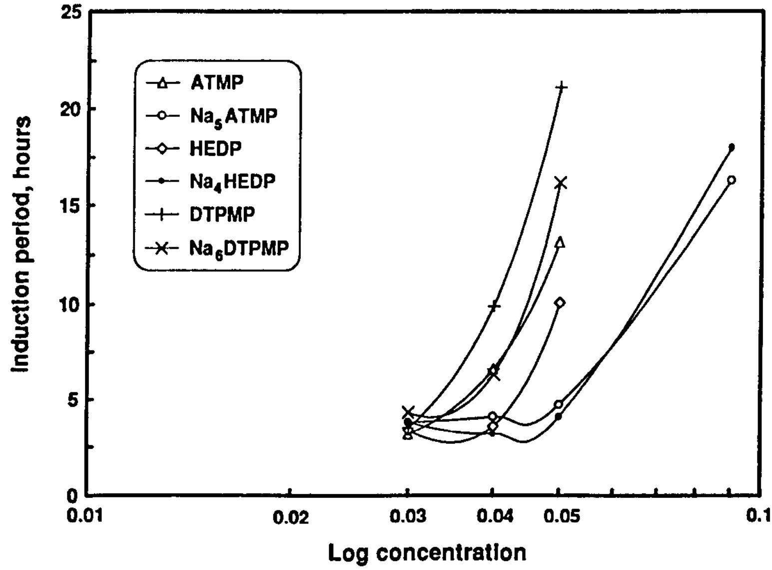

Figure 7. The induction periods for cement containing phosphonates.

The Na-salts of phosphonic acids are generally less effective than their acids in the retardation effects. In the presence of acids which induce lower pH in the hydrating system, the chelating or complexing effect with the cations is enhanced resulting in poisoning or stabilizing effects of the C-S-H product on the C_3S surface.

2.3 Water Reducers

Water reducers consist of Ca, Na, or NH_4 salts of lignosulfonic acid, Na, NH_4 or triethanolamine salts hydroxycarboxylic acid, and carbohydrates. Lignosulfonates containing (OH), (COOH) and (SO_3H) groups are more widely used than others. Hydroxycarboxylic acids such as citric acid, tartaric acid, salicylic acid, heptonic acid, saccharic acid and gluconic acid-based admixtures contain (OH) and (COOH) groups. Gluconic acid-based admixtures are used extensively. Carbohydrates include glucose, sucrose or hydroxylated polymers obtained by partial hydrolysis of saccharides. The role of water reducers (normal, accelerating or retarding) in terms of their effect on the hydration of cement is similar to that of accelerators and retarders.

The large amount of experimental data collected so far has indicated that the plasticizing action of water-reducing admixtures is related to their adsorption and dispersing effects in the cement-water system. In other words, some sort of interaction is evident.

Tricalcium aluminate, on hydration, produces a mixture of hexagonal phases that are converted to the stable cubic form. Addition of lignosulfonate retards the hydration of C_3A as well as the conversion of the hexagonal phase to the cubic form. In tricalcium aluminate hydrated in the presence of lignosulfonate, the hexagonal phases may be stabilized at least up to 14 days, whereas in that hydrated without the admixture, the cubic form appears at 6 hrs (peak in the thermogram at 300°C, Fig. 8).[5]

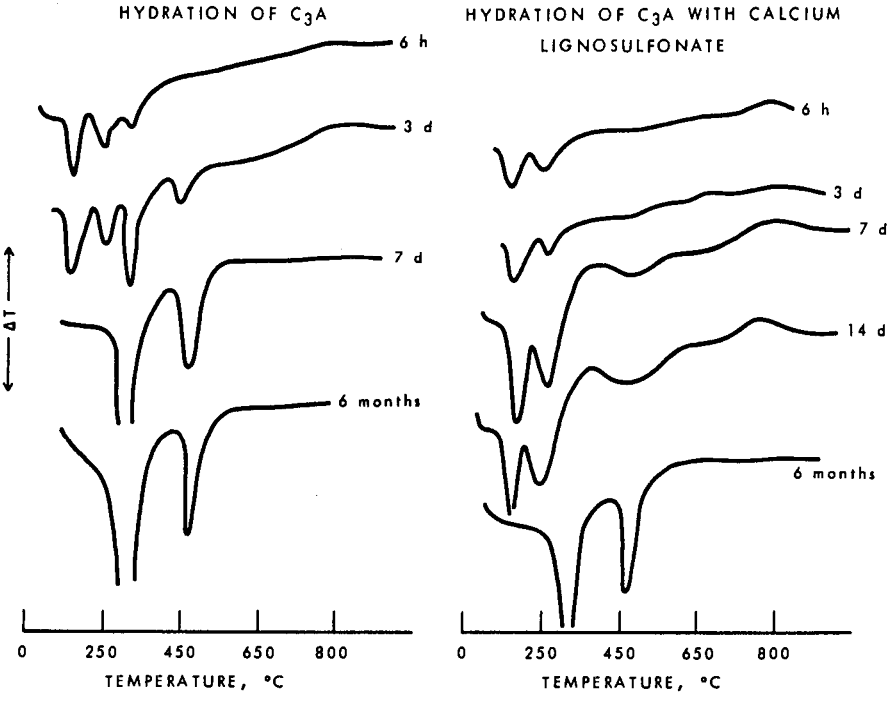

Figure 8. Effect of lignosulfonate on the hydration of tricalcium aluminate.

Adsorption isotherms cannot be obtained in the C_3A-lignosulfonate-H_2O system because the hydration of C_3A occurs during the measurements, especially at low admixture concentrations. At higher lignosulfonate concentrations, C_3A forms complex containing excess Ca^{+2} and Al^{+3}. It is possible to determine the adsorption-desorption isotherm in the system hexagonal aluminate-lignosulfonate-water, provided the concentration of lignosulfonate is kept between certain limits (Fig. 9).[38] Scanning loops in the isotherms show complete irreversibility indicating a complex formation. X-ray diffraction results indicate that the 7.9 Å (0.79 nm) peak for the hexagonal phase is shifted to 10.5 Å (1.05 nm), suggesting an increase in c-axis spacing of the hexagonal phase due to the formation of an interlayer complex. This complex would impede the conversion of the hexagonal phase to the cubic form. In a non-aqueous system, C_3A does not adsorb any lignosulfonate. The retarding effect seems to be due to the reaction between hydrating C_3A and lignosulfonate.

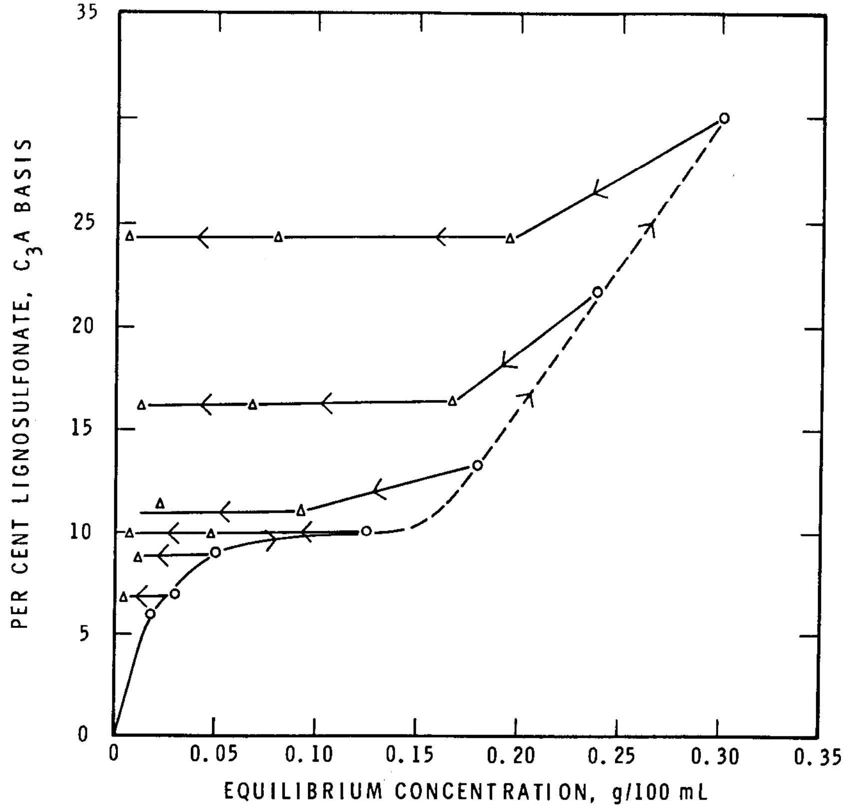

Figure 9. Adsorption-desorption isotherms of Ca-lignosulfonate on the hexagonal aluminate hydrate.

Jawed et al.[39] observed more fluidity in a cement paste containing a mixture of lignosulfonate and Na_2CO_3 than when each of them was added separately. In the presence of Na_2CO_3, the C_3A paste adsorbed lower amounts of lignosulfonate. They proposed that an ionic complex occurred between lignosulfonate and CO_3^{-2} and that it was more ionic than lignosulfonate, hence, it acted as a better dispersant. In the system C_3A-H_2O, the zeta potential in the presence of Na_2CO_3+lignosulfonate admixture combination is higher than that with lignosulfonate alone.[40]

Although there is some difference of opinion on the effect of lignosulfonate on the initial reaction between C_3A and gypsum to form ettringite, most investigations show that the conversion of ettringite to monosulfoaluminate is retarded. Adsorption of lignosulfonate on sulfoaluminate has shown that monosulfoaluminate adsorbs 4.3% and ettringite, 5.9%, indicating a retarding effect on ettringite. Considerable variation in the lattice dimensions occurs in monosulfoaluminate after adsorption.[41] One of the suggested mechanisms of the plasticizing effect may be related to a lower water demand caused by the retardation of ettringite formation and a decrease in the interlocking effect of the ettringite particles.

The hydration of tricalcium silicate is retarded by lignosulfonate. Adsorption-desorpton isotherms of the C_3S-lignosulfonate-H_2O system are plotted in Fig. 10.[42] The initial steep increase in adsorption at low concentrations of lignosulfonate is due to the formation of high surface area hydrated C_3S. At concentrations of about 0.15%, a decrease occurs followed by an increase beyond 0.3% lignosulfonate. There is no hydration at these concentrations but increased surface area from dispersion effects is responsible for adsorption. There is only partial reversibility during desorption, indicating the existence of a strongly bound surface complex involving C_3S, lignosulfonate and H_2O. Such a complex may cause retardation of hydration of C_3S.

That the hydrated C_3S paste irreversibly adsorbs substantial amounts of lignosulfonate may be concluded from desorption isotherms on the completely hydrated C_3S (Fig. 11). Even in a non-aqueous medium, the hydrated C_3S, unlike the anhydrous C_3S phase, adsorbs lignosulfonate. These results suggest that the retarding effect involves a reaction of lignosulfonate with the hydrating C_3S surface.

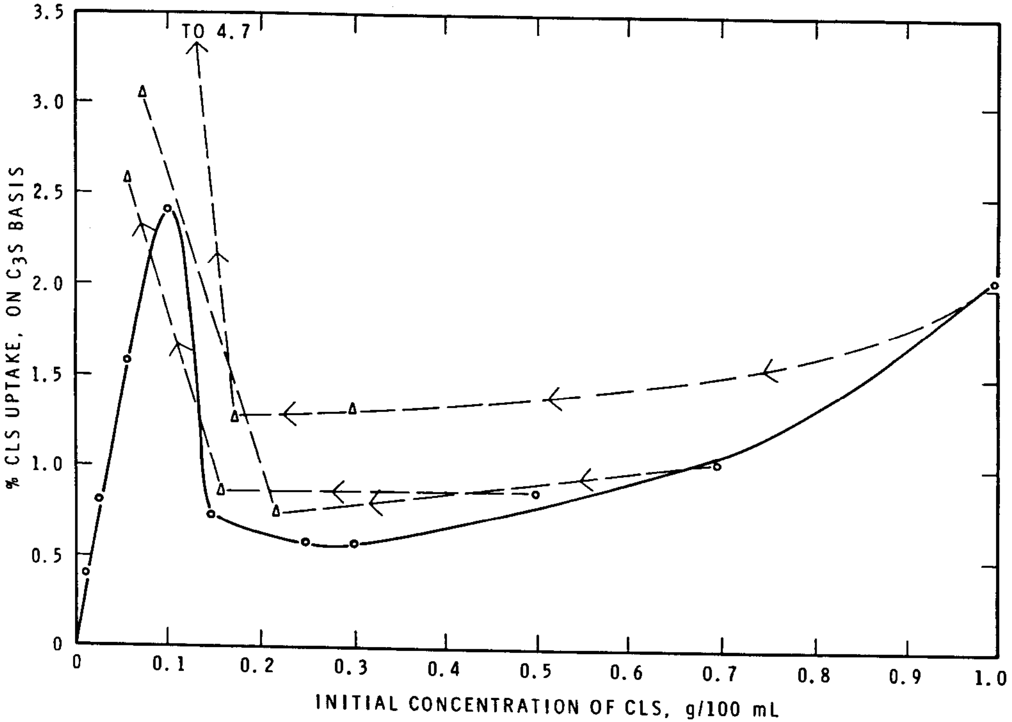

Figure 10. Adsorption of lignosulfonate on tricalcium silicate in aqueous medium.

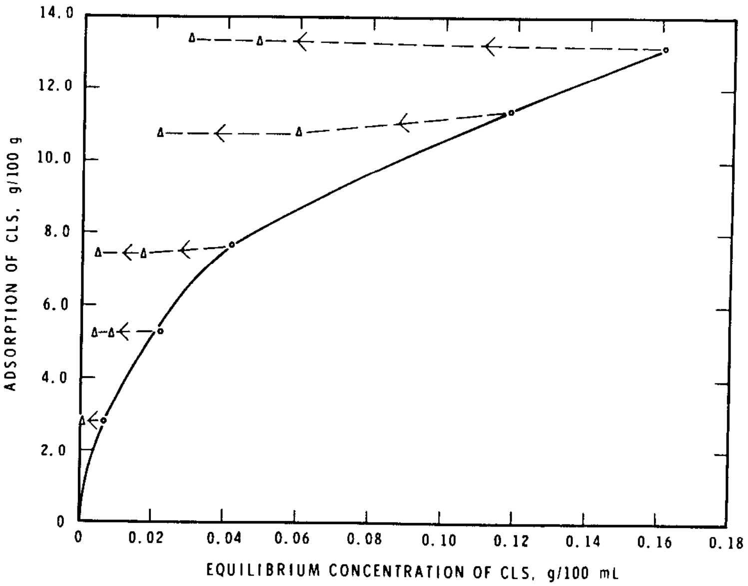

Figure 11. Adsorption-desorption isotherms of lignosulfonate on hydrated tricalcium silicate in an aqueous medium.

Since the C_3A phase adsorbs larger amounts of lignosulfonate (as soon as it comes into contact with lignosulfonate) than the C_3S phase, in the system C_3A-C_3S-H_2O, the C_3A phase may act as a sink for lignosulfonate. When lignosulfonate is added a few minutes after water has come into contact with cement, the hydration of C_3S is retarded more strongly. This would mean that the hydrated C_3A phase adsorbs lower amounts of admixture in the solution phase, leaving a larger amount of the admixture for a strong retardation of C_3S hydration. The adsorption effects of various water reducers on the hydration of C_3A and C_3S in the presence of gypsum has been studied.[42a] Lignosulfonate-K_2CO_3 combination has been used in gypsum-free cements. With this admixture combination, excess Ca^{+2} is precipitated as $CaCO_3$.[42b] The same combination of admixtures, when used with Type V cement, gave a structure of rubbery consistency. This was explained by the adsorption of lignosulfonate on the C-S-H gel.[42c] A general review of the effect of water reducers and their interaction with cement and fly ash has been discussed by Wang and Wu.[42d] The influence of organic water reducers such as Na gluconate in this system is similar to that of lignosulfonate.

The effect of lignosulfonate on cement depends not only on the amounts of C_3A and C_3S but also on the alkalis, the SO_3 content, the particle size of cement, etc. Depending on these factors and others, early set may be retarded or accelerated but the final set is generally retarded. The early acceleration of set is promoted in cements with higher aluminate/SO_3 ratios. At early times, due to the adsorption of lignosulfonate on C_3S, $Ca(OH)_2$ is not released and the rate of formation of ettringite is increased. This implies that the C_3A+gypsum reaction to form ettringite is faster than that containing $Ca(OH)_2$.

2.4 Superplasticizers

Normal water reducers decrease the water requirements of concrete by about 10–15%, whereas superplasticizers are capable of reducing the water requirements by about 30%. Most superplasticizers are based on sulfonated melamine formaldehyde (SMF), sulfonated naphthalene formaldehyde (SNF) and modified lignosulfonates. The action of superplasticizers is due to the adsorption and dispersion of the cement particles in the cement-water system. A study of the rate and amount of adsorption of superplasticizers on cement and cement compounds has provided some information on the rheological, setting, and hydration behaviors, as well as on the mechanism of hydration of cements.

Conduction calorimetric studies of the hydration of C_3A in the presence of SMF indicate that hydration is retarded. Figure 12 compares the rate and amount of adsorption of SMF on C_3A, C_3S and cement in an aqueous medium.[43] Adsorption of SMF on C_3A occurs as soon as the solution comes into contact with it. The rate and amount of adsorption on C_3A far exceeds those on the C_3S or cement. Even the hexagonal aluminate hydrate adsorbs large amounts of SMF but the rate of adsorption is lower than that on C_3A. In a non-aqueous medium adsorption is nil on C_3A but small amounts of SMF are adsorbed by the hexagonal phase. Adsorption is irreversible, indicating that a chemical interaction occurs between the hydrating C_3A and SMF. Thus, the retardation of C_3A may be explained by strong adsorption of SMF on the hydrating C_3A surface.

The reported results on the rate of hydration of C_3A+gypsum containing superplasticizers are contradictory. All three possibilities, acceleration, retardation, and neutral effects, have been reported. The rate of hydration and interconversion effects are known to depend on the types C_3A and gypsum and their proportions and methods of hydration. There is however, unanimity that the conversion of ettringite to the monosulfoaluminate hydrate is retarded by the superplasticizer. The possible interactions in the system have been investigated. Adsorption of SMF has been studied on the C_3A+gypsum system prehydrated for various periods (Fig. 13).[44]

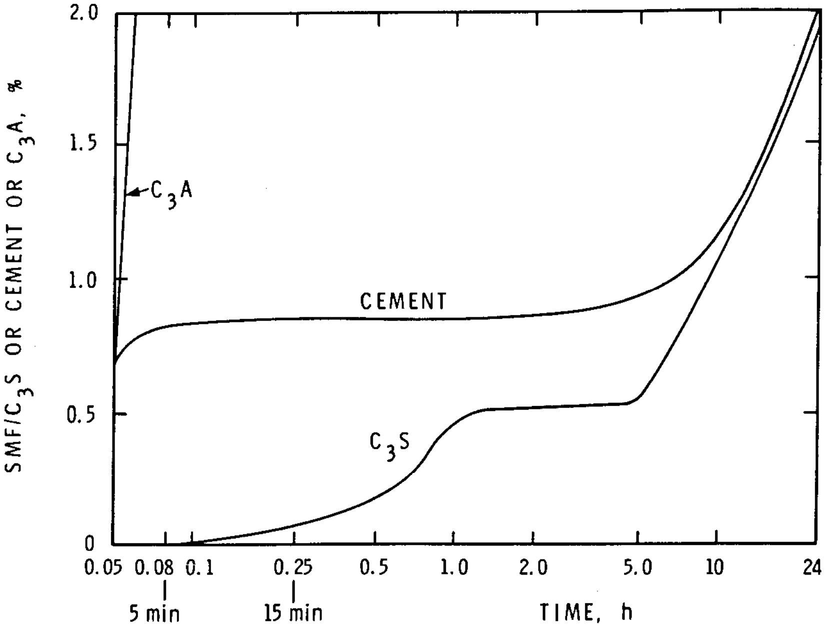

Figure 12. Adsorption of sulfonated melamine formaldehyde on cement, C_3S and C_3A.

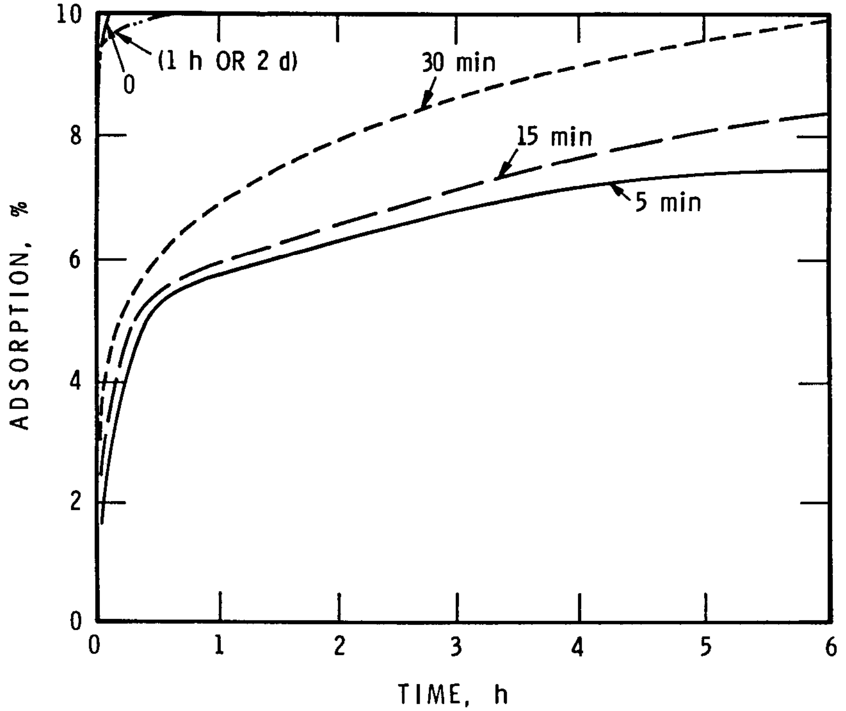

Figure 13. Adsorption of superplasticizer on C_3A+gypsum prehydrated for different periods.

The mixture that has not been prehydrated adsorbs almost all added SMF within a few minutes. The rate and amount of adsorption are lower for the mixtures prehydrated for 5–30 mins. In these samples, products are formed on the surface of C_3A so that diffusion of SMF is lowered. It is possible that if given sufficient time all SMF will be adsorbed. At 6 hrs to 2 days the main phases present are the low sulfoaluminate and C_3A. There is evidence that low sulfoaluminate adsorbs a large amount of superplasticizer.[45] The zeta potential is also increased as the adsorption increases. In other words, the repulsive forces increase as the amount of adsorption increases. Desorption experiments show that SMF is irreversibly adsorbed. A surface chemical or chemical reaction occurs between the hydrating C_3A or C_3A-gypsum mixture with SMF. The enhanced dispersion effect of superplasticizer added a few minutes after mixing water is added to concrete can be explained as follows: when it is added with the mixing water, the superplasticizer is rigidly attached in substantial amounts to C_3A-gypsum mixture, leaving only small amounts for dispersion of the silicate phases. In late addition, the admixture is adsorbed to a lesser extent on C_3A hydration products and there will be enough of the admixture to promote dispersion of the silicate phases and to lower the viscosity of the system.

The conduction calorimetric curves of C_3S hydrated in the presence of 0, 1, and 4% SMF are shown in Fig. 14. By the addition of SMF, both the induction period and peaks are shifted to later times, indicating a substantial retardation effect. Thermal studies also confirm that the formation of $Ca(OH)_2$ is delayed in the presence of SMF. Hydration characteristics of C_3S in the presence of SMF may be influenced by adsorption effects. The adsorption characteristics of C_3S exposed to an aqueous solution of SMF are plotted in Fig. 12. In the first hour a small amount of adsorption (0.5%) occurs on the surface of hydrating of C_3S and this may be responsible for the retardation of hydration of C_3S. Further adsorption after 5 hrs is due both to the increased dispersion of C_3S particles and to hydrated C_3S. Because of the increased surface created by dispersion, the concentration of SMF per unit surface area is gradually decreased and this may promote hydration after a few hours.

The interactions within the cement system are more complex because, in addition to the interfering effect of silicates and aluminates, the alkalis and SO_3 also play an important role. The effect of 0, 1, 2 and 4% SMF on cement hydration can be studied by conduction calorimetry (Fig. 15). The hump representing the accelerated reaction of C_3S is reduced or delayed in the presence of the superplasticizer. The induction period is also extended by one or two hours. Pure C_3S is retarded more effectively than cement by SMF. In cement, the C_3A and C_4AF components rapidly adsorb large amounts of SMF so that only low amounts of SMF are available in the aqueous phase to retard the hydration of the C_3S component.

The amount of adsorption of SMF on cement varies with the length of exposure to the solution (Fig. 12). Within a few seconds there is a steep increase in adsorption due to the C_3A-C_4AF components in the cement. Further adsorption does not occur for about four to five hours, after which it increases continuously. Adsorption beyond about five hours is due the hydrating C_3S component. These results suggest that the adsorption and interaction of SMF with the cement components are involved in the dispersion of the cement and retardation of cement hydration. The amount of adsorption on cement can be related to workability. With SNF superplasti-

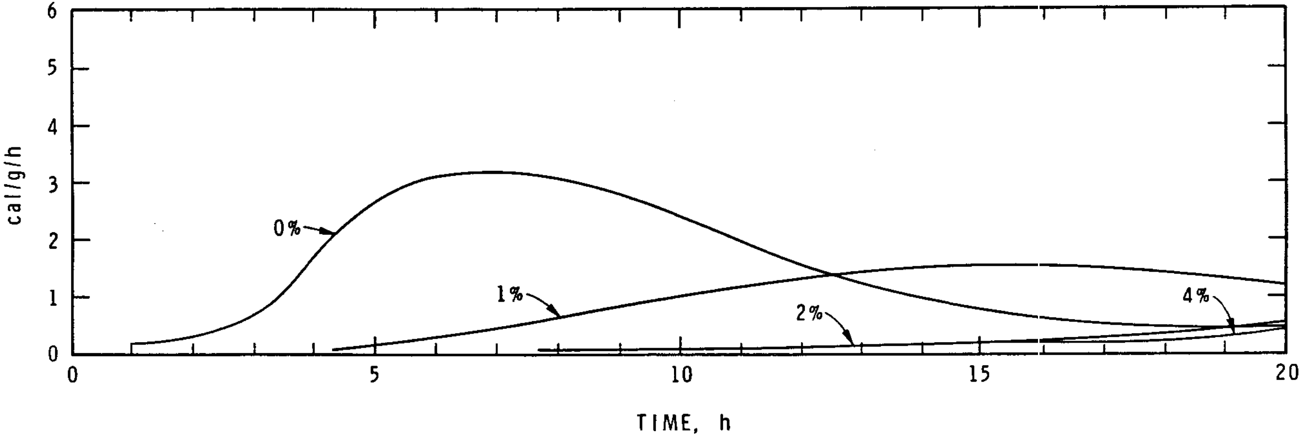

Figure 14. Conduction Calorimetric Curves of C_3S hydrated in the presence of superplasticizer.

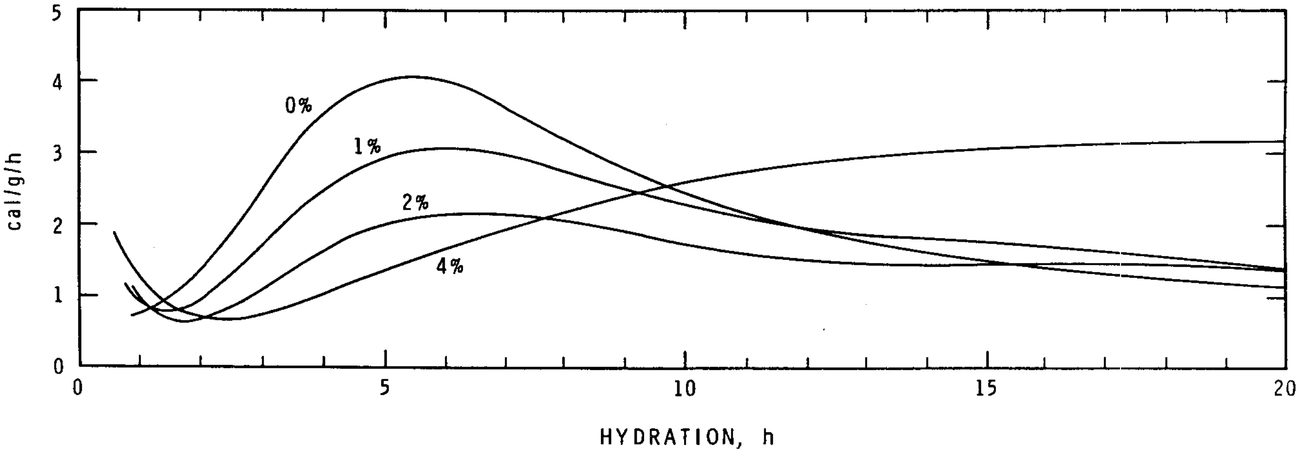

Figure 15. Conduction Calorimetric Curves of portland cement hydrated in the presence of SMF.

cizer, the minislump values increase as the amount of adsorption increases.[46] The adsorption characteristics of SNF on three types of cement reveal the role of C_3A and gypsum.[44] Figure 16 gives the amount of adsorption of SNF which decreases as follows: Type III > Type I >Type II. The C_3A/SO_3 ratios in the cements follow the same trend. That adsorption is dependent on C_3A content becomes clear considering that for the same workability, a higher dosage of superplasticizer is required for Type I than Type V cement. Using ^{35}S labelled superplasticizer and energy dispersive x-ray spectroscopy, studies have confirmed that a major portion of the admixture is taken up by the C-A-H phases and the Ca-rich C-S-H phase.[46a]

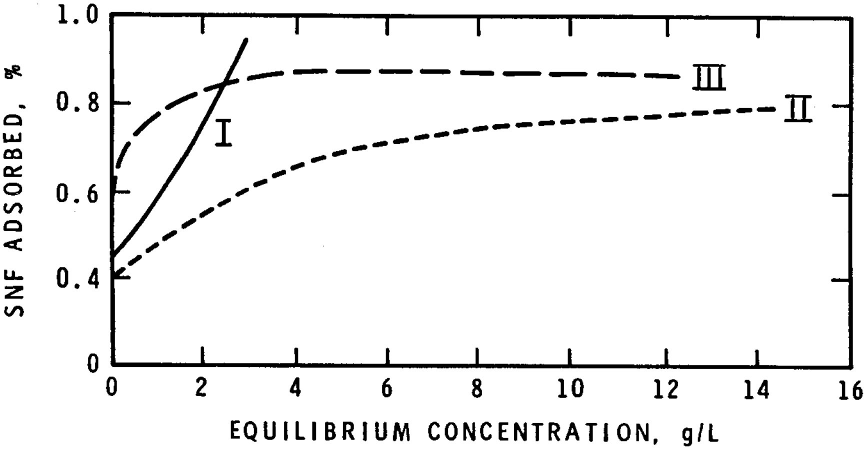

Figure 16. Adsorption characteristics of sulfonated naphthalene formaldehyde for three types of cement.

Zeta potential development in suspensions of cement, alite, C_3A and $Ca(OH)_2$ containing superplasticizers have been studied. Addition of superplasticizer results in a large negative potential. Large negative potentials are also registered in suspensions containing C_3A+gypsum. It has been suggested that a certain number of sulfonic groups linked to the polymer are adsorbed and cause dispersion. Attempts have been made to find a correlation between zeta potential and adsorption. Generally, both adsorption and zeta potential values increase as the concentration of superplasticizer added to cement is increased (Fig. 17).[47] The rate and the amount of adsorption depends on the molecular weight of the superplasticizer. The amount of adsorption increases with the increase in the molecular weight of the admixture.[47a]

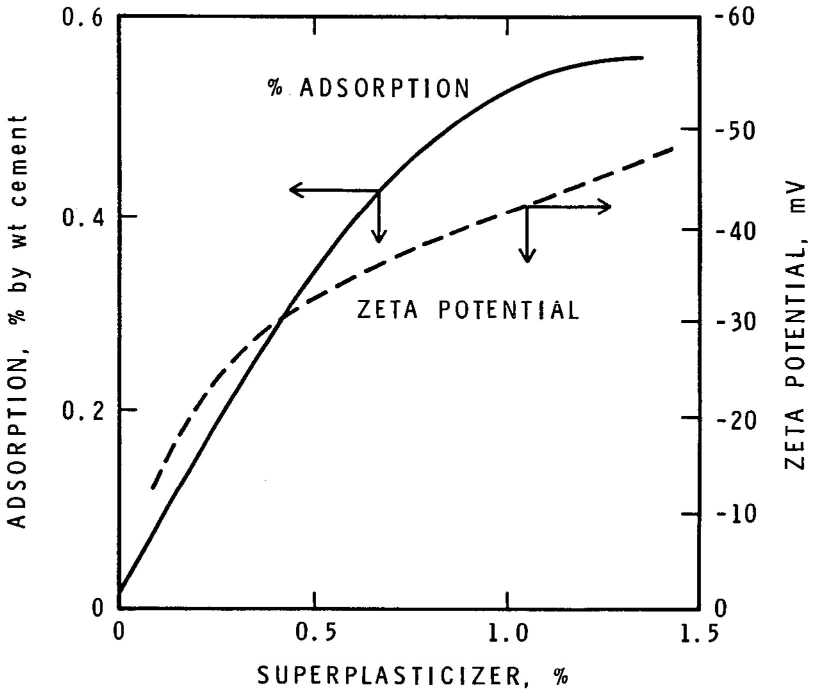

Figure 17. Influence of superplasticizer on the amount of adsorption and zeta potential.

Uchikawa et al. have tried to explain the physico-chemical properties of cement paste containing various amounts of a superplasticizer and lignosulfonate in terms of the superplasticizer-cement interactions.[47b] The fluidity of the cement paste with SNF was higher than that containing lignosulfonate. For cement flow in the range 100–200 mm, more SNF than lignosulfonate was required. More adsorption of SNF occurred for the same fluidity level. The setting time delay increased to a greater extent in the presence of lignosulfonate than with SNF. The lignosulfonate addition produced a larger amount of complex salt with Ca^{+2} in the liquid phase than the SNF addition and delayed the saturation of Ca^{+2}, resulting in the delay of setting times.

The mechanism of retardation of hydration and even dispersion may not be entirely due to the adsorption effects of the anions. In an SNF superplasticizer containing NH_4, Co, Mn, Li and Ni cations, the time for the development of maximum heat is 12.7 hrs with NH_4, and only 9.25 hrs with Ni.[48] The relative roles of cations in the superplasticizers are not well understood.

Higher than normal workability of concrete containing a superplasticizer is maintained for about 30–60 mins, after which the slump value decreases. The factors that determine slump loss are: initial slump, type and amount of superplasticizer, type and amount of cement, time of addition of superplasticizer, humidity, temperature, mixing criteria, and the presence of other admixtures in the mix. In the period during which slump loss is occurring, the C_3A phase reacts with gypsum. The product develops into a crystalline structure. The extent of reaction of C_3A and gypsum and the crystalline form of the product could have an important effect on the workability of concrete. Addition of the superplasticizer enhances the initial reaction between C_3A and gypsum. Alkalis also enhance this reaction. According to Hattori,[49] coagulation of the particles plays a more important role than the chemical bonding in slump loss. Experiments in the C_3S-SMF-H_2O system have shown rapid loss of slump occurs in this system.[50] Thus the contribution of the C_3S phase has to be taken into account. All these mechanisms involve some sort of interaction with the superplasticizer. One of the methods of maintaining the slump in superplasticized concrete is to add retarders, such as calcium gluconate to cement.[51] The retarder, although not interfering with dispersion caused by the superplasticizer, may adsorb on the cement components affecting the chemical or physical processes that cause agglomeration or interlocking of the cement particles.

3.0 AIR-ENTRAINING AGENTS

The air-entraining action is known to involve adsorption at the air-water and solid-water interfaces. The soluble surfactant ions are adsorbed on cement particles making them hydrophobic, so that as bubbles are generated during mixing, they adhere to cement. This process stabilizes bubbles, preventing their coalescence. Lowering of the surface tension may also stabilize bubbles. Anionic air-entraining agents such as sodium vinsol resin react with $Ca(OH)_2$ formed in cement hydration to form a precipitate of Ca salt. There is no general agreement on the effect of precipitation on air-entrainment. The precipitation forming around the bubble surface may help to stabilize the bubbles and prevent coalescence. If all the agent is precipitated nothing will be left over to lower the surface tension for the stabilization of the bubbles. Bruere,[52] however, found that during the mixing process, appreciable amounts of the precipitated calcium surfactant redissolve to replace the soluble surfactant ions, which are adsorbed. This implies that the air-entrainment action in concrete containing anionic agents is due to the action of soluble surfactant ions.

When air-entraining agents are used with other admixtures, the interaction between the admixtures and their interaction with cement become important for compatibility purposes. Calcium chloride should not be mixed with an air-entraining agent but should be added separately to concrete. When these admixtures are mixed together, a precipitation occurs rendering the admixture less effective.[53] In the use of fly ash concrete, excessive amounts of air-entraining agent may have to be added for the required amount of air, especially if the fly ash contains some free carbon. The carbon, being of high surface area, adsorbs a considerable amount of air-entraining agent. There is little published data on the effect of air-entraining agents on the hydration of cement. Nonionic agents do not appear to influence the hydration. A sodium oleate-based air-entraining agent is reported to retard ettringite and monosulfoaluminate formation due to the existence of an impermeable layer of a calcium oleate-aluminate hydrate salt. At high dosages, anionic surfactants may also retard C_3S hydration.[54]

4.0 POLYMER-MODIFIED CONCRETE

Polymer-modified cement is obtained by mixing either a polymer or a monomer in a dispersed, powdery or liquid form with fresh cement, and subsequent curing. Polymer latexes such as styrene butadiene, polyacrylic ester, polyvinyl acetate and others have been employed with success in concrete technology.

Not much data are available on the interaction between the polymer and the hydrating cement. In latex-modified cement, mortar and concrete, setting is delayed and this is attributed to the adsorption of polymer by the cement surface. Hydration of cement may also be retarded.[44] Generally the water permeation through the latex-modified mortar is lower than that through the unmodified mortar. Of the latexes such as styrene-butadiene, polyacrylic ester, polyethylene vinyl acetate and polyvinyl acetate, the polyvinyl acetate has the greatest permeability. This is explained by the hydrolysis caused by the reaction with $Ca(OH)_2$ and the polymer to form calcium acetate.[55]

In premix-polymer cement systems containing polyglycol and polyvinyl pyrrolidone, evidence has been obtained of the interaction between $Ca(OH)_2$ and polymer. The degree of hydration based on $Ca(OH)_2$ estimation may give lower values in these systems because some $Ca(OH)_2$ is bound by the polymer.[56] In systems containing methyl methacrylate and cement, $Ca(OH)_2$ may react with the methacrylate. In hydrating cements many other polymers may also interact with $Ca(OH)_2$. Substantial strength development in polymer-impregnated cement may involve surface interaction between monomer/polymer with the hydrated cement. The full implications of interactions between polymers and cement have yet to be explored.

5.0 MINERAL ADMIXTURES

The effect of mineral admixtures such as fly ash, silica fume, and rice husk ash is explained by their chemical reaction with the $Ca(OH)_2$ formed during the hydration of portland cement. This reaction results in increased strengths, lower permeability, better resistance to chemical attack and alkali-aggregate expansion.

A large amount of work has been carried out on the effect of fly ash on the properties of cement paste. Recent work has shown that in cement containing silica fume, the reaction between lime and silica fume results in microstructural changes. In normal portland cement pastes containing no silica fume, at all curing times, the porosity determined by helium does not differ from that by Hg porosimetry. In Fig. 18, the porosities (Hg or He) of cement pastes containing 0, 10 and 30% silica fume and hydrated for 1, 3,7, 14, 28, 90 and 180 days at two water-cement ratios are compared.[57] Table 3 gives the designation of these mixes. In pastes containing silica fume, porosity determined by Hg is lower than that by He, although He is a smaller molecule. This would indicate that the pore structure of the cement paste is changed in the presence of silica fume.

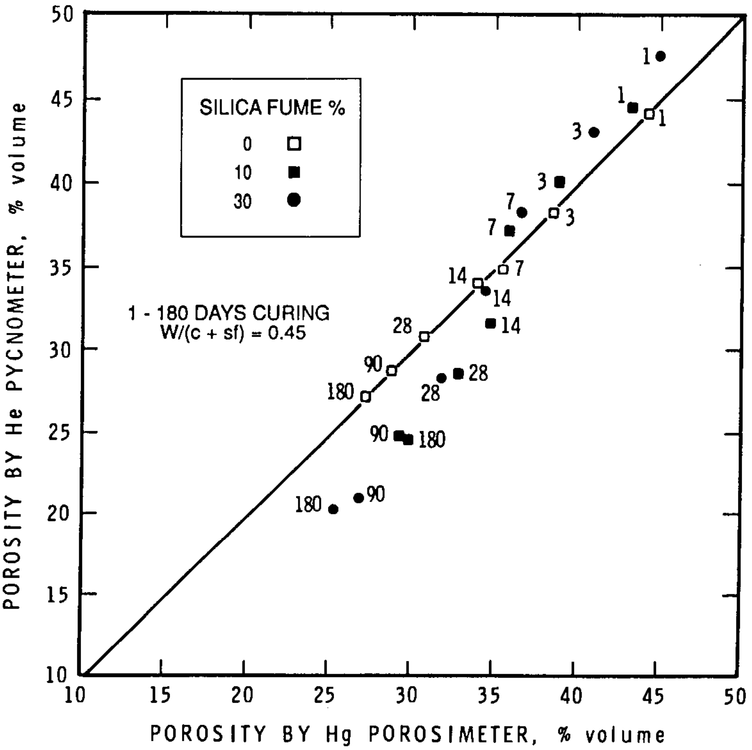

Figure 18. Comparison of porosities determined by He pycnometry and Hg porosimetry on cement-silica fume pastes.

Table 3. Nomenclature Adopted for Silica-Fume Cement Pastes

Silica Fume, %	Water/ (Cement + Silica Fume)	
	0.25	0.45
0	S^1	S^H
10	P^1	P^H_{10}
30	P^1_{30}	P^H

Figure 19 compares the first and second Hg intrusion curves for pastes cured for 90 days with 0,10 and 30% silica fume. The total porosity is the same after first and second intrusions, although pore-size distribution curves show differences. At larger dosages of silica fume, the second intrusion shows the development of larger pores. These pores are formed when high pressure Hg breaks some of the pores with narrow openings during the first intrusion. Consequently, the pore volume becomes greater in the range 3 x 10 to 3 x 10^4 nm. The presence of such pores must decrease permeability and resistance to chemical attack. Similar results have been obtained in fly ash-cement blends.

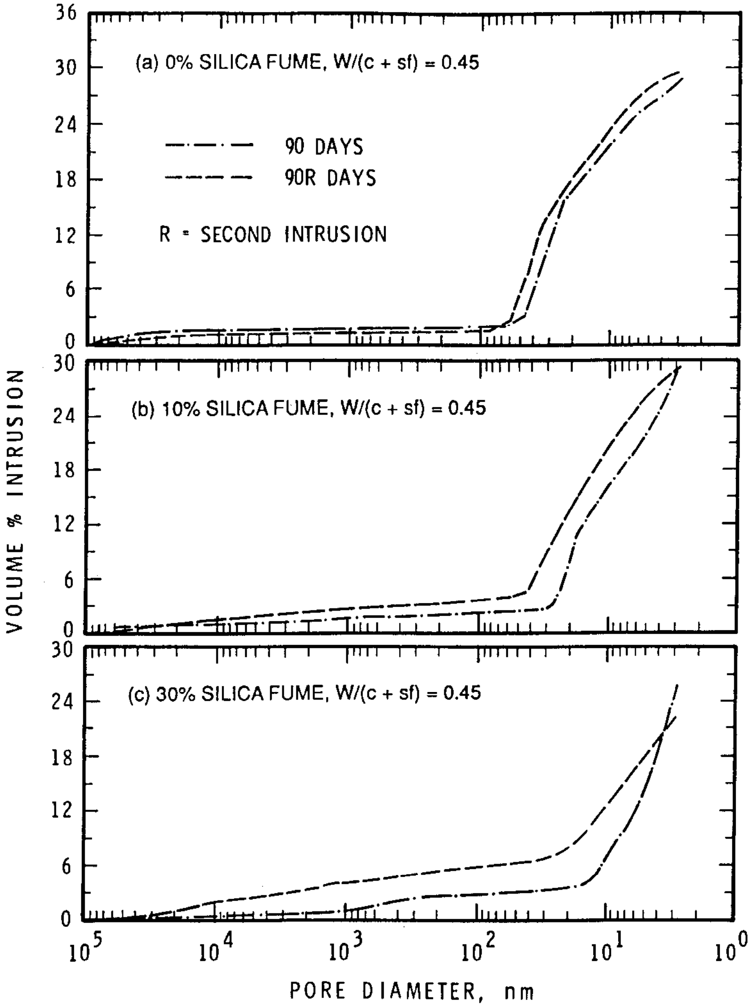

Figure 19. Pore structure of cement paste containing silica fume.

Another consequence of silica fume-$Ca(OH)_2$ interaction is an increased shrinkage of the paste with 30% silica fume. This may be due to the absence of $Ca(OH)_2$ which would have restrained shrinkage otherwise. Pozzolans are known to reduce alkali-aggregate reactions. This may be due to some chemical interactions. Potential explanations are: the presence of low amounts of alkali released by the cement, removal of $Ca(OH)_2$ by chemical interaction, lower permeability, and the formation of non-swelling lime-alkali-silica complex.

6.0 MISCELLANEOUS ADMIXTURES

Several types of admixtures which do not fall under any of the above categories are discussed below. Most of their action is related to chemical interactions.

Gas producing admixtures are used to reduce expansion of concrete in plastic or hardened state. A variety of metals such as Al,Mg,Zn is used for this purpose. These metals react with the alkali in the cement to produce H_2 by a reaction such as follows: $2Al+2OH+2H_2O = 2AlO_2^-+3H_2$. Expansion of concrete in the hardened state may be achieved by using iron filings containing rust-promoting agents. Rusting is an oxidation reaction. Other expansion-producing agents include $C_4A_3S+CaSO_4+CaO$, monosulfoaluminate + gypsum, and CaO. Their role depends on the production of ettringite or $Ca(OH)_2$.

Action of some of the waterproofing admixtures depends on chemical interactions. One of these admixtures, based on stearates, is applied as a coating on concrete. The stearate reacts with the $Ca(OH)_2$ formed in cements forming calcium stearate. This compound coats the surface of the pores and acts as a waterproofer.

The flocculating admixtures are used to decrease bleeding and laitance in concrete. Polyelectrolytes such as sodium polyelectrolyte are used. The mechanism of their action is based on the interaction of charged groups in the chain with cement particles. Adsorption and linking of cement particles result in the flocculating effect.

The quick-setting admixtures are different from the conventional accelerators in that they promote setting to occur within a few minutes to an hour. For very rapid setting occurring within a few minutes compounds such as sodium aluminate, sodium silicate or sodium carbonate are used. They accelerate the C_3A hydration as follows:

Eq. (1) $C_3A + 2NaX + Ca^+ + water = \underset{\text{(fast setting compound)}}{C_3A{\bullet}CaX_2{\bullet}H_{12}} + 2Na^+$

In addition, setting is accelerated by the interaction of Ca^{+2} and OH^- released by the hydration of C_3S to form an insoluble compound such as C-S-H, C_4AH_{13} or $CaCO_3$. Although they rapidly set, they do not develop strengths.

The water-retaining or viscosity modifying admixtures are high molecular weight soluble polymers which in aqueous medium have increased viscosity because of their interaction with water. These compounds are used to decrease the segregation/bleeding in cement paste or mortar. They comprise cellulose ethers, alginates and polyethylene oxides. Polyethylene oxide with expanded long chain molecules increases the viscosity of H_2O by interacting with each other and with water through hydrogen bonding.

Several compounds are suggested for use in concrete to retard or inhibit corrosion of the reinforcement. Anodic inhibitors consist of Ca/Na nitrite, Na benzoate, etc. The mechanism of their action may be related to the oxidation of ferrous oxide to form a protective layer on steel.

Calcium carbonate and other materials may be used to partially replace cement or gypsum. Although calcium carbonate is practically insoluble in water, depending on the particle size, it can have a significant effect on the hydration kinetics of C_3A and C_3S components of cement. Calcium carbonate chemically reacts with C_3A to form a carboaluminate complex. It also increases the rate of reaction of gypsum with C_3A and may cause acceleration of set and early strength development in concrete. Finely divided $CaCO_3$ accelerates the hydration of C_3S.[58] Figure 20 shows the acceleration effect with 5–15% $CaCO_3$ on the hydration of C_3S. The accelerating effect is also evident from the increased rate of heat development in C_3S containing $CaCO_3$. Some percentage of $CaCO_3$ added to C_3S is incorporated into the C-S-H phase (Fig. 21). Formation of this complex may be related to the mechanism of acceleration.

Various types of pigments are used to produce colored concrete. Some of them, such as ultramarine blue, have a high cation exchange capacity. Added to cement, ultramarine blue was found to react with $Ca(OH)_2$.[59] The strength increased from 1400 to 2390 lbs/sq.in. (9.7 to 16.5 MPa) at 7 days by the addition of 15% ultramarine blue.

Antifreezing admixtures are used in Russia for cold weather operations down to -30°C. Some of these admixtures such as $NaNO_2$ and $NaNO_3$ lower the freezing point of the liquid phase and some of them

(KOH+$CaCl_2$, carbamide, nitrite) act as accelerators. The accelerating admixtures are known to interact with the constituents of cement. The acceleration of C_3S may involve nucleation and incorporation in the hydrating C_3S. Some of these admixtures (carbamides and NH_3) form complexes with $Ca(OH)_2$. The retardation of reaction by some of them may be the result of adsorption on the hydrating C_3S. Complexes such as Ca-hydroxychloride, -hydroxy nitrite and -hydroxy nitrate are known to form in the presence of some admixtures.

Some aggregates in concrete are prone to an expanding reaction by the interaction of silica and alkali. Addition of lithium and barium salts has been advocated to reduce such deleterious expansions. One of the mechanisms operating in this system is the reaction of these salts with alkali hydroxide and silica to form insoluble Li and Ba silicates that do not imbibe water and swell.

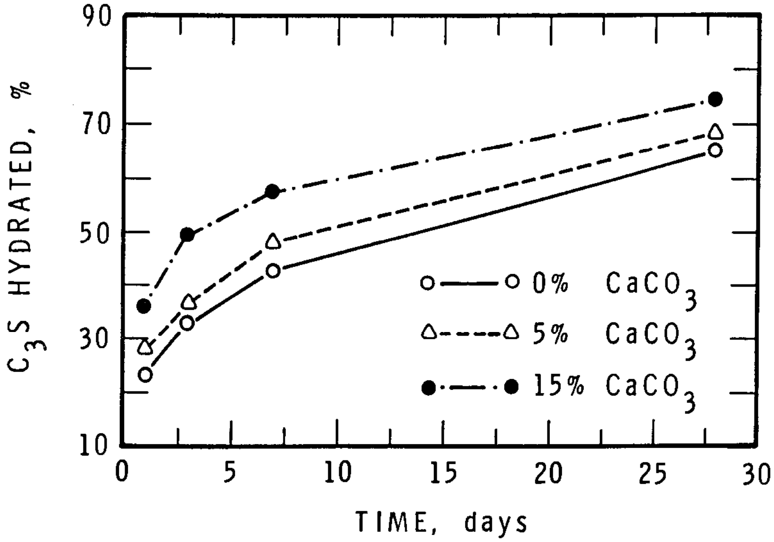

Figure 20. Degree of hydration of C_3S in the presence of $CaCO_3$.

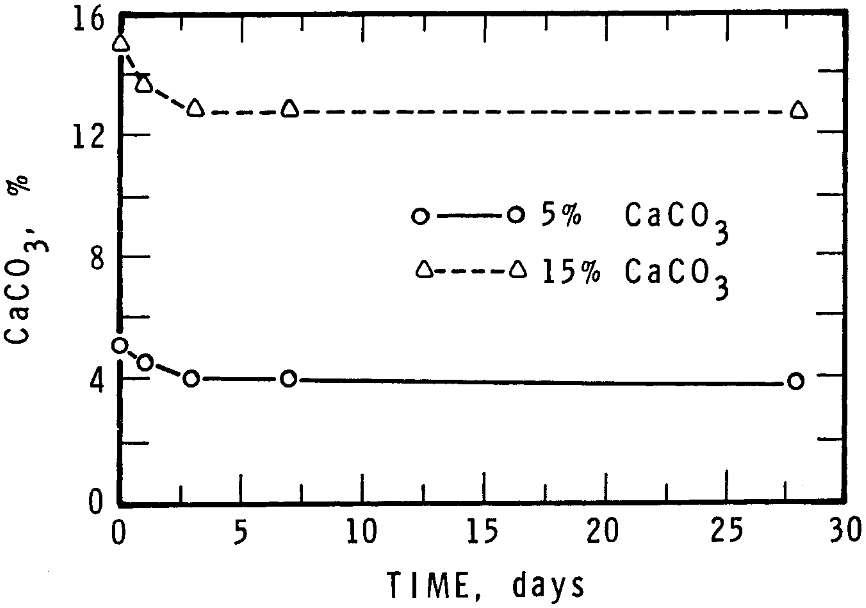

Figure 21. Amount of $CaCO_3$ in C_3S pastes hydrated for different periods in the presence of $CaCO_3$.

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Chemical Admixtures—Recent Developments

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1.0 INTRODUCTION

An admixture, defined as a material other than water, aggregate, hydraulic cement, and fiber reinforcement, is used as an ingredient of concrete or mortar, and added to the batch immediately before or during its mixing. Chemical admixtures, a very important group of admixtures used in small amounts, are water soluble or emulsified systems. Chemical admixtures include accelerators, retarders, water reducers, superplasticizers, etc. In a broad sense, chemical admixtures should also include among others, air entraining admixtures, pumping aids, coloring admixtures, alkali-aggregate expansion-reducing admixtures and others.

A brief account of the important developments that have taken place recently is emphasized. It is not meant to be an exhaustive survey but merely a review of the trends in the development of chemical admixtures. A more detailed treatment of these admixtures can be found in other chapters. Significant advances have particularly been made in the production and application of superplasticizers. Important developments are foreseen in such admixtures as lignosulfonates, accelerators, air entraining admixtures, alkali-aggregate expansion-reducing admixtures, admixtures for underwater concreting, polymer-modified and macrodefect free systems, extended set retarders and activators for reuse of returned concrete, activators for slags, corrosion inhibitors, etc. This chapter lays emphasis on the improvements in water reduction, dispersion, workability, strength development, durability, etc., in concrete containing the chemical admixtures. Aspects such as mechanisms, microstructural aspects, chemical reactions and new techniques of investigation are described under relevant chapters.

2.0 SUPERPLASTICIZERS

A large amount of work has been published on various aspects of the utilization of superplasticizers. Synthesis of new types of superplasticizers, application of superplasticizers for attaining high strengths, and methods to control the slump loss are some of the areas which have received special attention.

2.1 Superplasticizers Based on Lignosulfonate

In concrete applications, lignosulfonate admixtures are used widely as normal water reducers. At a dosage of 0.05–0.1% they reduce the water requirement by 6 to 10%. At higher dosages, excessive retardation of set and entrainment of air occurs and hence they cannot be used as high range water-reducing admixtures. On the other hand, synthetic polymers based on the sulfonated melamine and naphthalene formaldehydes, while decreasing water requirements by about 20 to 30%, do not adversely affect the setting and air entraining properties of concrete. Because of the relatively lower price of lignosulfonates there has been continued interest in developing a superplasticizer based on lignosulfonates. Superplasticizers known as modified lignosulfonates contain some amount of the conventional superplasticizer. The properties obtained using them are comparable to those using only superplasticizers. In Table 1 the properties of concrete containing a modified lignosulfonate are compared with those with melamine and naphthalene-based superplasticizers.[1] The results for two types of cement are similar.

It has been found that lignosulfonate-modified superplasticized flowing concrete with high slump and low cement contents may exhibit a higher degree of deterioration due to freezing and thawing action and de-icing chemicals, compared to the control concrete.[2] In Table 2 are given the durability data for samples exposed to 300 cycles of freezing and thawing according to ASTM C 666, Procedure A. The main type of deterioration is through the internal disruption of the specimens.

Table 1. Properties of Concrete Containing Modified Lignosulfonate and Other Plasticizers

	Admixture	W/C	Slump	Compr Strength, MPa		
			mm	7 days	28 days	91 days
I	None	0.49	75	26.8	32.8	37.8
I	Melamine-based	0.40	80	37.3	44.0	48.5
I	Naphth-base	0.40	80	36.3	42.6	49.9
V	None	0.48	90	19.1	32.2	38.0
V	Melamine-based	0.38	80	33.0	42.0	48.5
V	Mod-Lignosulf	0.38	85	32.8	42.4	50.3

Table 2. Freezing and Thawing Durability of Concrete Containing a Lignosulfonate-based Superplasticizer

Sample	Slump (mm)	Rel Dynm Modulus %	Weight Loss %
Control	100.0	94	3.2
Lignosol-modified	100.0	98	3.2
Control	195.0	87	2.2
Lignosol-modified	208.0	53	4.5

Attempts have been made to develop a synthetic superplasticizer based only on lignosulfonates. Rixom and Waddicor[3] prepared various types of lignosulfonates and studied their effect on concrete slump and water requirement. The significance of molecular weight, cationic species, degree of sulfonation and carbohydrate contents on initial set, workability and strength characteristics of concrete was studied. It was concluded that increase in molecular weight of lignosulfonate resulted in a more workable concrete, retardation of initial set and a slight reduction in compressive strength at 24 hrs. Increase in sulfonation did not affect workability or entrained air but it reduced the setting time. It was also found that sodium lignosulfonate was a better plasticizer than calcium lignosulfonate. Generally increased amounts of sugars in lignosulfonate resulted in longer setting times.

A comparison of the effects of lignosulfonate, melamine sulfonate and naphthalene sulfonate admixtures shows that sodium lignosulfonate is a more effective plasticizer than others. The slump retention is also higher with sodium lignosulfonate. Table 3 illustrates the effect of three admixtures when used at double the normal dosage.[3]

Table 3. Initial Set and Compressive Strength of Concrete Containing Superplasticizers

Admixture	Dosage (30% w/w)	W/C	Initial Set (hr)	24-hr Comp Str MPa
Reference	-	0.65	5.50	10.3
Melamine-based	2.67	0.65	7.75	11.2
Naphthalene-based	2.00	0.65	9.25	11.35
Na-Lignosulfonate	1.50	0.65	12.50	6.0
Na Lignosulfonate + Accelerator	1.50	0.65	11.50	9.8

When lignosulfonate is used at a lower dosage, it decreases early strengths and prolongs the setting times. Incorporation of an accelerator decreases the setting time and increases the compressive strength. At normal dosage the setting time was 8 hrs and the 24-hr compressive strength was 10.2 MPa for concrete containing only lignosulfonate.[3]

Ronneberg[4] has described the properties of concrete containing a lignosulfonate with low sugar contents. The plasticity was almost the same as that with other superplasticizers. When it was used as a water reducer, the air content and setting time were not different from those using other superplasticizers. When lignosulfonate was used to increase the slump of concrete the setting time was increased. At a dosage of 3 L/m^3 (40% dry material) the retardation of setting times with sulfonated melamine, sulfonated naphthalene, and lignosulfonate were 1.5, 3.5 and 7 hrs respectively. The 24-hr strength of reference concrete and that with lignosulfonate (1 L/m^3) was the same. However, at higher dosages of lignosulfonate the strength decreased. The same strengths were obtained when other superplasticizers were used at dosages 2–5 L/m^3.

Recently Bialski and Nayak[4a] attempted to synthesize a lignosulfonate for use as a superplasticizer. Spent liquor was subjected to heat treatment to reduce sugar content. The resultant product was subjected to ultrafiltration to remove low molecular weight materials including sugars. The molecular weight of the products was in the range 20,000 to 50,000. Several properties of the lignosulfonates and their effect on mortars were determined. The properties studied included surface tension, dispersion, and foaming characteristics of lignosulfonates. The properties studied on cement and mortar included viscosity, flow characteristics, setting times, water reduction and compressive strength. Of the many lignosulfonates studied, five preparations imparted better mortar flow characteristics than those with a melamine-based superplasticizer. Some of the properties of mortars containing a lignosulfonate are compared with those using a melamine formaldehyde-based superplasticizer (Table 4).

Table 4. Influence of Synthesized Lignosulfonate on Mortar

Additive	% Solid	Air %	Flow	Set Time hrs	Set Time min	Water-redn. (70%flow)
None	-	10.8	48	3	30	—
Melamine Formaldehyde	0.3	11.0	80	4	30	11.3
Lignosulfonate	0.3	0.8	87	6	00	12.8

Although a tailored lignosulfonate may qualify as a superplasticizer, several problems associated with its use have to be solved. It is known that some lignosulfonates may cause foaming and increase the air entrainment. The setting times are generally increased. If the dosages of normal superplasticizers and those of lignosulfonates are kept low, the compressive strengths of concrete will have about the same value. However, at higher dosages, concrete with lignosulfonate may show lower strengths. The use of defoamers and accelerators in lignosulfonate could offset some of the disadvantages mentioned above. Caution should be exercised in the selection of defoamers as some of them affect the aggregate-cement bond.

2.2 Synthesis of Superplasticizers

Continued attempts are being made to further improve the performance of superplasticizers. The effect of synthesizing conditions and molecular weight of superplasticizers on the behavior of cement, mortar and concrete have been reported.

A novel four step process has been developed for the synthesis of a sulfonated melamine formaldehyde. Over twenty superplasticizers were prepared by this process and the workability and mechanical properties of concrete incorporating them has been studied.[5] The four steps included hydroxymethylation, sulfonation, low pH condensation and high pH rearrangement. The results obtained with these superplasticizers were compared with those obtained with a standard concrete containing a melamine-based commercial superplasticizer.

Table 5 shows the relative water-reducing capabilities of three superplasticizers at a slump of 50 mm.[5]

Table 5. Relative Water-Reducing Capabilities of Superplasticizers at Different Dosages

Dosage (%) =	1	2	3	4	5
	Water Reduction (%)				
Commercial	9	19	29	36	38
Synthesized I	13	25	35	38	41
Synthesized II	13	24	34	37	40

A significant increase in water reduction occurs with the synthesized admixtures at lower dosages. It was also observed that the synthesized admixtures were effective in increasing the slump of concrete. For example, to obtain a slump of 200 mm, 1.3% commercial superplasticizer was required but the same value can be obtained with 1% of the newly synthesized superplasticizer. Slump retention, as well as strength was also greater with the synthesized admixture. At twenty-eight days, the strength of a neat mortar, that with 3% commercial superplasticizer and 3% synthesized admixture, was 30, 28, and 34 MPa, respectively. Andersen et al.[6] studied the effect of the molecular weight of sulfonated polystyrenes (4000–

70,000 g/mole) on their ability to disperse cement particles. The dispersion increased with the molecular weight and attained almost a constant value beyond the molecular weight of 40,000 g/mole.

Collepardi and coworkers[7][8] synthesized twenty naphthalene sulfonated formaldehyde samples of different degrees of polymerization. Both adsorption and zeta potential values of these admixtures increased with the molecular weight, up to a particular value. Strength of mortars increased with the degree of polymerization. A plot of the monomer content vs minislump of cement paste showed a steady decrease in values as the monomer content increased, the minislump values being 175 and 25 cm^2 at monomer contents of 10 and 100%, respectively.

It appears that the relationship between the degree of polymerization and strength development varies from one polymer to the other. In an investigation of the effect of seven water soluble polymers on concrete properties, it was observed that the low molecular weight polymers were more effective dispersants.[8a]

As has already been discussed, the molecular weight of the superplasticizer has a strong influence on the rheological properties of the cement systems. The cement composition, the alkali content, and particle distribution are other factors that have to be considered. Ferrari and others[9] found that sulfonated naphthalene-based superplasticizers exerted the best fluidizing effect in the molecular weight range 6000–8000 (weight average), but at higher range the effect decreased. These cements were rich in C_3A. Cements that had a high C_4AF content did not show this drop at higher molecular weights.

A superplasticizer has been synthesized by Phatak, et al., from the cashew nut shell liquid.[9a]

2.3 Concretes Containing High Dosages of Superplasticizers

Important benefits result in certain concrete systems by using higher than normal dosage of superplasticizers. In an investigation of the possibility of using high volume fly ash in concrete, Malhotra[10] succeeded in making durable fly ash concrete comprising 50–60% class F fly ash (of the total cementitious material), low unit water content equal to $w/c < 0.35$, and a superplasticizer content of up to 7.1 kg/m^3. Although the early strength gain of control mixes containing no fly ash was higher than that with fly ash, a significant gain in strength for the fly ash concrete occurred from 7 to 28 days. For example, the mixture with 150 kg/m^3 cement and 190 kg/m^3

fly ash showed a strength of 23.9, 41.6 and 53.1 MPa at 7, 28 and 91 days. In spite of the relatively low cement factor, the fly ash concrete showed desirable mechanical properties, satisfactory freeze thaw resistance and low permeability to chloride ions. The long term strength development in concrete containing more than 55% fly ash was investigated by Sivasundaram et al.[10a] up to a period of 3.5 years. The concrete reached a strength of 70 MPa at 1.5 years. The modulus of elasticity at 2 years was 47 GPa. The carbonation depth was only 4 mm at 3.5 years and there was negligible chloride ion penetration. This type of concrete has been used in several applications in Nova Scotia, Canada.

Rodway and Fedirko[11] also examined concrete containing up to 70% fly ash (high calcium) and a superplasticizer (twice the normal dosage) and studied properties such as compressive strength, flexural strength, air-void parameters, creep and permeability. The main drawback was delayed setting time. Otherwise the properties were adequate for structural applications.

Fly ashes are incorporated into concrete to counter the expansion caused by alkali-aggregate reactions. Alasali and Malhotra[12] studied the effect of higher than normal additions of fly ash (50–60%) in concrete (by using higher than normal dosages of a superplasticizer) and determined the inhibiting effect of this concrete on alkali aggregate expansion. For example, the reference concrete containing alkali and exposed to normal sodium hydroxide at 80°C for 275 days showed an expansion of 0.409% whereas that containing fly ash and alkali exhibited an expansion of only 0.083%.

Mine tailing dumps and some rock outcrops are susceptible to attack by penetrating rain and surface water. The leachates that result from this action may be potentially toxic and cause environmental and health problems. A new capping technology, using high volume fly ash shotcrete has been suggested.[13] Several mixtures were used in which cement contents ranged from 123 to 152 kg/m^3, fly ash contents between 193 and 328 kg/m^3, polypropylene addition from 4 to 5 kg/m^3 and superplasticizer dosage between 3.6 and 7.8 L/m^3. Properties such as compressive strength, flexural strength, flexural toughness, impact behavior, drying shrinkage, chloride permeability, and freezing and thawing durability were determined. The economics and advantages of using this mixture were analyzed with reference to other methods. This technology has been used in several applications in British Columbia and Nova Scotia, Canada.

The use of superplasticizer and excess air entraining agent permits production of high volume blast furnace slag. In the work of Nishibayashi et al.,[14] concrete containing 85% slag was used. Regardless of the percentage of the slag used the compressive strength of superplasticized concrete was almost equal to that of the control concrete. The initial setting time was unaffected but the final setting time increased as the amount of slag increased.[14] Sivasundaram and Malhotra[14a] studied the properties of air-entrained high volume slag concrete containing 50–75% of slag. The reference concrete containing 292–428 kg/m^3 cement needed 4.7–5.9 kg/m^3 of superplasticizer, whereas the mixtures containing 147–301 kg/m^3 slag needed up to 9.1 kg/m^3 superplasticizer. At seven days and after the high-volume slag concrete achieved similar strength to that of the reference concrete. Most slag concrete had a strength of 50 MPa at 91 days. The flexural strength of most slag concretes reached a value of 8 MPa, being higher than that of the reference concrete. The penetration resistance of slag concrete to chloride was exceptionally high.

2.4 Control of Slump Loss

Superplasticizers are known to increase the initial slump of concrete considerably. This increase however, is only transient because it is generally not maintained beyond about 30–60 min. One method is to add the superplasticizer at the point of discharge. There are some problems associated with this approach. Several other methods can be adopted to control slump loss. They include adding a higher than normal dosage of superplasticizer, redosing the superplasticizer at different intervals of time or by including some type of retarder in the formulation. Continued interest is evident from the research carried out on various methods of controlling slump loss and the number of patents appearing annually. A few of the recent developments are discussed below.

The effectiveness of superplasticizer is related to its concentration in the liquid phase. The concentration of superplasticizer decreases considerably, especially through strong adsorption in the early periods of hydration of cement. Fujiu et al.,[15] and Fukuda and others,[16] have developed a polymeric dispersant which by itself is insoluble but under the alkaline environment during cement hydration forms a product which has a superplasticizing effect. Thus, by this time-delay mechanism, the admixture is capable of maintaining the slump for a longer period. The polymer precursor has ester, acid chlorides, amides, and acid anhydrides as functional groups. The slump retention increases with the decrease in particle size as shown in Fig. 1.

Several types of polycarboxylic acid dispersants have been examined for their effect on slump increase and slump retention. Both the initial slump values and slump retention times were found to increase by the use of polycarboxylic acids at a level of 0.12% by weight of cement. The optimum molecular weight of the superplasticizer was found to be 10,000.[17] In general, this admixture in comparison with the naphthalene-type superplasticizer, imparted lower bleeding, higher slump and slump retention but the concrete had higher air content and longer setting times. An additive containing olefin and unsaturated carboxylic acid as a monomer has been suggested by the Chinese workers.[17a]

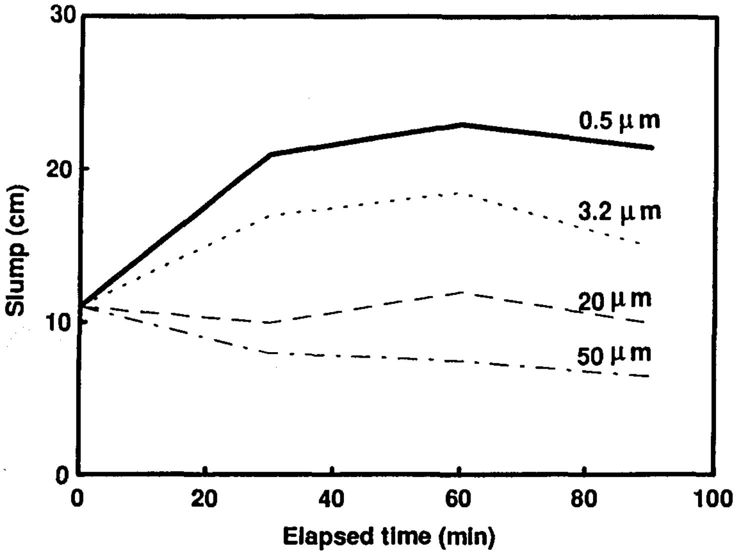

Figure 1. Dependence of particle size on slump retention.

Ramachandran and co-workers[18] investigated the effect of different dosages of various latexes on the slump of superplasticized concrete. The styrene-butadiene (P_1) latex was most effective in controlling the slump loss in a melamine formaldehyde-based (S_1) superplasticized concrete. The initial slump increased further when 2% latex was added to concrete containing 0.3% superplasticizer. Figure 2 compares the slump retention characteristics of concrete containing 0.3% S_1, 0.3% S_1+1% or 2% P_1. The concrete containing no P_1 has a steep rate of slump loss, attaining a value of about 5 cm at 4 hrs. By adding 1 and 2% P_1 to 0.3% S_1, the slump retention at 4 hrs is relatively higher than that without P_1, being about 8 cm and 14 cm, respectively.

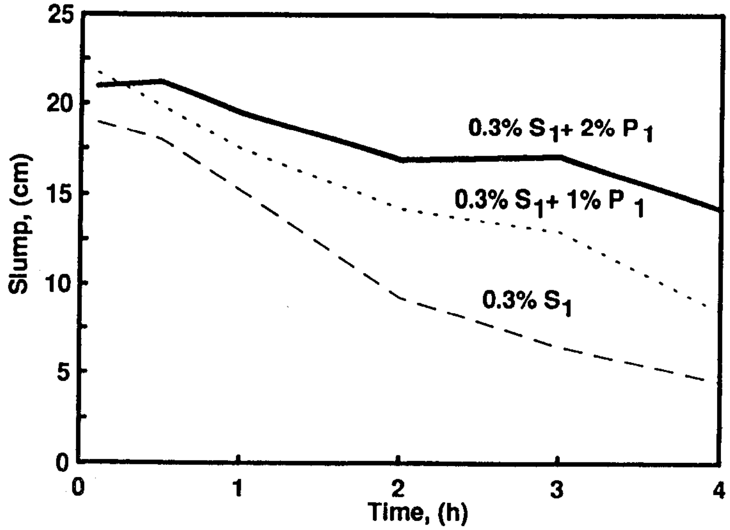

Figure 2. Effect of commercial superplasticizer and polymer on slump.

2.5 High-Strength Concrete

Normal weight structural concrete members have strengths between 23.5 and 35.2 MPa. Utilization of superplasticizers enables field-placed concrete to attain strengths of 60 MPa.[19] Ultra high-strength concrete, defined as that having compressive strengths from 68 to 124 MPa and a flexural strength of 14 MPa, may be fabricated at a water:cement of 0.22. In concrete containing silica fume, addition of a superplasticizer decreases the water requirement, thus increasing the strength. The pozzolanic action of the highly reactive silica fume also contributes to concrete strength. Further enhancement of strength is achieved using a high cement factor and stronger aggregates. With 593 kg/m^3 ASTM Type I cement, 119 kg/m^3 silica fume (W/C = 0.22, slump 11.9 cm) a strength of 111.4 MPa at 28 days and 124 MPa at 128 days may be achieved.[20]

Mitsui and coworkers[21] have carried out a comprehensive investigation on the production of high-strength silica fume concrete utilizing an admixture consisting of a sulfonated naphthalene formaldehyde and a copolymer with a functional sulfonic and carboxylic group. In Fig. 3 the strength development at 28 days for concrete made at different water:cement + silica fume ratios and superplasticizer dosages 0.8% to 5% is given. It is obvious that the highest strength is attained in the presence of 20% silica fume. At a W/C+SF (W = water; C = Cement; SF = Silica Fume) of 0.25, a strength of 105 MPa is obtained. The percentage increase in strength with silica fume is very high at a W/C+SF of 0.35. The influence of silica fume on the strength development is particularly significant when concrete is fabricated at a moderate W/C.[22] Figure 4 shows the effect of W/C ratio on the 28-day compressive strength of concrete containing 0, 8 and 16% silica fume. In the W/C range of 0.4 to 0.9, compressive strength is always much higher in concrete containing 16% silica fume. The influence of silica fume on strength development increases as the W/C is decreased. However, at a very low W/C, the effectiveness is low.

Several other reports confirm that superplasticized silica fume concrete develops very high strengths. Aitcin and Riad[23] obtained a strength of 85.9 MPa at a W/C of 0.21. Malhotra[24] found that concrete containing 3.89% naphthalene-based superplasticizer (42% solids) and with 8% silica fume and fabricated at a W/C = 0.25 developed a strength of 74.2 MPa and 89.9 MPa at 28 and 91 days, respectively. The mixture containing 8% silica fume and 20% slag exhibited a strength of 95.8 MPa.

Strengths of about 100 MPa were obtained by Collepardi et al.[25] in concrete (slump of 20 cm) containing 10–20% silica fume, 2.4% superplasticizer and 400 kg/m^3 of cement. Generally, silica fume concrete develops strengths at a low rate in the early periods of curing. Collepardi and coworkers,[25a] working with silica fume concrete, concluded that the strengths are about the same with 2% of sulfonated melamine formaldehyde (SMF) or sulfonated naphthalene formaldehyde (SNF). At 4% dosage however, addition of SMF yielded better strengths. Durekovic[25b] obtained strengths of about 110 MPa in cement pastes containing 4% superplasticizer and up to 15% silica fume. High early-strengths may be obtained using a rapid hardening cement in combination with a superplasticizer. Concrete containing 8% silica fume, a rapid hardening cement and a superplasticizer may develop a strength of 34 MPa in 1 day.[22]

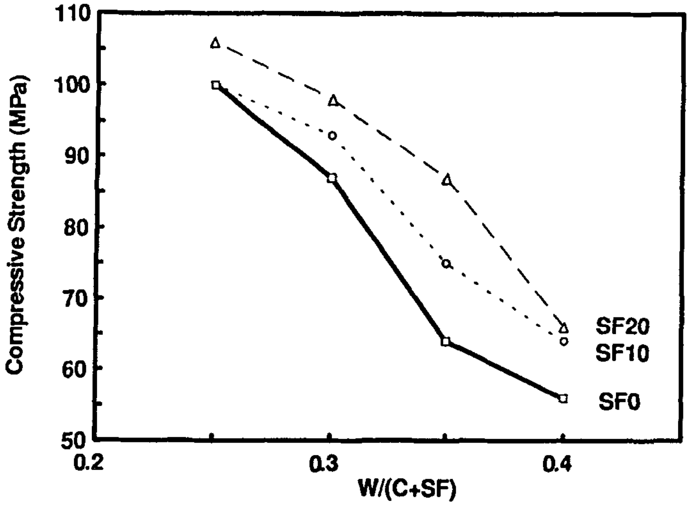

Figure 3. Effect of silica fume on compressive strength development.

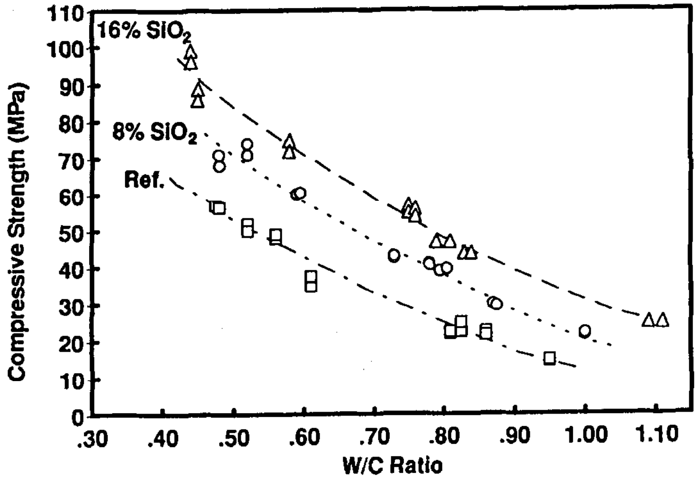

Figure 4. Effect of silica fume on strength of concrete at different W/C ratios.

Formulations for high-strength concrete include a mixture of Na lignosulfonate, Na gluconate, β naphthalene and melamine sulfonic acid salts to produce concrete of strength 152 MPa; further strength development is obtained by utilizing the same admixtures but with added silica dust.

2.6 Densified Low Porosity Cement Systems

Densified cements containing homogeneously mixed ultrafine particles (DSP) represent a class of ceramics that are bonded at or near ambient temperatures. These systems, developed by Bache et al., are produced from portland cement, finely divided silica and a dispersing agent at a very low water-solid ratio.[25c] Densification is accomplished with cement of particle size of about 0.5–100 mm and silica fume of size 5 nm to 0.5 mm. In this system, the spaces normally occupied by water are occupied by finely divided silica. The dosage of superplasticizer used may be as high 4%. The water requirements may be as low as 0.13% by weight of cement+silica. The C-S-H phase formed in the paste is amorphous. Few distinct crystals of calcium hydroxide can be seen. The DSP mortar and concrete develop very high strengths. A cement mortar containing 4 mm bauxite and cured for 4 days at 80°C produces a product of compressive strength 269 MPa and a dynamic modulus of elasticity of 108,000 MPa. The durability of DSP binder is significantly higher than that of the normal mortar or concrete. Just as ordinary concrete, the DSP cement system is also attacked by acids, but the deterioration occurs very slowly.

3.0 ANTIFREEZING ADMIXTURES

Accelerating admixtures such as calcium chloride are used in cold weather concreting. A significant increase in the early strength development at normal and low temperature enables reduction in the curing and protection periods necessary to achieve specific strengths in concrete. Calcium chloride cannot be considered an antifreezing admixture. For example, at a dosage of 2% and a water-cement ratio of 0.50, the freezing point of water is lowered by about 1.4°C which is negligible from practical considerations.

Antifreezing admixtures are capable of depressing the freezing point of water in concrete considerably so that their use is of practical significance. Antifreezing admixtures are used in Russia at temperatures as low as -30°C.[1] These admixtures allow earlier stripping and use of forms, earlier completion of construction projects and occupancy. They are particularly useful in the fabrication of precast elements, for patching and repairs, foundation work, and slabs on grade for garages. Improved cohesiveness, plasticity, minimization of cold joints and sand streaking are some of the advantages.

The mode of action of the antifreezing admixture is *(a)* to lower the freezing point of water in concrete and act as either a weak accelerator or retarder of setting and hardening using sodium nitrite, sodium chloride, weak electrolytes and organic compounds such as high molecular weight alcohols and carbamide, or *(b)* to accelerate significantly the setting and hardening with good antifreezing action using chemicals such as calcium chloride, sodium chloride, sodium nitrite, calcium nitrite-calcium nitrate and urea.

The Russian literature contains a significant amount of information on antifreezing admixtures.[1] Only recently has some interest been evident from other sources. The RILEM committee recognizes antifreezing admixtures for cold weather concreting.[26] It also includes cautions to be taken in the use of these admixtures. Generally, larger dosages of antifreezing admixtures are used compared to chemical admixtures. For example, with 8% sodium nitrite, 50% of water will still be in the liquid state in concrete at a temperature of -15°C. In Table 6, the strengths (as a percentage of designed strength) are given for concrete cured at -5°C which contains sodium nitrite (SN), calcium nitrite-nitrate-chloride (CNNC), and calcium chloride-calcium nitrate (CC+SC). The binary admixture addition at lower dosages imparts higher strengths than when used singly.

In Finland premixed dry mix mortars containing antifreezing admixtures are marketed. They can be used even at -15°C and are specially applicable for joints and repair purposes.[27] Figure 5 shows the strength development in mortars with this product at -5, -15 and 20°C. Even higher strengths are achieved at -15°C beyond 28 days of curing.

Table 6. Strength Gain in Concrete Containing Antifreezing Admixtures

Admixture	Amount (%)	Percent of designed strength		
		7 days	28 days	90 days
SN	4–6	30	70	90
CNNC	3–5	40	80	100
CC + SC	2–3	35	80	100

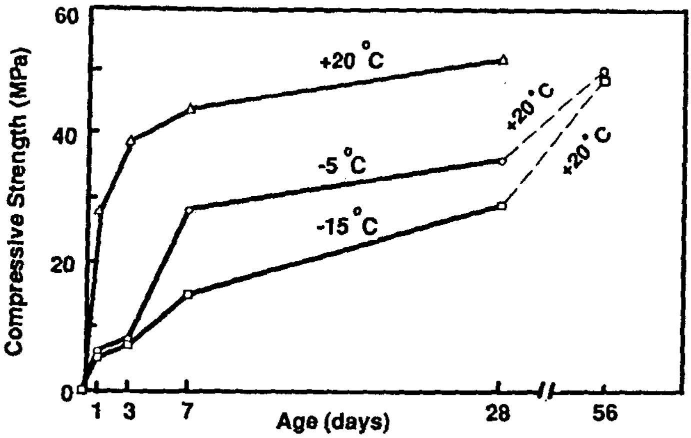

Figure 5. Strength development of dry-mix mortar at low temperature.

It has also been shown that, with the antifreezing admixtures, the strength of concrete with ordinary cement may exceed that obtained with the rapid hardening cement containing no admixture. Table 7 compares the results obtained with the two types of cement at -10°C. Best results[28] are obtained using a mixture of potassium carbonate and a retarder. Brook et al.[29] have described an admixture called ATA, a non-chloride admixture that is noncorrosive, water-reducing, and set-accelerating. With this admixture (10% solids) ice formation at -6.7°C can be prevented. In another publication, Scanlon and Ryan[29a] have provided data on a new freeze-protection admixture. This admixture accelerates set time and accelerates strength development at subzero temperatures as shown in Table 8. Korhonen et al.[29b][29c] have recently carried out work on the effect of antifreezing admixtures in concrete. They determined the strength developed in concrete at 5°C after 7, 28 and 56 days of curing, and found the values that were respectively 40, 80 and 100% of those developed at the same ages at room temperature. The dosages required to attain this strength level with the antifreezing admixtures was determined (Table 9). It is evident that 3 to 9% calcium nitrite produces adequate strengths at or above -5°C. Sodium nitrite, although, as a freezing point depressant, it is not as efficient as calcium nitrite, it promoted significant strengths down to -10°C.

An antifreezing admixture composed of a superplasticizer and inorganic salts has also been reported in the Japanese literature.[30] Concrete containing this admixture when cured at -10°C showed strengths of 14, 75, 165 and 213 kg/cm^2 at 3, 7, 14 and 28 days respectively and the corresponding values for untreated concrete were 2, 3, 4 and 6 kg/cm^2.

Continued interest in antifreezing admixtures is evident from other formulations such as potash-lignosulfonate-sodium tetraborate,[31] potassium carbonate-lignosulfonate,[32] nitrite-nitrate-alkali[33] and polyamine-lime-alumina cement-potash.[34]

Much more information has to be obtained before these admixtures can be used widely. Antifreezing admixtures are expensive, especially as they are used in higher dosages. The hardening rate is sometimes too slow, the accelerating rates may be affected by plasticizers, and compatibility with other normal admixtures as well as their effect on long-term durability has to be established for each mixture and curing regime.

Table 7. Strengths of Concrete Containing Some Antifreezing Admixtures (Expressed as % of Dry Day Strength)

Admixture Type	Ordinary Cement	Rapid Hardening
Sodium nitrate + Sodium sulfate	85%	70%
Sodium nitrite + Calcium chloride	63%	63%
Potassium carbonate + Retarder	74%	48%
Calcium nitrate + Sodium sulfate	75%	43%

Table 8. Concrete with Freeze-Protection Admixture

	Plain	New Admixture
Time of set	11 hr 55 min	5 hr 45 min
(-4°C)	Strength (MPa)	
3d, -4°C	3.4	9.24
7d, 10°C	8.3	39.3
28d, 10°C 18.1	49.9	

Table 9. The Dosage of Antifreezing Admixture Required to Produce Strength Equivalent to Concrete Cured at 5°C

Admixture	Dosage, %	Lowest fabrication Temp, °C
Calcium Nitrite	3–9	-5
Sodium Nitrite	3	-5
	6–9	-10
Sodium Nitrite/Calcium Nitrite	6/2	-10
Sodium Nitrite/Potassium Carbonate	6/0.06	-10
Urea	6	-5

4.0 AIR-ENTRAINING AGENTS

The general method of counteracting freezing and thawing attack on concrete is to use air-entraining admixtures. Factors such as variability in the material, mixing, placing methods, and temperature may make it difficult to adjust the required amount of air with the right bubble size and spacing. It is also not easy to adjust the air in blended cements, superplasticized concrete, and high strength concretes. Whiting and Stark[35] have listed 23 factors that affect air entrainment.

A new air entraining admixture, commercially known as micro-air, has been developed, and it is claimed that it provides concrete extra protection by creating ultra stable air bubbles that are small and closely spaced.[35a] It is basically a multicomponent mixture of fatty acids, salts of sulfonic acid and stabilizing agents.[35b] In addition to many advantages, it can be used in fly ash concrete containing high amounts of carbon, concrete containing a high alkali cement, and concrete with extended mixing times. It has been reported that, with this admixture, air content increased rapidly during the first 20 minutes of mixing. The air content increased from 5% at 8 minutes to 7% at 20 minutes and then remained stable.[35b] The air content measured at 20 mins is more representative of the final air content than that obtained at 15 mins. In fly ash concrete, if the fly ash contains carbon, problems arise because of the variation in the amounts of carbon from batch to batch and the adsorption of the surface active agent on the high surface area carbon particles. Some of these problems have been circumvented by adding polar compounds such as sodium octonate.[35c]

An innovative approach in the area of air-entraining admixtures is the use of preformed bubble reservoirs in the form of porous particles. In one method, hollow plastic microspheres with diameters between 10 and 60 μm are added to concrete.[36] The voids in the particle are smaller than those in the air-entrained concrete (10–3000 μm). Addition of 1% by weight of cement of these microspheres to concrete corresponds to 0.7% by volume of concrete. The spacing factor equivalent using these spheres is 0.07 mm, well below the permissible maximum. Sommer[36] compared the losses in weight of concrete (due to freezing and de-icing salt attack) containing 5% entrained air with that containing 0.3, 0.6, 0.9, 1.2 and 1.5% hollow microspheres. Adequate frost resistance was attained using 0.9% of the microspheres. No further advantage was observed using higher proportions. Thus 1% hollow sphere was found to be as effective as 5% entrained air. The workability as a measure of consistency was increased by the microsphere addition to the same extent as that provided by 5% air. The 28-day strength was higher with microspheres, being 40 MPa/mm^2 and 38 MPa/mm^2 with 1% hollow spheres and 5% air, respectively.

Vanhanen[37] confirmed some of the findings of Sommer.[36] Using 0.3, 0.6, 0.9 and 1.2% microspheres by weight of cement, concretes were made. The resulting compressive strength and frost resistance of these mixtures were compared with those of reference concretes (with and without air entrainment). The frost resistance was improved considerably in concrete containing microspheres. A minimum amount of 0.6% microsphere was needed for good frost resistance. It was also concluded that the compressive strength of air-entrained concrete (with respect to the plain non-air entrained concrete) was less than that containing the microspheres.

Recently Litvan[38] demonstrated that porous particles made with fired clay bricks, diatomaceous earth, vermiculite, pumice and perlite can be added to concrete to increase its frost resistance. These results show that concretes containing porous particles are generally more durable than the plain concrete.

Table 10 gives the particulate admixture used, its concentration in concrete, and the compressive strength. Two concentrations were added to concrete to assess their effect on freezing and thawing durability. In general, the addition of particles (with the exception of brick) lowered compressive strength. At lower particle concentration, the reduction of compressive strength is 7.7%, 6.1% and 19.5% for vermiculite, pumice I and perlite, respectively. These differences will be lower if comparison is made with respect to the air-entrained concrete. The lower strengths should not be a problem for applications related to sidewalks, roadways and other horizontal surfaces where better durability promoted by these particulates is expected to compensate for a slight decrease in compressive strength.

The expansion and dynamic moduli of elasticity of concrete specimens exposed to different number of cycles of freezing and thawing cycles are shown in Figs. 6a and 6b.[39a] Results indicate that concrete containing higher concentrations of particulates (Table 10) showed high freezing and thawing resistance even after exposure to 350 to 400 cycles. The only exception was concrete with pumice II. The plain reference concrete (containing no air-entrainment) failed after 60 cycles at a w/c = 0.60 and that fabricated at a w/c of 0.56 failed after 300 cycles using ASTM C-666 Procedure B (freezing in water and thawing in air). Kuboyama, et al., examined the effect of the incorporation of porous, fine expanded shale (porosity = 33%) into concrete and found it to have increased frost resistance.[39a]

Table 10. The Effect of Particulates on Spacing Factor and Compressive Strength

Low Water/Cement

Sample	W/C	Concentration	Spacing Factor (mm)	Comp.Str. MPa (28d)
Brick	0.60	4.33	0.58	31.3
Vermiculite	0.63	0.55	0.32	28.9
Pumice I	0.63	2.15	0.43	29.4
Pumice II	0.63	4.21	0.43	25.1
Perlite	0.63	0.51	0.43	25.2
Plain Conc.	0.60	——	——	31.3

High Water/Cement

Sample	W/C	Concentration	Spacing Factor (mm)	Comp.Str. MPa (28d)
Brick	0.68	8.66	0.29	30.2
Vermiculite	0.76	1.10	0.16	20.5
Pumice I	0.69	4.30	0.2	25.1
Pumice II	0.66	8.42	0.22	21.7
Perlite	0.64	1.02	0.20	24.4
Plain Conc.	0.60	——	——	31.3

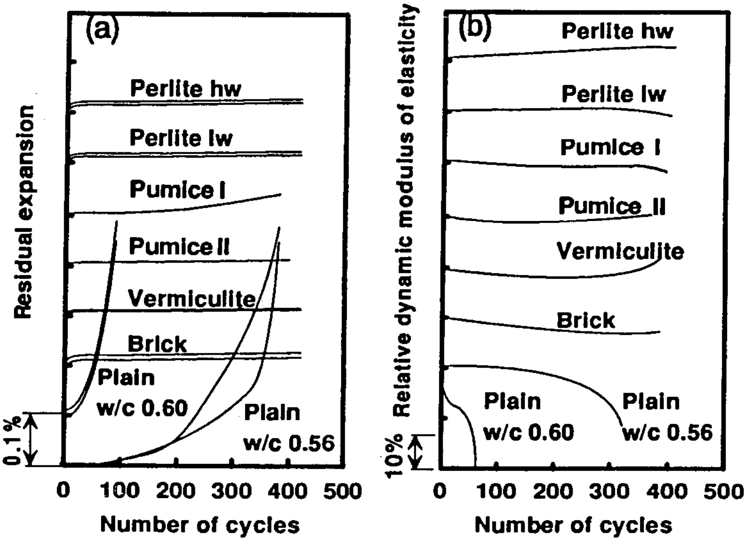

Figure 6. Concrete with and without particulate admixture. *(a)* Residual expansion and *(b)* relative dynamic modulus of elasticity as a function of freeze/thaw cycles (hw: high W/C; lw: low W/C).

5.0 POLYMER-MODIFIED MORTAR AND CONCRETE

Polymer-modified mortars and concretes are used as construction materials for finishing and repair purposes. They are widely used for bridge deck overlays and patching, and also as adhesives, anticorrosive liners, decorative coatings and integral waterproofers. It is estimated that annually 1.2 million sq meters of bridge decks are overlayed with polymer-modified concrete.[40] The polymers are usually added to the mixing water just as other chemical admixtures, at dosages of 5 to 20% by weight of cement. There is evidence that interactions occur between polymers and hydrating cement.[41][42] Polymers influence the setting, bleeding, workability, hydration and mechanical properties of cement. There is continued interest in developing polymer-based admixtures for various new applications in concrete.

The polymers consist of lattices, liquid resins, and those that are water soluble. The lattices are more widely used than others. The major types of lattices (dispersed suspensions of solid polymer microparticles in water) comprise styrene butadiene (SBR), ethylene-vinyl acetate (EVA), polyacrylic ester (PAE) and epoxy resin (EP).

Ohama, et al.,[43] have developed a highly durable concrete using polymer dispersions containing 0.5% alkyl silane. The polymer dispersion consisted of SBR latex, EVA emulsion and PAE emulsion at polymer/cement from 5 to 20%. Properties such as strength, chloride-ion penetration, carbonation and drying shrinkage were determined. All polymer-modified concretes showed superior properties to those of the unmodified concrete. In the EVA and SBR concrete, the chloride penetration depth was significantly lower than that in PAE-modified concrete. The penetration depth in the polymer-modified concrete was almost half of that in the unmodified concrete (Fig. 7). In another study Ohama et al.[43a] reported the fabrication of a "super-durable" polymer concrete containing an amino alcohol derivative, an alkyl alkoxy silane, and calcium nitrite. Very substantial reduction in carbonation depth and chloride ion penetration was realized with such polymer-modified concretes.

Polymer-modified mortars may be used for repairs but they harden slowly, so that their application on substrates with flowing or leaking water is not very effective. An ultrarapid hardening shotcrete (URH) has been developed which contains magnesium acrylate in combination with sodium persulfate and sodium ascorbate.[44] The URH was reported to stop water leaking at a water pressure up to 0.01 MPa. The adhesion in tension of

URH shotcrete was 2 MPa, which was about 10 times that of the unmodified mortar. The flexural strength and the freezing and thawing resistance of URH shotcrete were also higher than those of the unmodified mortar. Shotcretes containing silica fume and latex are known to have a better rebound and bond strength characteristics.

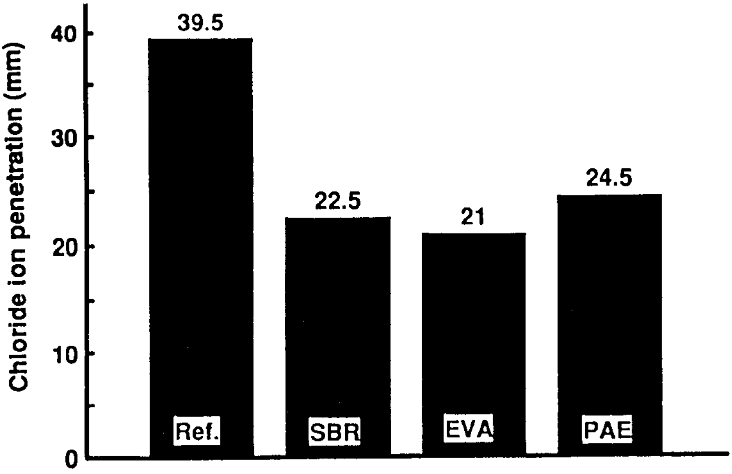

Figure 7. Chloride ion penetration in polymer-modified concrete.

Significant increases in compressive strengths in concrete are possible utilizing polymer admixtures. Adequate strength increases are achieved using an epoxy resin, in combination with a superplasticizer or an accelerator. Figure 8 compares the rate of strength development in a control concrete, epoxy-modified concrete, and epoxy-modified concrete with a superplasticizer.[45] High strengths were obtained with a mixture of epoxy and the superplasticizer; the 7 day strength was 60% higher than that of the control concrete and 23% higher than that of the epoxy-modified concrete without a superplasticizer. Use of a chloride-free accelerator also produced strength increases of 10–20% at 28 days. Generally, incorporation of polymers is known to increase the flexural strength of concrete. Significant increases in flexural strengths were achieved with polymethyl methacrylate copolymer (0–20%) and an antifoaming agent.[46] A cement containing these admixtures yielded a flexural strength of 30 MPa, Young's modulus of 15 GPa, and the work of fracture of 555 Jm^{-2}. The corresponding values for the cement paste containing no admixtures were 12 MPa, 8 GPa and 125 Jm^{-2} respectively. The possibility of increasing the ductility of concrete by incorporating a mixture of natural rubber latex and a superplasticizer has been examined.[47] The addition of superplasticizer prevented premature coagulation and increased the flow of cement mortar. With dry rubber contents up to 2%, the compressive strength and tensile strengths remained unaltered but the strain capacity increased significantly. This was reflected in the marked improvement of the ductile behavior of latex concrete. It was found that up to 2% rubber content, there was no difference in the compressive and tensile strengths of latex and normal concretes (Fig. 9); however, there was a marked increase in the strain capacity in the latex concrete. Thus there is an impressive increase in the ductile behavior of polymer-modified concrete. Beyond 2% rubber addition, although strength decreases by about 15–30%, the ductile behavior remains very pronounced.

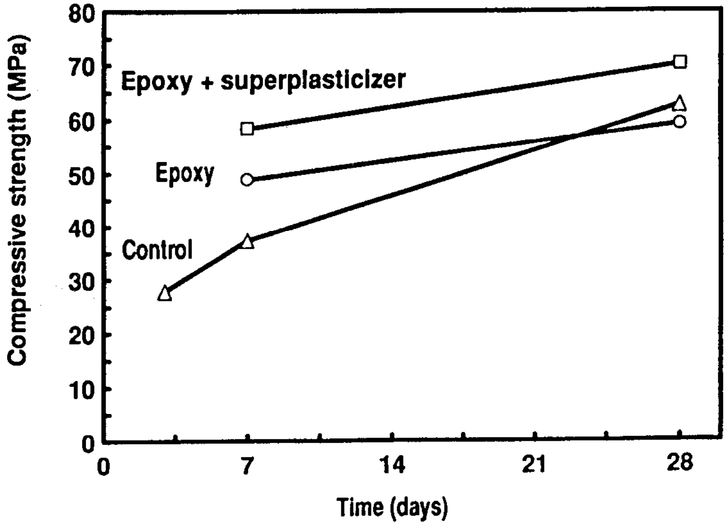

Figure 8. Compressive strengths in epoxy-modified concretes.

Extension of workability, superior bonding strength and increased bonding to compressive strength ratio have been demonstrated in a polymer-modified mortar containing an acrylic latex and a superplasticizer.[48] For example, the reference mortar containing 0% polymer had a bonding to compressive strength ratio of 0.2, whereas the mortar containing 15% polymer, 15% polymer + superplasticizer and 15% polymer + silica fume developed ratios of 0.38. 0.31 and 0.37 respectively. A new type of polyester-modified concrete developing high strengths has been reported recently.[48a]

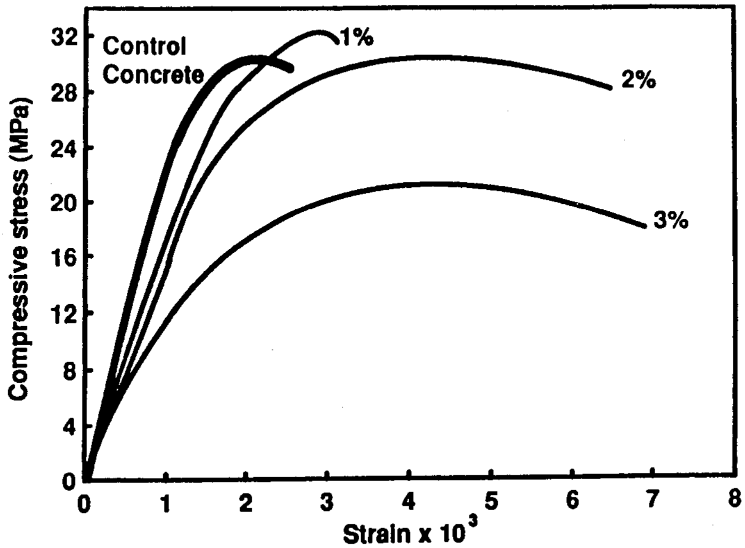

Figure 9. Stress-strain behavior of concrete containing superplasticizer and different amounts of rubber latex.

6.0 MACRODEFECT-FREE CEMENTS

The compressive strength of portland cement paste ranges from 27.5 to 55 MPa, which increases to about 138 MPa with silica fume. The macro defect-free cement having high strength was reported in the early 80's by the Imperial Chemical Industries.[49][50] Compressive strength surpassing 276 MPa was obtained with MDF cements. In the MDF cement, the constituents include the cement and a polymer such as PVA, polyacrylamide, or hydroxypropyl methyl cellulose. A low water-cement ratio of about 0.10 to 0.15 is used. The cement acts as a reactive filler and it is only partially hydrated. Since the hydrated cement may act as a cross-linking agent with the polymer, the polymer should be considered as an admixture, although it is used in large amounts. Special processing techniques are necessary for fabricating MDF cements. Roll milling and mixing at high shear rates are involved. Full strength development is achieved by curing at about 80–120°C for about 24 hrs.

The cement containing PVA and high alumina cement is sensitive to moisture, the flexural strength decreases with exposure to moisture. Improvements are achieved by insolubilizing PVA matrix with cross linking or coupling agents. Improved strengths are obtained by inclusion of an epoxy functional group and boric acid or organic chromium complexes as cross-linking agents.[51] A flexural strength as high as 250–300 MPa has been obtained with epoxy functional silane coupling agent (Fig. 10).[51] The value for the reference specimen is high because it was not exposed to moisture. On exposure to moisture, the strength of the reference specimen decreases by 50% of the original strength whereas that of the treated specimen will not be affected much.

Attempts have been made to fabricate MDF cements by using inorganic polymers such as $(NaPO_3)n$ and $(NaPO_3)n\ Na_2O$.[51a] The samples were made at a water-solid ratio of 0.182, at a phosphate-cement ratio of 0.1. The flexural strength with the former additive was 33.7 MPa, and with the latter, 20.1 MPa, at one day. The reference had a strength of 7.3 MPa at one day.

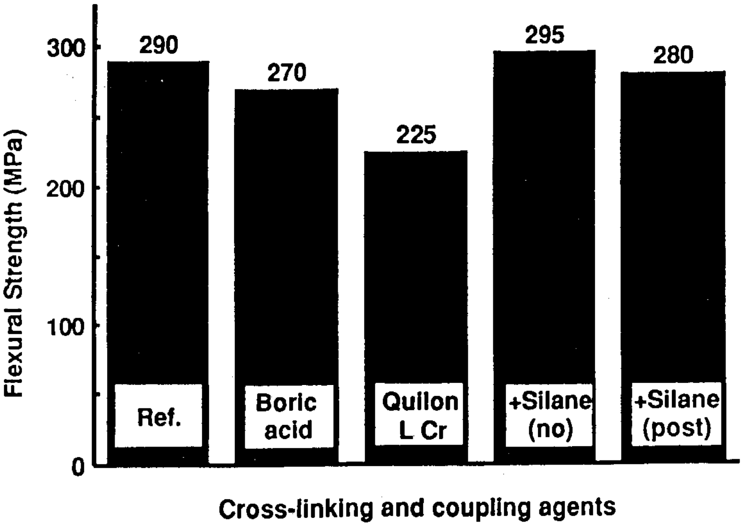

Figure 10. Flexural strengths of MDF cements.

7.0 ACTIVATOR ADMIXTURES FOR SLAGS

The activation of granulated, blast furnace slag in slag concrete is generally based on the alkalis released from the hydration of portland cement. Use of slag as a cement without portland cement has advantages. Because the strength development of slag by itself occurs at a slower rate than that of portland cement, much attention has been directed to a study of the activation of slag containing no cement. Activators are of three types: caustic alkalis (Na, K or Li hydroxide), non-silicate salts of weak acids (R_2CO_3, R_2SO_3, R_2S or RF; R = Na, K or Li), and silicate salts of type $(R_2O)(n)\cdot SiO_2$. All three types are used for basic slags (containing larger proportions of lime, aluminum oxide, magnesium oxide, alkalis, etc.) but for neutral or acid slags (containing larger proportions of silica, phosphorous compounds, etc.), non-silicate salts of weak acids are not recommended.

The types of activators used include sodium hydroxide, sodium carbonate, F-activator produced in Finland (contains NaOH, Na_2CO_3 and lignosulfonate) sodium silicate, sodium sulfate, potassium sulfate, lime and their combinations. For better workability and low water requirements admixtures such as lignosulfonates, gluconates and superplasticizers have also been added with activators. The rate of hydration of slags is enhanced using finely ground slag and higher temperatures. The degree to which the slag is activated depends not only on the type and amount of the activator, temperature and fineness but also on the chemical composition and glass content of slag. In view of this, the best activator suggested for a particular slag may not be applicable for another slag.

With F concrete (Finnish formulated concrete) using alkali activators, Byfors et al.[52] concluded that best strengths are obtained with 2% NaOH + 2% Na_2CO_3. Talling[53] achieved optimum strengths in slag-mortars with sodium silicate activators containing 3–6% Na_2O. Gjorv[54] studied the alkali activator in combination with the Finnish formulation F on physical and mechanical properties of slags of different Blaine surface areas, and at different temperatures. With a Blaine surface area of 640 m^2/kg, strength (at 24 hrs) attained a value of 22.6 MPa. A review of alkali-activators was published by Talling and Brandstetr.[55] The strength development in a normally-cured slag mortar containing sodium silicate of M_s = 2 (SiO_2/Na_2O) and made at a water-slag ratio of 0.32–0.35, was reported to be 10–20 MPa at eight hours, 30–42 MPa at one day, and 55–85 MPa at twenty-eight days. Further increase in strength occurred at higher temperatures. It was also found that the mixture was sticky when sodium silicate was used; addition of limestone powder, fly ash, silica fume, granite, etc., improved the workability. In another study, high strengths were obtained using 7% NaOH for a slag of Blaine 1000 m^2/kg. Also in an alkali-activated fly ash mixture with 7% NaOH, the strengths at 3, 7 and 28 days were reported to be 12–13, 14–15 and 20 MPa, respectively, and the corresponding values for slags were 16, 18 and 36 MPa.[56] Activation of phosphorus slag is also possible with cement clinker, Na_2SO_4 and sodium silicate.[57] Douglas and Brandstetr[58] have found that activated slag mortars with a dilute solution of sodium silicate, 2% lime, and 1% Na_2SO_4 gave compressive strengths comparable to ASTM C-109 portland cement mortars. For example, the strengths of mortars at a water-binder ratio of 0.48 were 13.4, 29.4 and 35.7 MPa at one, seven and twenty eight days respectively. Investigating slags with surface areas between 147 and 654 m^2/kg and seven NaOH activator concentrations from 1.6 to 30% and water-slag ratios of 0.3, 0.4, 0.6 and 0.7 and a superplasticizer, Isozaki et al.[59] obtained effective strengths with 2–3% NaOH. Accelerated heat effects were also observed with NaOH or Na_2CO_3-NaOH mixtures in slags. Tango and Vaidergorin[59a] used a mixture of lime and sodium sulfate (10% and 5% respectively) to obtain a strength of about 30 MPa in slags at seven days.

In a comprehensive investigation, using pastes and mortars, Andersson et al.[60] evaluated the activation of slags using NaOH, Na_2CO_3 and water glass of general composition, Na_2O (n)•SiO_2, where n varied between 0.9 and 3.35. Properties such as setting time, compressive strength, flexural strength, porosity, dynamic modulus of elasticity and shrinkage were studied. In general, setting time decreased in activated slag mortars. In several cases, activated mortars produced higher strengths than the reference mortars. The strength development in reference mortar and that containing 8% sodium silicate or 11% NaOH were comparable. The mortars were all cured at 20°C. The water-binder ratio was 0.43 for the activated mortars and 0.50 for the reference mortar. Only slag containing NaOH had sufficient strength for it to be stripped from the form at an early age. However, at seven days and after, the sodium silicate-activated slag had higher strengths (Fig. 11).[60] At twenty-eight days, sodium silicate-activated slag had strength in excess of 50 MPa, whereas the reference concrete showed a strength of about 40 MPa. Shrinkage values (at 231 days) of activated mortars were generally higher, the values being in the range 0.093–0.22% compared to 0.068 for the reference mortar.

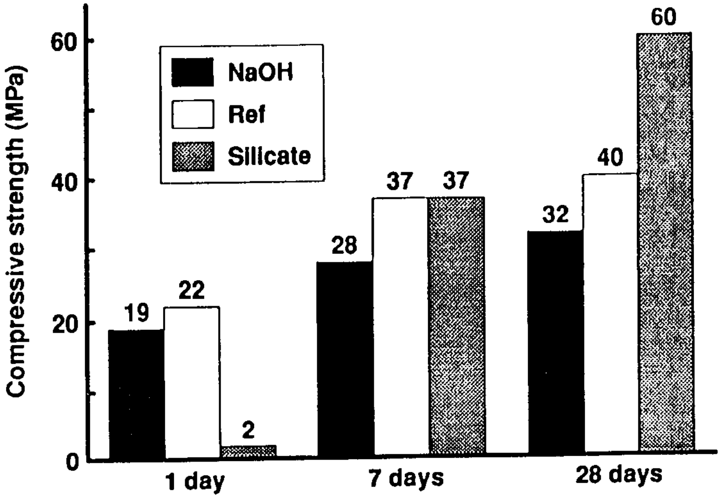

Figure 11. Effect of activators on compressive strength of slags.

The properties of the sodium silicate-activated slag containing a Na-silicate-slag ratio = 0.32–0.48, silicate modulus = 1.22 or 1.47, and containing air between 4.5 and 7.3% was evaluated by Douglas, Bilodeau and Malhotra.[60a] It was found that the compressive strength (activated by silicate) beyond 7 days was equal or higher than that of the reference concrete. Drying shrinkage was higher than that of the normal concrete. At low silicate-slag ratios, the specimens showed poor freezing/thawing resistance although they exhibited improved resistance to chloride-ion penetration.

The products formed in the activated slags are reported to be low-basic calcium silicates, alkali-alumino silicate hydrates, calcium-rich magnesium silicate hydrate, $2CaO{\bullet}Al_2O_3{\bullet}2SiO_2{\bullet}8H_2O$, hydrogarnet, silicic acid, zeolite type compounds, etc. At high temperatures, crystalline compounds abound. No $Ca(OH)_2$ is detected.

Although there are several advantages of using activated slags there are some problems associated with their use: quick setting, sticky consistency, efflorescence effects, increased alkali-aggregate expansion, higher carbonation, irritation to the skin by the use of some activators, and higher costs.

Much more work needs to be done on activators for resolving some of the apparently contradictory results reported in the literature.

8.0 ALKALI-AGGREGATE EXPANSION-REDUCING ADMIXTURES

One of the well known methods of reducing the expansion of concrete caused by alkali-aggregate reaction is to incorporate pozzolans in a concrete mixture. The possibility of using chemicals to reduce expansion was first suggested in the early 50's. The materials that have been studied include salts of lithium, barium and sodium, proteinaceous air-entraining admixtures, aluminum powder, copper sulfate, and water-reducing and set-retarding admixtures. The expansion of concrete containing reactive limestone aggregate could be reduced by adding lithium and ferric chloride.[1] Any chemical that is used should not only reduce expansion but also not adversely affect other concrete properties such as setting times, mechanical characteristics and durability. Because of limited laboratory data, no recommended practices have been formulated pertaining to the use of these admixtures.[61]

There has been a resurgence of interest in the development of a chemical to reduce the expansion caused by alkali-aggregate reaction. Ohama et al.[62] investigated the effect of sodium silicofluoride, alkyl alkoxy silane, lithium carbonate, lithium fluoride, styrene-butadiene rubber latex and lithium hydroxide on the expansion of mortar containing cement with 2% equivalent Na_2O. Compressive strength measurements were also carried out. In Fig. 12 the results are plotted in terms of expansion per unit length. The reference mortar without the chemical shows an expansion of 48×10^{-4}. The expansion is only 26×10^{-4} with 0.5% sodium silicofluoride. This was attributed to the formation of an insoluble compound with strong siloxane linkages. The alkyl alkoxy silane is also very effective in reducing the expansion of the reference mortar by 95%. Of the silanes, the most effective expansion-reducing compound is reported to be hexyl trimethoxy silane.[62a] Lithium compounds reduce expansion, but to a lesser extent than other compounds. The results of the relative compressive strengths indicate that the mortar with sodium silicofluoride shows the highest strength, being about 50% higher than that of the reference. The addition of other admixtures did not result in changes in strengths.

The work by Sakaguchi et al.[63] on the effect of lithium carbonate, lithium nitrite and lithium hydroxide showed that all these compounds effectively decreased the expansion due to alkali-silica reactions. For example, at a $LiOH \cdot H_2O$ dosage of 0.65%, the expansion reduced from about 0.25% to 0.1%. The effect of lithium compounds is attributed to the formation of lithium silicate that dissolves at the surface of the aggregate without causing swelling.[63]

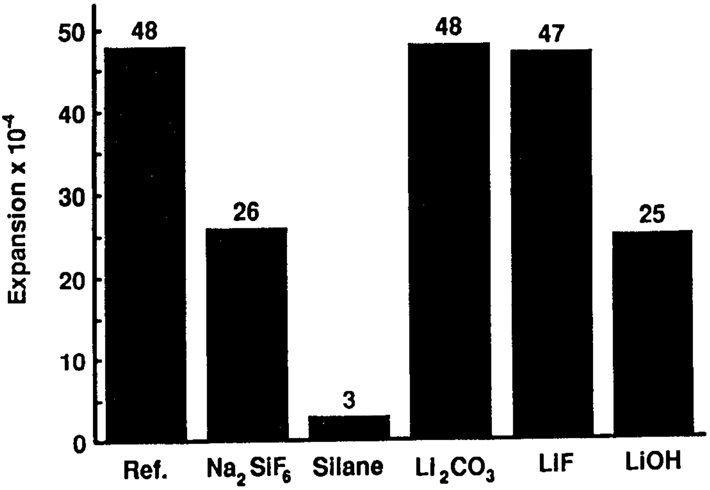

Figure 12. Effect of chemicals (0.5%) on alkali-aggregate expansion.

The effect of accelerators and retarders on the alkali-aggregate expansion has recently been reported.[63a] Addition of sucrose decreased expansion whereas $CaCl_2$ increased expansion. Other admixtures, lactic acid, EDTA, and oxalic acid, had no effect.

A method of treating the reactive aggregate before making concrete or treating the hardened concrete with calcium phosphate has been proposed as a method of countering the alkali-silica expansion. The expansion of a reference concrete containing a non-reactive aggregate was compared with that containing a reactive aggregate treated with monocalcium phosphate monohydrate. The aggregate treated with phosphate even for a minute had almost no expansion at 28 days, compared to an expansion of about 1% in the reference concrete.[64] This method was less effective for concrete containing reactive carbonate aggregates. Phosphate addition may interfere with the dissolution of silica gel and the formation of gel. It is also possible that phosphate reduces the osmotic potential and the swelling pressure in the gel.

Nakajima and coworkers studied the effect of air-entraining admixture, air entraining admixture containing a water reducer and a superplasticizer on the expansion due to alkali-aggregate expansion.[64a] All the additives decreased expansion. Hasni and Salamon[64b] found that by complexing the potassium ions with an agent such as β-cyclodextrine, the expansion could be reduced. A combination of silica fume and an air-entraining admixture has been shown to be effective in decreasing the expansion.[64c]

9.0 ADMIXTURES FOR UNDERWATER CONCRETING

Dewatering of hydraulic structures for repair is difficult and expensive. Recent advances in cohesion-inducing admixtures have allowed placement of concrete under water without the use of conventional tremies. The concrete is cohesive enough to allow limited exposure to the water, yet has good mobility to move underwater with little loss of cement. Such cohesion-inducing admixtures are referred to as antiwashout admixtures (AWA's).

Most AWA's are composed of water soluble cellulose ethers or water soluble acrylic-type polymers as the main component.[65] The action of admixtures is to increase the viscosity of water in the mix. This results in an increased thixotropy of the concrete and an improved resistance to segregation. Dosage of the admixture ranges from 1 to 1.5% by weight of the water in the mixture and it is frequently used in combination with a superplasticizer.[66] The magnitude of the effect produced is dependent on the admixture dosage and the molecular weight of the main component. It is usually discharged into the mixer at the same time as the other materials.

Laboratory evaluation of non-dispersible concretes has been carried out to study the effect of various combinations of water reducers and superplasticizers.[65]-[68] Conventional lignosulfonate and hydroxycarboxylic acid water reducers and naphthalene formaldehyde sulfonate and melamine formaldehyde sulfonate-based superplasticizers were used in these studies. The Tatterstal two point workability test and wash out test were used to evaluate the mixture characteristics. Best results were obtained with lignosulfonates and melamine formaldehyde. The naphthalene-based superplasticizers produced erratic results in flowability and cohesion.[66]

Field tests have also been carried out on commercially available antiwashout admixtures.[67] The trials evaluated bonding capability, pumpability and flowability around reinforcement. The quality of the recovered test pieces and strengths of cores show AWA concrete to be suitable material for in-situ structural concrete construction at considerable water depths.[68]

Other investigations have centered on the use of auxiliary admixtures to reduce the amount of polymer used in the concrete for cost reduction purposes.[69] This admixture reportedly reacts with the polymer in the AWA to increase the apparent molecular weight of the polymer thereby improving its cohesion inducing properties. Table 11 shows the results obtained from a study of concrete mixes containing the auxiliary admixture glutaraldehyde combined with a polyacrylamide AWA. It can be seen that the auxiliary agent increases resistance to cement washout (as measured by transmittance) permitting a reduction of the polymer by 0.8% by weight, without any adverse effect on strength.

Table 11. Results of Concrete Containing Glutaraldehyde

Polymer (%)	Glutaraldehyde (%)	Transmittance*	Slump (mm)	Strength (28 days)
0.6	—	92	130	34.5
	0.5	95	125	34.8
	1.0	97	125	35.0
0.8	—	95	180	33.5
	0.5	98	170	34.0
	1.0	100	160	34.2
1.5	—	99	225	33.2
	0.2	100	220	33.8
2.0	—	100	220	32.0
	0.1	100	215	32.5
3.0	—	100	145	29.0
	0.1	100	140	29.2

* Measured as a turbidity by photoelectric photometry

10.0 NON-CHLORIDE ACCELERATING ADMIXTURES

A large amount of data is available on the use of calcium chloride as an accelerator in concrete.[70] The presence of chloride ions in concrete however, tends to increase the potential for corrosion of the embedded steel and hence there has been continued interest in developing an alternative to calcium chloride that accelerates cement hydration but does not promote corrosion of steel. Soluble salts such as bromides, fluorides, carbonates, thiocyanates, nitrates, nitrites, thiosulfates, silicates, aluminates and alkali hydroxides are known to accelerate the setting of cement. Organic compounds such as triethanolamine and formates also act as accelerators. Commercial non-chloride accelerators contain a combination of admixtures and their short and long term effects on concrete are yet to be completely assessed.

Calcium formate is a popular non-chloride admixture used commercially. It may not be as efficient an accelerator as calcium chloride. For example, a concrete containing 2% Ca-chloride or 2% Ca-formate may have one day strengths of 384% and 88 % strength over the control, respectively.[70a] The effect of formate on strength development in concrete depends on the tricalcium aluminate-sulfate ratio of the cement. Table 12 illustrates how the early strengths depend on the C_3A/SO_3 ratio. At a ratio of about 3.0 in concrete containing 2% formate, there is reduction in strength with respect to the control. Addition of chloride does not have such an adverse effect.[70a]

Table 12. Concrete Strength using Ca-Chloride or Ca-Formate (Influence of C3A/SO3 Ratio)

ADMIXTURE	C3A/SO3	COMP. STR. (%) 1 DAY	3 DAYS
CONTROL	2.44	——	——
2% FORMATE	2.44	3	15
2% CHLORIDE	2.44	30	24
CONTROL	3.32	——	——
2% FORMATE	3.32	-14	8
2% CHLORIDE	3.32	18	3
CONTROL	4.34	——	—
2% FORMATE	4.34	44	47
CONTROL	4.70	——	—
2% FORMATE	4.70	36	32
2% CHLORIDE	4.70	117	29

Rear and Chin[71] tested three commercially available non-chloride admixtures for their effect on early strength development of concretes with five ASTM Type I and Type I/II cements, two ASTM class F fly ashes and two ASTM C fly ashes. The testing was carried out at 22°C and 10°C. The three accelerators studied were Ca-nitrite, Ca-nitrate and Na-thiocyanate. At 22°C with the Ca-nitrite and Na-thiocyanate admixtures, the one day strength of concrete increased by 128 to 144% and the 7 day strength by 109 to 131%. Not much improvement resulted with Ca-nitrate. At 10°C however, all the admixtures promoted higher strengths with respect to the reference concrete at one and seven days. In class C fly ash concrete containing three types of cements, the Ca-nitrite based admixture promoted strength in two of them. In class F fly ash concrete, two cements showed higher strengths at one day and all cements showed higher strengths at seven days with respect to the reference concrete containing no calcium nitrite. At twenty-eight days, generally, calcium nitrite enhances the strengths of concrete containing all three cements.

Brook et al.[72] have described the effect of a new non-chloride accelerating admixture on concrete containing a fly ash (called class CF) in which the CaO content was 5–15%. The setting, strength and other characteristics of the concrete were investigated at 21°C and 10°C. The accelerator shortened the setting times by 80–180 minutes and increased the compressive strengths at 3, 7 and 28 days. For example, the 3-day strength of the plain concrete was about 24 MPa and that containing an accelerator dosage of 2.8 L/100 kg of cement, had a strength of about 31 MPa. The corresponding values at twenty-eight days were 41.4 and 44.8 MPa. Although the flexural strength at three days was higher for concrete with the accelerator, the 7- and 28-day strengths were only equal to those of the plain concrete. There was no deleterious effect of the accelerator on shrinkage and air-void characteristics. The accelerator had also beneficial effects on concrete made with class F and C fly ashes.

Many other non-chloride accelerators have been studied for their action on the hydration and strength development in cements, mortars and concrete. Kuroda et al.[73] found acceleration of setting and strength development using a multicomponent calcium nitrite-calcium rhodonate-triethanolamine admixture in concrete. Triethanolamine was found to be an accelerator for the slag cement.[74] A water soluble organic material of the carboxylic acid-type was investigated for its effect on cement, mortar and concrete by Popovics.[75][75a] At a dosage of 2%, the 3- and 7-day strengths increased in comparison to the reference mortars. Setting time was reduced by 50% with respect to the control. It was compatible with superplasticizers and epoxies, produced greater strength with ASTM Type III cement than with Type I cement, and yielded greater strength with delayed addition. Sodium molybdate as well molybdenum oxides have also been found to be accelerators for cement but they are not as efficient as calcium chloride.[76][77]

11.0 EXTENDED SET CONTROL ADMIXTURES

Every year very substantial amounts of the ready-mixed concrete produced are returned for disposal in dump sites. There are now increasing environmental concerns and restrictions regulating the disposal of returned plastic concrete. Disposal of fresh concrete is now a major problem for the ready-mixed concrete industry.[78] Admixture manufacturers have developed a cost effective alternative to the disposal problem. The technique keeps concrete fresh for longer periods making possible its storage and later use. The system uses two non-chloride admixtures (stabilizer and activator), which alternately suspend and reactivate cement hydration. In this system, a stabilizer coats cement particles to suspend hydration and interacts with hydration products that are in solution. Depending on the dosage, the mix can be maintained in a deactivated state for hours or days. An activator is then used to remove the coating, allowing hydration to proceed. The admixture system may be used the same day during long hauls or long waiting periods as a consequence of pump, truck or equipment breakdown, thus permitting the reuse of aged fresh concrete. Overnight/weekend stabilization of both returned fresh concrete and truck wash water for reuse as part of the mix batched the next day, is another important application.

The stabilizer is usually used at a dosage ranging from 0.325 to 8.47 L/100 kg of cementitious materials. Dosage is influenced by a number of factors including, *(a)* mixture proportioning, *(b)* elapsed time between batching and stabilizing, *(c)* average ambient temperatures, *(d)* quantity of reclaimed concrete and *(e)* desired time of stabilization. The activator dosage range is 0.65–0.98 L/100 kg of cementitious material and is also governed by most of the factors influencing the stabilizer dosage. Unlike conventional retarders, the stabilizer can be used at high dosages without the attendant adverse effects such as flash set and poor strength development characteristics resulting from the use of normal retarders.[79]

The stabilizer may consist of carboxylic acids and phosphorus-containing organic acid salts. The mechanism of action of the stabilizer admixture is thought to be related to the inhibition of CSH and CH nucleation. It is claimed that the nucleation process is controlled more comprehensively than that obtained with conventional retarders.[80] Cement hydration is arrested by the admixture acting on all phases of cement hydration including the C_3A fraction. The claim is supported by conduction calorimetric data and scanning electron microscopic examination of the surfaces of stabilized and activated alites. The stabilizer is a surface active agent designed to prevent surface nucleation of calcium ion rich hydrates. When nuclei have already formed, the stabilizer retards their growth and alters the external morphology of subsequently formed hydrates. The ability of the stabilizer to stop formation of primary CSH hydrates and its moderate slowing of C_3A suggests that in portland cement, the stabilizer prevents epitactic growth of primary CSH on C_3S, while only slightly slowing C_3A hydrates from precipitating out of solution. Although the action on hydrate nucleation cannot be directly attributed to these admixtures, there are data which indirectly illustrate these effects. For example, the alteration of ettringite morphology on alite, and the more open texture of ettringite on C_3A suggests that these admixtures strongly influence how the hydrates are formed.[80]

Manufacturers claim that the admixture has been tested for its effect on setting, air entrainment, freezing-thawing resistance, mixtures containing fly ash and slag, flexural and compressive strengths, length change, susceptibility to cracking and corrosion and creep. The reported field and laboratory data show that no adverse effects are produced by the admixtures on these properties.[79] Under same experimental conditions the same cement produces identical hydration products both with treated and control cement pastes. The physical structure as revealed by water vapor sorption and mercury porosimetry was also the same for both pastes.

Recently Ramachandran and co-workers[81] studied the extended retarding effect of phosphonate-based acids and their salts. Of the phosphonates studied, diethylenetriaminepenta-methylene phosphonic acid was found to be the best retarder. The conduction calorimetric curve shows that at a dosage of only 0.05%, this chemical extended the induction period of cement hydration to 21 hours.

12.0 CORROSION INHIBITORS

Corrosion of steel in concrete is enhanced in the presence of chlorides added in excess as an admixture and through the permeation of de-icing salts. Corrosion inhibiting admixtures are added in small amounts to check, decrease or prevent corrosion of the reinforcement.

A number of reports have dealt with the use of nitrite-based inhibitors. Alonso et al.[82] have suggested that in order to protect steel from corrosion due to carbonation, nitrite at a dosage of 3% should be used. Although Ca-nitrite is known to be a good inhibitor, the dosage at which it should be used for effectiveness depends on the concentration of the chloride. At 2% calcium nitrite, and 391 kg/m^3 cement, corrosion may be initiated if chloride ion per cubic meter exceeds 0.6 to 1.2 kg.[83] Recent work on the use of sodium nitrite on the corrosion of concrete exposed to sea water has shown that, in cracked concrete, corrosion actually increases with this inhibitor.[84] Sodium nitrite is also reported to be deleterious to strength development, to cause efflorescence and also expansion due to alkali-aggregate expansion. The inhibitive action of Na_2PO_3F has been reported and it appears to act as an anodic inhibitor.[85] Mortars prepared with 0.1–0.2% ZnO are reported to inhibit corrosion on exposure to sea water or 3% chloride solution.[86] Zinc oxide acts through an anodic protection mechanism.

Mixed inhibitor systems have a good potential for use in reinforced concrete. A mixture of Ca-nitrite and Na-molybdate effectively protects steel from corrosion. For example $Ca(NO_2)_2$/Na-molybdate in the ratio of 1:11 is reported to be more effective than Ca-nitrite.[87] The mixed inhibitors are more effective than the individual inhibitors because of the synergistic effects. The feasibility of injecting synergistic inhibitors has been tried to protect steel in concrete.[88] The compounds found to be effective included tetramethyl phosphonium nitrite, tetraethyl phosphonium nitrite, tetrabutyl phosphonium nitrite and tetraphenyl phosphonium nitrite. El-Sayed and Ali[89] have reported that calcium formate, calcium nitrate, sodium benzoate and sodium nitrite are good corrosion inhibitors. Although it was found that incorporation of these admixtures in concrete increased its strength up to 180 days, there was a subsequent decrease in strength. The results are shown in Table 13.[89]

Table 13. Strength Development in Concrete Containing Some Corrosion-Inhibiting Admixtures

	Strengths at Different Curing Times (MPa)				
Admixture	7	28	90	180	365 (days)
Ref	13.6	16.3	16.8	19.9	23.0
2% Ca Formate	20.7	21.1	26.1	31.2	25.2
2% Na Benzoate	15.6	19.9	22.9	23.5	15.9
2% Na Nitrite	14.4	21.2	24.6	26.4	21.7

13.0 CONCLUDING REMARKS

There has been continuous activity in the development of admixtures as evidenced by published literature and patents. In the years 1985–1989, nearly 600 patents were taken on concrete admixtures and the enormous interest in their development is evident from 242 patents reported in 1989 and 140 in 1992.

In construction, there will be an increasing demand for the development of concrete with high performance characteristics. Such concrete should be able to perform adequately against hostile environments when used in ocean sea floor tunnels, offshore structures, sewage pipes, and in structures exposed to hazardous chemicals and radioactive materials. Special types of concrete have also to be developed for repairs, and for infrastructural applications. Utilization of waste materials in concrete and solidification of hazardous materials in concrete will also require special mixtures. For all such applications utilization of novel admixture combinations will have to be developed. Multifunctional admixtures for various purposes, in which a combination of admixtures would be necessary will be developed in the coming years. Greater attention will be directed to the production of more economical admixtures utilizing new techniques and raw materials derived from chemical wastes. The production of some of the admixtures presently used, such as lignosulfonates, may pose environmental concerns; hence new methods will have to be devised to synthesize them or alternative admixtures have to be developed. Although non-chloride admixtures are being used presently, they are not as efficient and economical to use as calcium chloride. Therefore there is a great need to develop an admixture as efficient as calcium chloride. Efforts will continue in the field of advanced cement systems to produce materials of very high strengths and for such systems novel admixtures will have to be developed. The antifreezing admixtures are not popularly used in North America. Some work has been carried out on these admixtures and it can be foreseen that more attention will be directed towards the production of these admixtures in the future. Also, more work will be carried out to develop economical admixture combinations for the reuse of returned concrete in the ready-mixed concrete plants. Although research has shown that some chemicals retard the alkali-aggregate expansion reaction, much more long-term work will have to carried out before they will be applied in practice. Interesting work has been done on the activation of slags using admixtures but a more exhaustive work has to be carried out in North America for large scale applications. Corrosion inhibitors are being used to counteract the corrosion of the reinforcement. The long term corrosion aspects and also the possibility of using dual inhibitors are expected to receive more attention in the coming years. Improved properties are obtained by the use of polymers in concrete and further improvements and the possibility of new applications will be sought by using novel types of polymers in combination with other admixtures. Further attention will be directed to the development of admixtures for purposes such as roller compacted concrete, shotcrete, oil well cementing, grouting and materials for repair and restoration. Extended set retarders have been used for various purposes, such as in hot weather concreting, in concretes containing large amounts of cement, for long hauls, in large placements, and for preventing cold joints. Work is expected to be carried out on the development of more efficient retarders that will not have any adverse effects on concrete.

There has been an increased activity in the production of ultra high strength concrete with strengths of the order of 120 MPa, and having high workability and good durability. This is accomplished with ASTM type II cement, superplasticizers, a retarder, silica fume, low air content and specially chosen aggregates.[90] Further research can be foreseen in this area. Another important development is related to the application of superworkable concrete.[91] In such a concrete, the segregation resistance and self-compactibility is provided by the addition of an admixture based on a water soluble cellulose ether and flowability is ensured with a superplasticizer. A typical mixture consists of blast furnace slag cement, fine aggregate (fineness modulus of 2.87), coarse aggregate (fineness modulus of 6.65), water soluble ether, superplasticizer and air entraining agent (anionic surfactant).

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5

Accelerators

V. S. Ramachandran

1.0 INTRODUCTION

An accelerating admixture is a material that is added to concrete for reducing the time of setting and accelerating early strength development. Accelerating admixtures are used in cold water concreting operations and also are components of antifreezing admixtures and shotcreting mixes. In cold weather concreting, there are other alternatives such as the use of type III cement, use of higher than normal amount of portland cement type I, or warming of the concrete ingredients. Of the above, the most economical method is the use of type I cement in conjunction with an accelerator. The advantages include: efficient start and finishing operations, reducing the period of curing and protection, earlier removal of forms so that the construction is ready for early service, plugging of leaks, and quick setting when used in shotcreting operations. Many substances are known to act as accelerators for concrete. The American Concrete Institute Committee 212 (Chemical Admixtures for Concrete, Report ACI-212, American Concrete Institute, Detroit, p. 31, 1990) has divided accelerators into four groups as follows: *(i)* soluble inorganic salts that include chlorides, bromides, fluorides, carbonates, thiocyanates, nitrites, nitrates, thiosulfates, silicates, aluminates and alkali hydroxides that accelerate the setting of portland cement; *(ii)* soluble organic compounds such as triethanolamine (TEA), calcium formate, calcium acetate, calcium propionate and calcium butyrate. The other two groups are used in combination with water reducers:

(iii) quick setting admixtures used in shotcrete applications and which promote setting in a few minutes and may contain sodium silicate, sodium aluminate, aluminum chloride, sodium fluoride, strong alkalis and calcium chloride; and *(iv)* miscellaneous solid admixtures such as calcium aluminate, seeds of finely divided portland cement, silicate minerals, finely divided magnesium carbonate and calcium carbonate. To these could be added multifunctional admixtures that improve the properties of concrete in more than one way. Of these, calcium chloride is the most widely used because of its ready availability, low cost, predictable performance characteristics and successful application over several decades. It is obtained as a by-product in the manufacture of Na_2CO_3 by the Solvay Process. In a British document of 1977, of the sixteen commercial accelerators listed, twelve had calcium chloride as an active ingredient.[1]

Calcium chloride has been used as an admixture for a longer period than most other admixtures. The first documented use of calcium chloride in concrete can be traced to the year 1873[2] and the first patent to the year 1885.[3] Prior to 1900, there were only about seven publications concerning the use of calcium chloride in portland cement, but since then the literature has grown substantially. Interest in this admixture is evident from innumerable papers, patents, reviews, chapters in books, and symposia; a book has been published recently discussing the science and technology related to the use of calcium chloride in concrete.[4] Cook (private communication) prepared a bibliography of accelerating admixtures for the years 1960–1986 in which 240 references were listed.

There is considerable disagreement and even misunderstanding on the effect of calcium chloride on many properties of concrete. For example, whereas in some countries the use of calcium chloride is prohibited, in some others, such as Canada and the USA, the use of calcium chloride is permitted provided certain precautions are taken. In the Russian literature, use of relatively larger additions of calcium and sodium chloride has been advocated.[5] Many aspects of the action of calcium chloride are controversial, ambiguous or incompletely understood. In spite of the above, to this day enormous interest is being shown on various aspects of calcium chloride because it is not only very economical to use but also is the most efficient of all accelerators. Attempts have continued to find an effective alternative to calcium chloride because of some of the problems associated with its use.

2.0 INFLUENCE OF CALCIUM CHLORIDE ON THE HYDRATION OF CEMENT MINERALS

2.1 Tricalcium Silicate

Although calcium chloride influences the hydration behavior of all cement components, the early strength development and setting is related to its effect on the tricalcium silicate phase. It is thus important to gain an understanding of the influence of $CaCl_2$ on this phase. Calcium chloride is somewhat unique because the cation-anion Ca^{+2}/Cl^- combination ranks as one of the best accelerators for the hydration of C_3S. The accelerating effect of cations is in the decreasing order $Ca^{+2} > Sr^{+2} > Ba^{+2} > Li^+ > Na^+ > K^+$ and that of the anions, $SO_4^{-2} > OH^- > Cl^- > Br^- > I^- > NO_3^- > CH_3COO^-$.[6] There is some evidence that Cl^- is a better accelerator than SO_4^{-2} in the hydration of portland cement.[7][8] Calcium chloride not only alters the rate of hydration of cement minerals but may also combine with them. It also influences such properties as strength, chemical composition, surface area, morphology, and pore characteristics of the hydration products.

Hydration Behavior. The silicate phases C_3S and C_2S, together constituting the major portion of the components in portland cement, influence considerably its hydration and strength development. The accelerating influence of $CaCl_2$ on the hydration and hardening behavior of C_3S was observed in 1931 by Sloane et al.,[9] and Haegermann,[10] and has been confirmed by subsequent work.[11]-[41] Addition of $CaCl_2$ also results in a decrease in the dormant or induction period in the hydration of C_3S. The accelerating influence of $CaCl_2$ on the hydration of C_3S is conveniently followed by estimating, at different times, the amount of residual unhydrated C_3S, the amount of $Ca(OH)_2$, non-evaporable water content, electrical conductivity, heat liberation, etc.

The techniques of Differential Thermal Analysis (DTA) and Thermogravimetry have proven to be useful in following the hydration of C_3S in the presence of calcium chloride.[7][11][13][14][16][24][28][33][42] The DTA method estimates the amount of calcium hydroxide and the amount of C_3S present during the course of hydration. Estimation of the silicate phase involves determining the peak intensity associated with the reversible crystalline transition at about 915°C.[42a] Typical DTA results are illustrated in Fig. 1 and 2.[4][13] Thermograms of C_3S hydrated for different times in the presence of $CaCl_2$ enable a study of the progress of hydration, identification and estimation of some of the products. Unhydrated C_3S exhibits endothermal effects at about 680°, 930° and 970–980°C representing crystalline transitions. The onset of hydration is indicated by endothermal effects below 300°C. This effect is caused by the removal of loosely as well as firmly bound water from the C-S-H gel. The increase in the intensity of this effect with time is indicative of the formation of larger amounts of C-S-H product. A very small endothermal effect at about 480°C appears within a few minutes, becomes more evident at 1 hr and is attributed to the dehydration of $Ca(OH)_2$. In the first eight hours, the amount $Ca(OH)_2$ produced is about 25% of that formed in thirty days.

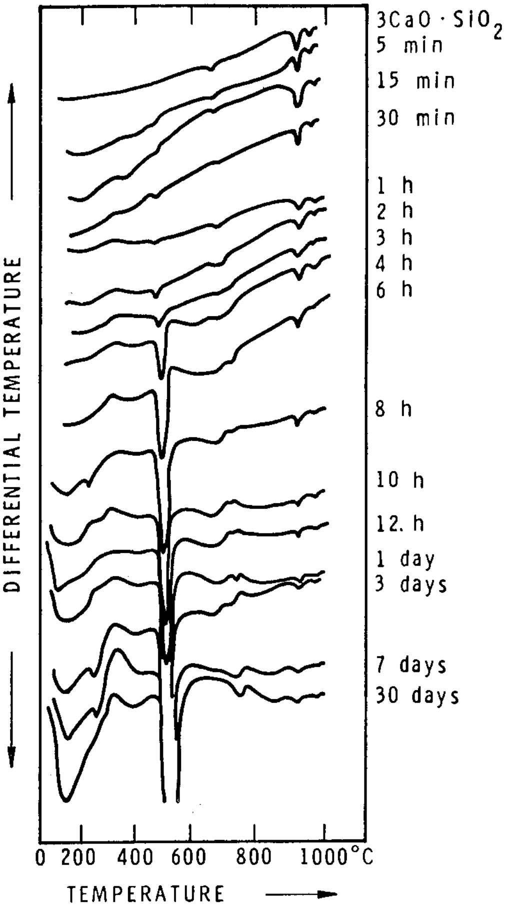


Figure 1. DTA curves of $3CaO{\bullet}SiO_2$ hydrated in water.

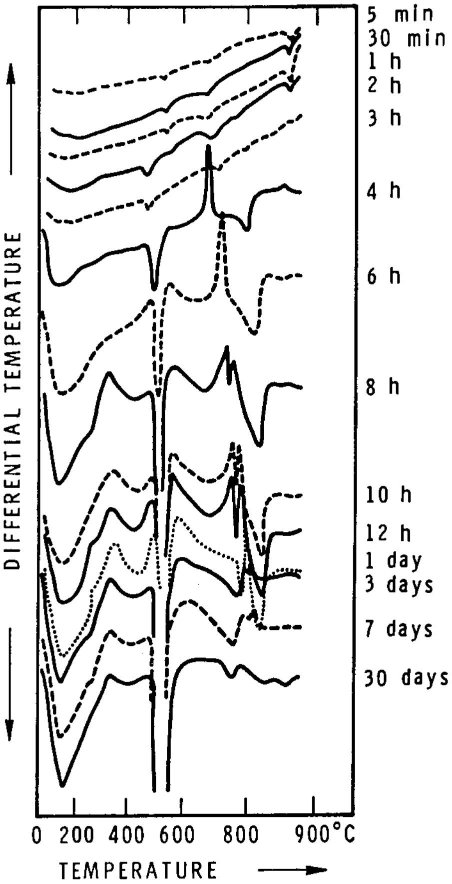


Figure 2. Hydration of $3CaO{\bullet}SiO_2$ in the presence of 1% calcium chloride.

In the presence of 1% $CaCl_2$, the thermograms of hydrating C_3S show significant differences from those obtained without $CaCl_2$. The endothermal effects below 300°C in the presence of $CaCl_2$ are much larger than those obtained in the hydration of $C_3S + 0\% \ CaCl_2$ (Figs. 1 and 2). An endotherm at 550°C, appearing up to two hours in the presence of 1% $CaCl_2$, is absent in C_3S hydrated without $CaCl_2$. There is also evidence that the endothermal effect due to $Ca(OH)_2$ is more intense in samples containing 1% $CaCl_2$ than without it; of the estimated total $Ca(OH)_2$ at thirty days, 33% is formed within 6 hrs of hydration. The onset of an intense exothermal dip at a temperature of 690°C is always followed by a large endothermal dip at about 800–840°C. There is suggestion that it may be caused by the chemisorbed chloride on the C-S-H surface and possibly also by chloride ions in the interlayer positions.[14] The detailed mechanism of the decomposition of this complex is not known.

In the presence of 4% $CaCl_2$, some of the thermal effects become more intense at earlier times than the corresponding ones hydrated in the presence 1% $CaCl_2$. The possibility of a surface complex of chloride on the hydrating C_3S is suggested by an endotherm in the range 570–590°C. A larger endothermal effect at 810–850°C following an exothermal effect is present from three hours to thirty days.

The amount of $Ca(OH)_2$ formed at different periods may be determined by measuring the endothermal areas of $Ca(OH)_2$ decomposition.[13] If the amounts of $Ca(OH)_2$ formed at different periods represent the degree of hydration, then at 30 days, $C_3S + 1\% CaCl_2 > C_3S + 0\% CaCl_2 > C_3S + 4\% CaCl_2$. If the rate of hydration is determined by the disappearance of C_3S, then at 30 days it would be $C_3S + 4\% CaCl_2 > C_3S + 1\% CaCl_2 > C_3S + 0\% CaCl_2$. This apparent anomaly can be explained by the formation of higher C/S products in the presence of 4% $CaCl_2$. The sample hydrated in the presence of 4% $CaCl_2$ will have a lower amount of calcium hydroxide because some of it is in a combined state in the C-S-H phase. The rate of hydration of C_3S (determined by estimating unhydrated C_3S) with 2% $CaCl_2$ shows the formation of an increased amount of C-S-H at all times up to 1 month[4][20] (Fig. 3). In Fig. 4, the fraction of tricalcium silicate hydrated (in the presence of various admixtures) is plotted against the estimated percentage of calcium hydroxide.[42b] The reference material and the pastes containing ZnO, sucrose, lignosulfonate and a superplasticizer exhibit a linear relationship. In the sample containing 3% calcium chloride at any time of hydration, much lower amounts of $Ca(OH)_2$ are formed, indicating that the C-S-H product has a higher C/S ratio.

It has been observed that the DTA peak caused by the presence of $Ca(OH)_2$ shifts to a higher temperature especially at earlier times of hydration.[42c] In the presence of $CaCl_2$ the shift in temperature is lower than that in the reference material. This difference is attributed to the variation in the bonding of calcium hydroxide to the surface of C_3S and C-S-H, especially at earlier periods.

Calcium chloride accelerates the hydration of C_3S even at higher temperatures. The effect is particularly greater at earlier periods of hydration. At twenty-four hours with no added $CaCl_2$, C_3S hydrates approximately to the extent of 30% and 60% at 22°C and 80°C, respectively. With the addition of 2% calcium chloride, the degree of hydration at the same period at 22°C and 80°C is 60% and 70% respectively.[25] Heat evolution curves also show that at temperatures of 25°, 35°, and 45°C, addition of 2% $CaCl_2$ not only intensifies the total heat developed at early periods but also reduces the times at which the maximum heat evolution peak occurs.[41]

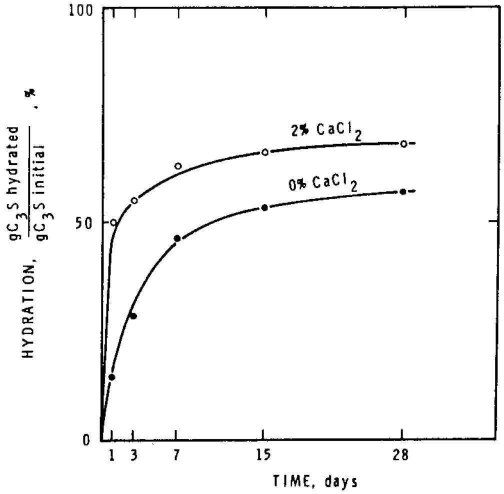


Figure 3. Effect of calcium chloride on the hydration of C_3S.

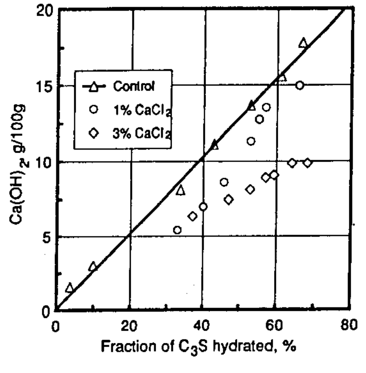


Figure 4. Calcium hydroxide content as a function of the hydrated C_3S. *(Reprinted from* Cement Concrete Res., *9:38-43, I. Odler and A. Maulana, © 1987, with kind permission from Elsevier Science Ltd, The Boulevard, Langford Lane, Kidlington 0X51GB.)*

The hydration behavior is modified if C_3S is precured at ambient temperatures and then autoclaved. Some tricalcium silicate samples were precured and then subjected to autoclave treatment at about 190°C for 5 hrs.[43] The degree of hydration of C_3S + 2% $CaCl_2$ (precured for 0–8 hrs and then autoclaved) was much less than that of a sample of C_3S hydrated similarly. Formation of a relatively more impermeable layer of hydration product on the C_3S phase caused by the presence of $CaCl_2$ is thought to be responsible for this phenomenon. Presence of $CaCl_2$ inhibits the formation of a C_2SH and $C_3SH_{1.5}$ that is formed in the reference C_3S sample.

The accelerating effect of $CaCl_2$ is not just confined to hydration of C_3S at low W/S ratios, and low $CaCl_2$ concentrations. The accelerating effect is also observed at W/S ratios as high as 10; with a 0.72N $CaCl_2$ solution, the degree of hydration of C_3S at 20 hrs is more than double that with no $CaCl_2$.[17]

Increasing the concentration of $CaCl_2$, even up to 20%, with respect to C_3S has been found to accelerate intensely the hydration of the silicate.[4][23] Increasing the amount of $CaCl_2$ not only accelerates the appearance of the conduction calorimetric peak at earlier times but also intensifies the peak (Fig. 5).

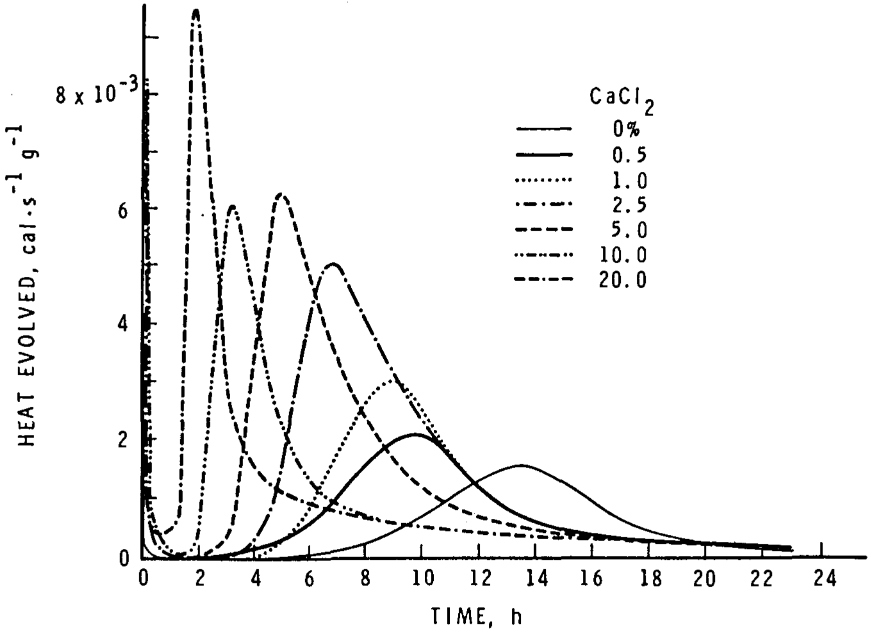


Figure 5. Influence of $CaCl_2$ on the heat evolution characteristics of C_3S.

The addition of $CaCl_2$ to C_3S not only alters the rate of hydration but also influences the chemical composition of the C-S-H phase. The C/S ratio depends on the initial W/S ratio, the amount of $CaCl_2$ and degree of hydration. It also depends on the techniques used for determining this ratio. Kurczyk and Schwiete,[24] working at a W/S ratio of 0.5, found a value of about 2.0 and 1.93 for C-S-H formed with 0% and 2.0% $CaCl_2$ respectively. There was a steep increase in the C/S ratio at dosages above 2% $CaCl_2$. Collepardi and Massida[18] also found that at earlier times addition of 2% $CaCl_2$ accelerates the formation of low C/S ratio product but the values were much lower than those reported by Kurczyk and Schwiete.[24] Odler and Skalny[15] found however, that up to about 30% hydration, addition of 2% $CaCl_2$ lowered the C/S ratio of the product, but beyond this stage the product formed with $CaCl_2$ showed consistently much higher C/S values (about 2); addition of 5% $CaCl_2$ showed even higher C/S values than those formed with 2.0% $CaCl_2$.[15] A general increase in the C/S ratio for products with 0.5 to 5% $CaCl_2$ has also been reported, although the absolute values are not in accordance with those observed earlier.[27] In a recent work[44] on the hydration of C_3S with 2% $CaCl_2$, it was found that the C/S ratio of the product containing $CaCl_2$ was lower in the induction period, but only marginally higher or equal to that hydrated without $CaCl_2$. In the ball mill hydration, significant reductions in the C/S ratio occur in the presence of $CaCl_2$ within a few hours.[18] The H/S ratio of the C-S-H product is also influenced by $CaCl_2$.[27]

The kinetics of hydration of tricalcium silicate in the presence of calcium chloride seems to follow the Avrami equation during the acceleratory period and that of Jander during the deceleratory period.[44a]

Additions of SO_4^{-2} or Cl^- individually increase the rate of hydration of C_3S. The combination of these cations may further accelerate hydration.[25]

Because of the accelerated hydration, the silicate phases show rapid setting characteristics in the presence of $CaCl_2$. In a C_3S:C_2S mixture containing 0, 1% and 2% $CaCl_2$, the setting times have been found to occur at 790 and 525 and 105 minutes, respectively.[14]

Mechanism of Hydration. In the earlier literature, the accelerating action of $CaCl_2$ was ascribed to the formation of the calcium oxychloride hydrate.[45]-[48] In the system CaO-$CaCl_2$-H_2O, two oxychlorides, $3CaO{\bullet}CaCl_2{\bullet}16H_2O$ and $CaO{\bullet}CaCl_2{\bullet}2H_2O$ are formed, the former being stable at $CaCl_2$ concentration of 18% or more and the latter at 34% or more.[14] The concentrations of $CaCl_2$ normally used to accelerate the hydration of C_3S do not attain such a high value and hence this mechanism is discounted. Conditions of higher $CaCl_2$ concentrations may result when hydration is carried out at a low W/S ratio and with higher amounts of $CaCl_2$.[33] Under normal conditions of hydration, no evidence has been reported for the existence of these complexes using the usual techniques adopted for cement investigations.

In the absence of an evidence for the existence of a complex, it is suggested that $CaCl_2$ acts catalytically.[19][39][47][49][50][55][56] The exact mechanism by which this occurs in the C_3S-$CaCl_2$-H_2O system is not clear. This mechanism is based on the premise that $CaCl_2$ does not go into any chemical combination. There is however, some evidence that $CaCl_2$ may, in fact, be rigidly bound in the hydrating C_3S. Leaching with water may instabilize the complexes that may be formed. Based on the results of leaching with alcohol (which presumably dissolves only free $CaCl_2$) or H_2O, Ramachandran[16] speculated about the possible states of chloride in the hydrating C_3S. The chloride may be in the free state, as a complex on the surface of C_3S during the dormant period, as a chemisorbed layer on the C-S-H surface, in the interlayer spaces of C-S-H and in the lattice of C-S-H. In the acceleratory period, adsorption of Cl^- ions may lead to an autocatalytic effect or splitting of the layer, nucleation centers or increased permeability so that hydration proceeds at a fast rate. The increase in surface area and modifications in the morphological features of hydrated C_3S in the presence of $CaCl_2$ may perhaps be due to Cl^- being chemisorbed or existing in the interlayer positions. The inhibition of formation of afwillite in the presence of $CaCl_2$ during C_3S hydration may be related to the existence of Cl^- in the C-S-H lattice.

Applying the pressure techniques in conjunction with leaching experiments, Ramachandran et al.[56a] found that substantial amounts of added chloride are strongly bound or immobilized (Fig. 6). In another investigation by Beaudoin et al.,[56b] chloride was added to synthetically-prepared C-S-H compounds with C/S varying between 0.68 and 1.49. Depending on the C/S ratio, different amounts of Cl^- were bound to the C-S-H phases. All the Cl^- treated samples exhibited exothermal peaks for the formation of wallostonite. The temperature difference of this peak varied between 0 and 30°C, compared to that without chloride. This indicated the possibility of chloride substitution in the lattice of C-S-H.

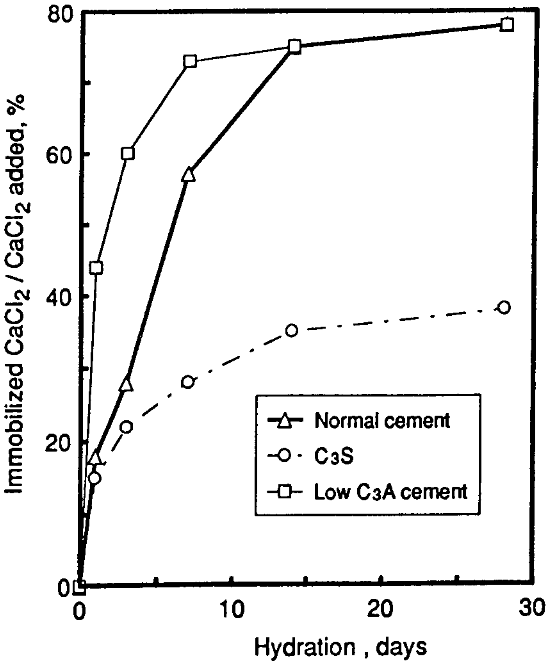


Figure 6. Amount of immobilized $CaCl_2$ in C_3S and cement paste. *(Reprinted with permission.)*

According to Collepardi et al.,[6] the accelerating action of $CaCl_2$ is due to its ability to promote the instability of the primary hydrosilicate, thus enhancing the formation of nuclei of a lower lime and a more porous hydrosilicate. This explanation is based on the observation that the addition of $CaCl_2$ to a prehydrated C_3S does not accelerate further hydration.

The addition of $CaCl_2$ reduces the alkalinity of the aqueous phase in the hydrating C_3S. For example, without the addition of $CaCl_2$, the pH values at 1, 2, 3 and 4 hrs are respectively 12.31, 12.38, 12.41 and 12.43, and the corresponding values decrease to 11.67, 11.77, 11.85 and 11.91 in the presence of calcium chloride.[24] It is thus possible that, by a reduced pH, the system would compensate by liberating more lime through increased rate of hydration of C_3S. Acceleration can also be achieved in an environment of higher pH values and hence it is doubtful whether acceleration can be explained by pH effects only.

The condensation characteristics of silicate ions in the hydration of silicates with or without $CaCl_2$ may have a role in the mechanism of hydration and strength development. Calcium chloride seems to promote higher condensation initially in the hydration of C_3S, thus possibly enabling a high level of water diffusion through the gel.[37]

There is some evidence that among the cations studied for the hydration of C_3S, those with smaller ionic radii are more effective accelerators.[6] This would indicate that solid state diffusion plays a role in the accelerating mechanism.[41]

Kondo et al.[51] suggested that Cl^- ions diffused through the initially-formed hydrates on the silicates into the zone of active reaction and this would increase the rate at which OH^- ions would diffuse outwards. Thus the precipitation of $Ca(OH)_2$ would occur more rapidly, resulting in an accelerated decomposition of the calcium silicates in the inner reaction zone.[51]

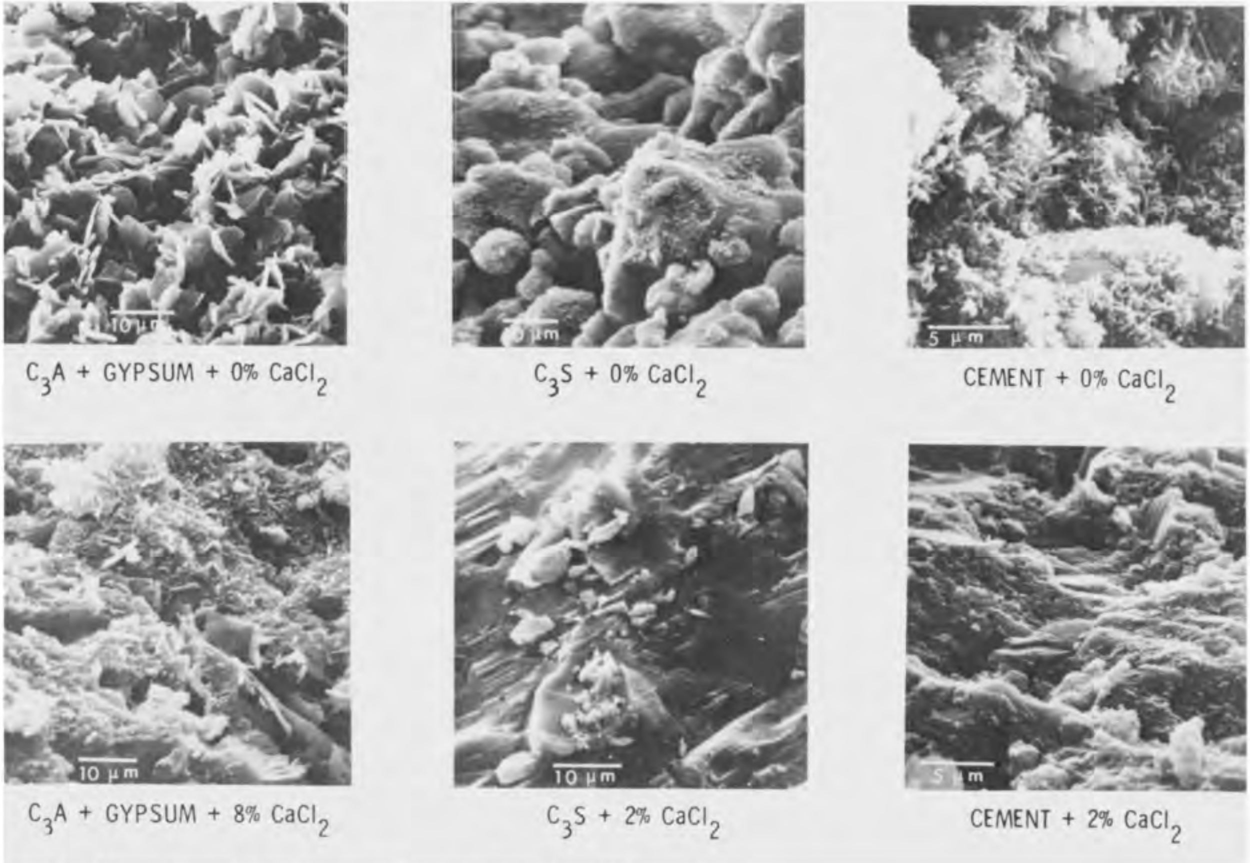
Singh and Ojha[56c] have reported that the zeta potential values for tricalcium silicate differ depending on whether it is hydrated in the presence of water or water containing calcium chloride. The potential values at earlier times are low but during the induction period are higher and then decrease after the acceleratory period. The chloride-containing pastes showed higher values than those without the chloride. The full implications of these observations have yet to be resolved.

It thus appears that no single mechanism can explain the effect of $CaCl_2$ on the kinetics of hydration of C_3S, and the morphological features, pore volume and surface area changes and strength development in C_3S pastes. Possibly a combination of mechanisms may be operating depending on the experimental conditions and the period of hydration.

Microstructure. A number of investigators have studied the effect of different concentrations of $CaCl_2$ on the morphological characteristics of hydrated calcium silicate. There has, however, been a variance in the actual description of the morphology.[4] According to Odler and Skalny,[52] hydrated C_3S normally forms spicules or sheets rolled into cigar-shaped fibers 0.25–1.0 μm long, and in the presence of $CaCl_2$, a spherulitic morphology is facilitated. Kurczyk and Schwiete[24] reported that needle-like products change to spherulites in the presence of $CaCl_2$. Young[53] described the change of morphology of hydrated C_3S + 0% $CaCl_2$ to hydrated C_3S + 2% $CaCl_2$ as occurring from needlelike C-S-H to lace-like structure. In contrast to the above, Murakami and Tanaka[7] found the existence of a fibrous cross-linked structure in C_3S pastes treated with $CaCl_2$. According to Le Sueur et al.,[56d] during the early periods, the morphological features of C_3S with and without $CaCl_2$ do not vary. After 4 hours, C-S-H is much more fibrillar and consists of open latticework, similar to a sponge (honeycomb) in the presence of calcium chloride.

Using the transmission electron microscopy, Ramachandran[14] found that C_3S hydrated at a W/S ratio of 0.5 showed needlelike morphology, whereas that hydrated in the presence of 1% of 4% $CaCl_2$ exhibited a platy or crumpled foil-like morphology. Collepardi and Marchese[54] and Berger et al.[55] came to similar conclusions. These changes in morphology may have resulted from the chemisorption of Cl^- ions on the C-S-H surface and introduction of these ions into the C-S-H lattice. In Fig. 7 the effect of $CaCl_2$ on the microstructural features of cement, C_3S and C_3A + $CaSO_4{\bullet}2H_2O$ is compared.[56] Addition of 2% $CaCl_2$ to cement results in a 50% increase in strength and is attended by a highly consolidated structure. A similar structure develops in C_3S + $CaCl_2$ pastes but with a 70% increase in strength. In the C_3A + gypsum system treated with 8% $CaCl_2$, the strength increases by 100% and small needles and plates develop in place of a platy structure.

The morphological features become less distinct when the hydrated products are formed in a confined space, as for example, when the pastes are prepared at low W/S ratios. This is because the particles are so close to each other that there is not enough space for crystals to grow into larger dimensions. In the micrographs of C_3S hydrated at a W/S ratio of 0.3 and obtained with 0, 2 and 5% $CaCl_2$, a dense structure for pastes with 2 and 5% $CaCl_2$ is evident and this feature may be responsible for a 50–150% increase in microhardness values over the paste containing no $CaCl_2$.[33] It may, however, be argued that a lower porosity and better contact or bonding of the particles are factors causing strength increases. Bendor and Perez[57] have ascribed the higher strengths in C_3S pastes with $CaCl_2$ to a honeycomb nature of the paste as opposed to a sponge-like feature in the reference C_3S paste. Berger[58] and Young[53] compared the microstructure of C_3S hydrated with or without $CaCl_2$ at the same degree of hydration and concluded that differences in external morphology indicated the differences in pore-size distribution. Porosity and pore-size distributions are recognized as important parameters affecting the strength development. However, in this work[58] it is not easy to assess pore sizes below 0.1 µm. Lawrence et al.,[31] on the other hand, have concluded that the outer morphology observed by SEM is not as important as the contact points closest to the unhydrated grains (which cannot be resolved by SEM) in assessing the mechanical properties of the C_3S paste. It is, hence, important to recognize that morphology, porosity, density, and chemical composition are mutually dependent factors that determine strength characteristics.



C_3A + GYPSUM + 0% $CaCl_2$

C_3S + 0% $CaCl_2$

CEMENT + 0% $CaCl_2$

C_3A + GYPSUM + 8% $CaCl_2$

C_3S + 2% $CaCl_2$

CEMENT + 2% $CaCl_2$

Figure 7. Microstructural development in cement containing calcium chloride.

Addition of $CaCl_2$ modifies the morphology of autoclaved C_3S. Fibrous crystals and rectangular block-shaped crystals normally present are not found with $CaCl_2$. In the presence of $CaCl_2$, $C_3SH_{1.5}$ and a C_2SH are not formed.[43]

Young and co-workers[31][34] studied the effect of various anions containing Ca^{++} as the common cation. The anions included perchlorate, thiocyanate, propionate, maleate and chloride. There was a change in the C-S-H morphology from an acicular to a lacy and honeycomb structure in the presence of some admixtures. Other changes such as the number of CH crystals/mm^2, their relative sizes and crystal axis ratios, also occurred (Table 1). The relevance of the above changes to strength development is not completely clear.

Table 1. Influence of Admixtures on the Morphology of C3S Pastes

Admixture	Hydration Kinetics (24 hrs)	Effect on Morphology C-S-H	CH	Approx. No of CH Crystals/mm^2
Calcium chloride	Strong Accelerator	Modified	Large c <a	
Calcium thiocyanate	Accelerator	Modified	Large c <a	2.5
Calcium propionate	Accelerator	Unchanged	Small irregular	14.0
Calcium perchlorate	Weak Accelerator	Unchanged	Large c <a	3.0
Calcium sulfate dihydrate	Weak Accelerator	Unchanged	Small c <a	4.0

Berger and McGregor[59] have made an extensive study of the microstructure of the C_3S paste, with particular reference to the CH component. The paste that resulted by the use of sixty-two admixtures could be divided into four groups, based on the c/a axis ratios. The morphology was found to be dependent more on the type of anion than on the cation. There is need to investigate how the above differences influence the engineering properties. It has often been reported that in C_3S pastes containing various admixtures, the hexagonal phase typical of CH may not be present. According to Bendor and Perez,[57] in pastes containing CdI_2 the hexagonal CH phase formed, whereas it was absent in the presence of $CaCl_2$ and $CrCl_3$. The mechanism responsible for these differences is not clear. In some instances the CH crystals may be obscured by the C-S-H gel.

Pore Structure. The pore structural studies are valuable because porosity and pore size distribution are known to bear a relationship with strengths. In a study of the effect of 2–5% $CaCl_2$ on the properties of C_3S hydrated at W/S ratios of 0.3 and 0.5, Traetteberg and Ramachandran[33] found that an approximate linear relationship exists between porosity and logarithm of microhardness. They also found that microhardness and compressive strength are linearly related. Working on C_3S containing 1% $CaCl_2$, Berger et al.[58] found that at equal degrees of hydration, the porosity of the paste containing $CaCl_2$ was lower than that of the reference paste. A plot of gel space ratio vs compressive strength indicated a linear relationship for pastes with or without $CaCl_2$ hydrated to different degrees. It was assumed that the specific volume of the pastes was not changed by the addition of $CaCl_2$. Work of Ramachandran and Feldman[60] has shown that in cement pastes, $CaCl_2$ influences the specific volume of the pastes. There is evidence that pastes containing $CaCl_2$ can have a substantial portion of total porosity in pores of diameter below 0.0065 µm.[21][61][62] Collepardi[63] found that with C_3S hydrated with 2% $CaCl_2$ at 1 day, the hydrated product had most of the pores in the range of 10–50 Å radius. Skalny and co-workers[64] using N_2 isotherms also concluded the C_3S hydrated in the presence of $CaCl_2$ has a lower hydraulic radius (31.8 Å) than that of the reference paste (53.3 Å).

Figure 8[53] shows the total porosity and effective pore diameter relationship obtained for C_3S hydrated to different times in the presence of 1% $CaCl_2$. As hydration progresses, porosity decreases due to the hydration products filling the pores and at 30 days the product contains a higher percentage of pores of diameter less than 0.01 µm.

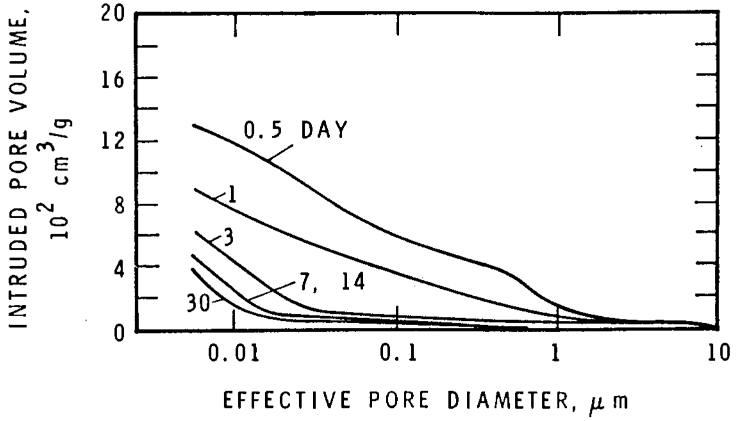


Figure 8. Mercury intrusion curves of C_3S pastes hydrated with calcium chloride.

Surface Area. The surface area of hydrated C_3S or C_2S is increased in the presence of $CaCl_2$.[17][37][52][54][61][63]-[65] The extent of this increase differs depending on factors such as particle size and purity of the silicate, W/S ratio, amount of $CaCl_2$ added, extent of hydration, temperature of hydration, and drying conditions. If water is used as the adsorbate, surface area values are found to be much higher than N_2 values. There is controversy over the significance of water as an adsorbate in determining the surface area of tricalcium silicate and cement pastes.

Figure 9 shows the N_2 surface area values as a function of the time of hydration of C_3S.[54] In the presence of $CaCl_2$ in the first day, the surface area is about 220 m^2/g, which decreases to a value of about 80 m^2/g in 3 months. This value is still about three times that determined for C_3S + 0% $CaCl_2$. Nitrogen area for C_3S + 5% $CaCl_2$ is even higher than that for C_3S containing 2% $CaCl_2$.[14][66] Although surface area decreases as the temperature of hydration is increased, at any temperature, samples containing $CaCl_2$ show higher surface areas than those without it.[66] In Fig. 9, C_3S samples show a decrease in surface area as hydration progresses, and this is due to the "aging" effect involving formation of physical and/or chemical interlayer bonds.

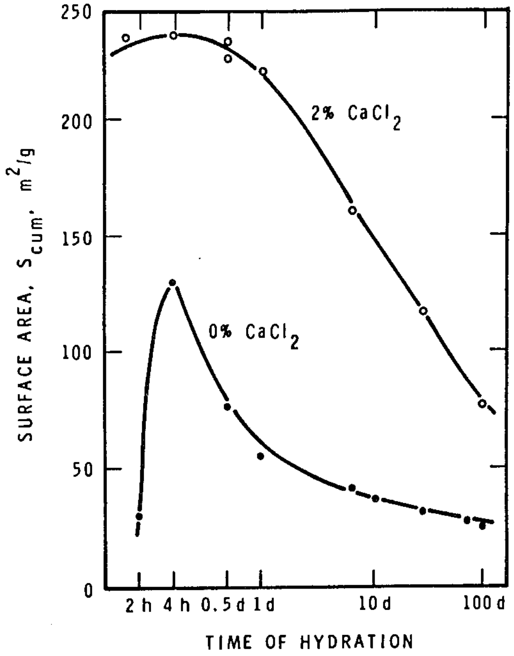


Figure 9. Surface area of a C_3S paste containing calcium chloride.

The higher surface area of the C_3S paste in the presence of $CaCl_2$ may partly be contributed by the formation of less crystalline $Ca(OH)_2$. In the differential thermal curves, it has been found that (at curing periods less than 1 day) the peaks for $Ca(OH)_2$ decomposition shift towards higher temperatures as the curing period increases, indicative of better crystallinity. In the presence of $CaCl_2$, the temperature shift occurs to a lesser extent.[44] It is also observed that the pastes containing $CaCl_2$ have a larger amount of fine pores which contribute to the high surface area.

Surface area (by H_2O vapor) of hydrated C_3S carried out at a hydration degree of 64% shows a value of 324 m^2/g for C_3S + 0% $CaCl_2$ and a value of 261 m^2/g for C_3S + 2% $CaCl_2$.[64] The lower surface area is explained by the formation of C-S-H of higher C/S ratio and increased average thickness of the gel unit.[15] A higher C/S ratio in the gel need not necessarily mean that it would have a lower surface area. For example, the gel with 5% $CaCl_2$ has a N_2 surface area of about 15 m^2/g larger than that formed with 2% $CaCl_2$, though the C/S ratio of the gel at 5% $CaCl_2$ is higher. At normal dosages of calcium chloride, it has been found that compressive strength of tricalcium silicate paste increases as the surface area of tricalcium silicate increases (Fig. 15).

Strength Development. A small addition of $CaCl_2$ to portland cement is known to accelerate the setting and hardening characteristics in the cement. This is mainly attributed to the action of $CaCl_2$ on the silicate phase. This has since been confirmed by others.[14][16][19][20][24][31][33][37][40][67] Figure 10 compares the rate of strength development in C_3S pastes hydrated without and with $CaCl_2$.[20] At all times up to 28 days the strength in the paste containing 2% $CaCl_2$ is higher than that hydrated with the chloride. The percentage increase of strength, however, decreases as the hydration proceeds. The increase in strengths at earlier periods (with $CaCl_2$ addition) may be explained by the increased amount of hydration products formed. Increased rate of hydration by itself does not assure increased strengths. This is evident from Fig. 11 which shows that although the amount of hydration with 2% $CaCl_2$ is at least as high as that with 1.5–2.0% $CaCl_2$, higher concentrations of $CaCl_2$ generally lower the strength.[4][24] This may be ascribed to the change in the C/S ratio of the product and the microstructure.

The hardening behavior of C_3S + $CaCl_2$ + H_2O system not only depends on the percentage of $CaCl_2$ but also on the initial W/S ratio. At a W/S ratio of 0.5, 2% $CaCl_2$ addition gives better strengths than 5% $CaCl_2$. At a W/S ratio of 0.3, however, 5% $CaCl_2$ gives strength nearly as much as 2% $CaCl_2$ addition (Table 2).[33]

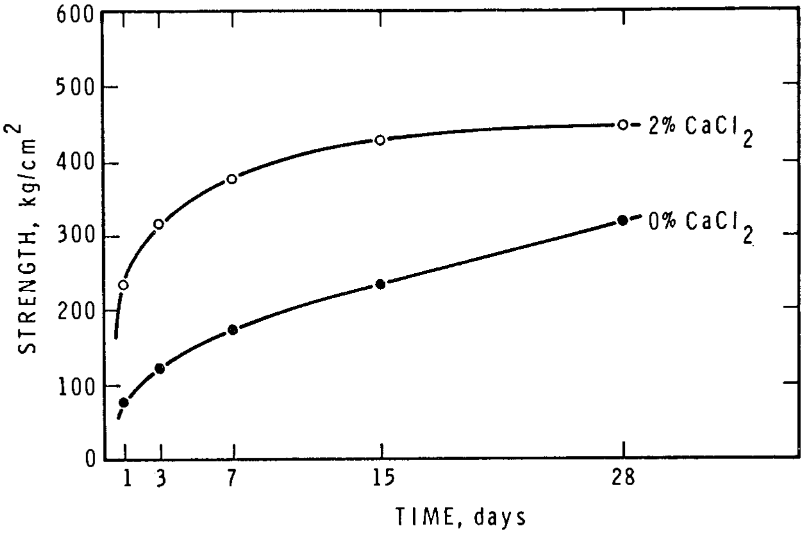


Figure 10. Compressive strength of a tricalcium silicate paste containing $CaCl_2$.

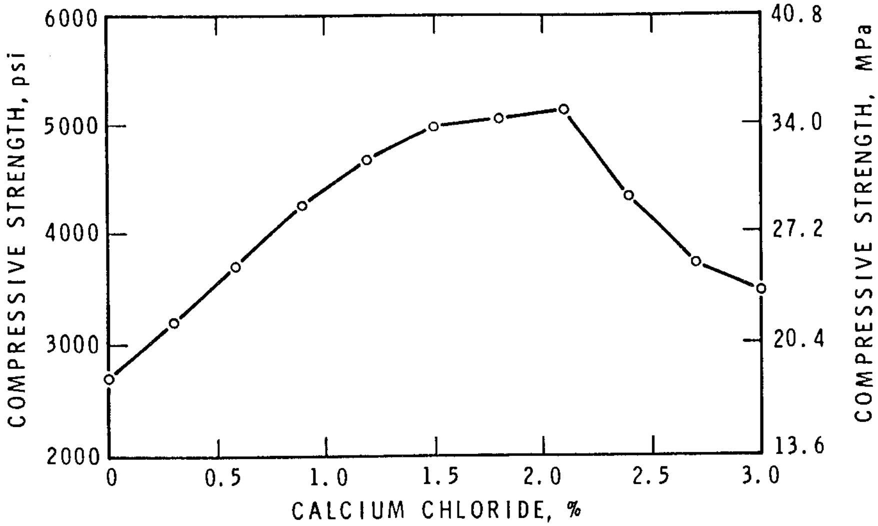


Figure 11. Effect of calcium chloride on the 28-day strength development in C_3S pastes.

Table 2. Microhardness for C_3S Pastes Containing Different Amounts of $CaCl_2$

Hydration Time (Days)	Microhardness (N/nm^2)			
	Water/Solid = 0.5		Water/Solid = 0.3	
	C_3S + 2% $CaCl_2$	C_3S + 5% $CaCl_2$	C_3S + 2% $CaCl_2$	C_3S + 5% $CaCl_2$
1	113	13	132	98
2	83	23	221	155
3	98	27	271	225
7	117	41	292	284
10	150	57	360	346
15	186	92	311	353

The enhancement of strengths in C_3S + 1–2% $CaCl_2$ pastes cannot be explained only in terms of the degree of hydration. For alites containing 1% $CaCl_2$, the strengths at equal degrees of hydration are similar at lower degrees of hydration, but at higher degrees of hydration some divergence is evident (Fig. 12).[58] It may be related in a complex way with porosity, morphology, chemical composition, surface area, density, etc. Odler and Maulana[42b] studied the effect of various admixtures on the strength development in cement pastes. The fraction of hydrated C_3S had a linear relationship with the compressive strength, irrespective of the type of admixture (Fig. 13).

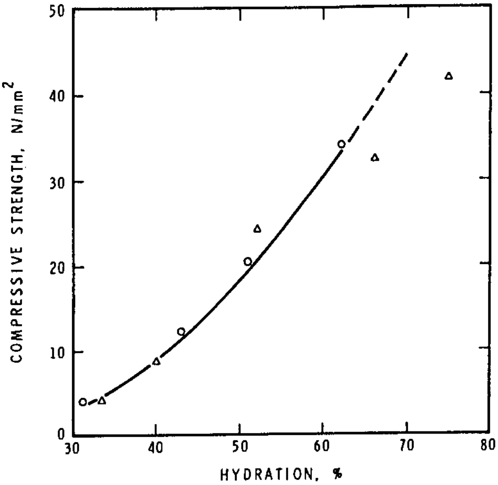


Figure 12. The dependence of degree of hydration on strength in alite containing calcium chloride.

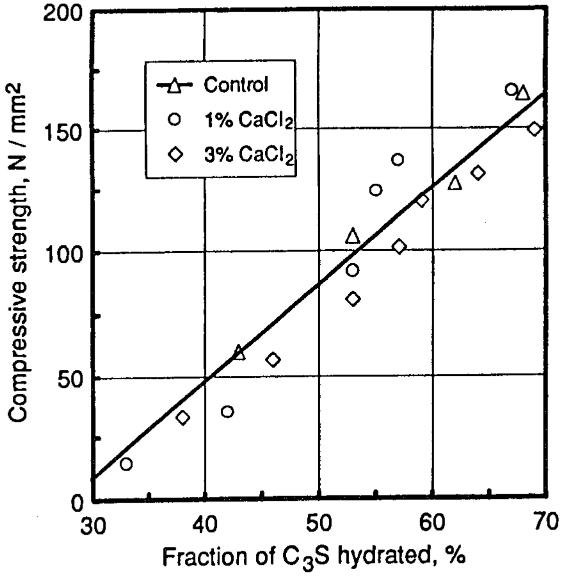


Figure 13. Compressive strength as a function of the degree of C_3S hydration. *(Reprinted with permission.)*

The silicate structure changes occurring in the hydrated cements was determined by Lentz[68] using the trimethylsilylation reaction. It was found that with time of hydration, the orthosilicate content gradually decreased, giving rise to disilicate and polysilicate structures. As an extension of this idea, polymerization of silicates in pastes containing C_3S or C_2S and admixtures $CaCl_2$, citric acid and thionyl chloride, was examined by Tamas et al.[69] The hydrated products were found to contain mainly the dimeric $Si_2O_7^{6-}$ ions with small amounts of tetrameric rings. In both C_3S and ß-C_2S, the ratio of the monosilicate/disilicate peak heights was lower for pastes containing $CaCl_2$, indicating the increase in the disilicate formation with the progress of hydration. It is known that there is an increase in strength in the pastes containing larger amounts of polymerized silicates.

Modulus of elasticity of a cementitious system can be obtained by the ultrasonic pulse velocity technique. In a study of C_3S hydrated with calcium salts of thiocyanate, propionate, maleate, perchlorate, and chloride, Lawrence et al.[31] found that the velocities were higher with pastes containing admixtures. The velocity-time behavior could partly be explained by the higher degree of hydration. Results with $CaCl_2$ were anomalous; compared to other admixtures, it promoted the development of lower velocities and lower porosity at equal degrees of hydration. Since the velocity depends on the density of the product and the number of contact points, it is possible that in the presence of $CaCl_2$, the higher density product that is formed reduces the contact points. Hence the applicability of the ultrasonic technique for the cementitious systems containing admixtures should be reexamined, especially since the hydrate product is changed.

Shrinkage. Shrinkage of a C_3S paste is increased in the presence of $CaCl_2$. If the measurements are carried out at a particular time, the values may reflect the extent to which the hydration has progressed. Hence, Berger et al.[58] compared the shrinkage of the C_3S paste and C_3S paste + 1% $CaCl_2$ at equal degrees of hydration. At any degree of hydration the paste containing $CaCl_2$ showed a higher shrinkage. One reason is that the hydration product in the presence of chloride has a higher surface area. In the absence of calcium chloride, shrinkage increases with the degree of hydration but in the presence of $CaCl_2$, the value decreases (Fig. 14).[58]

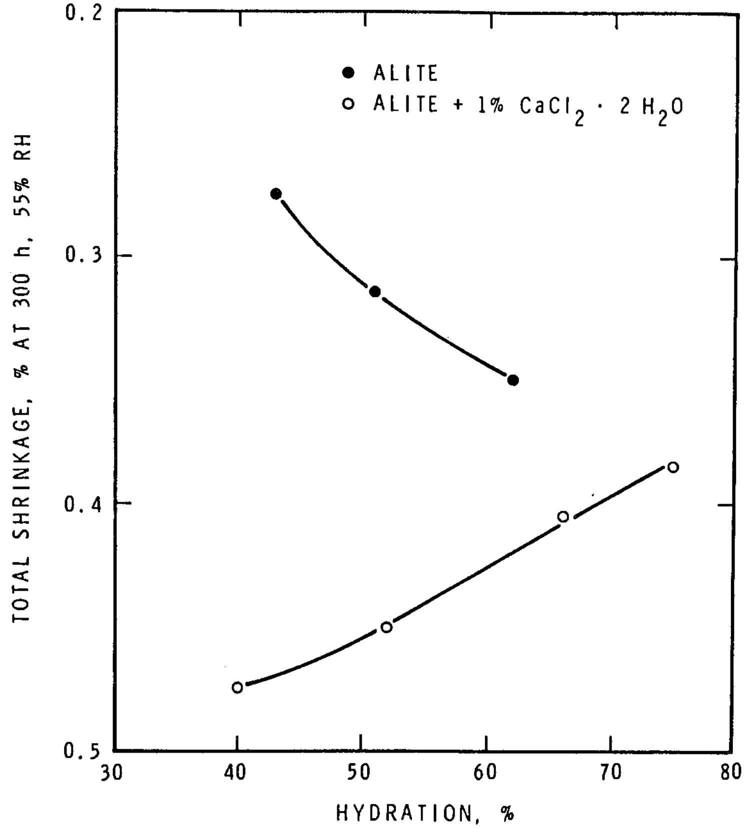


Figure 14. Shrinkage vs degree of hydration of alite pastes containing 1% $CaCl_2 \cdot 2H_2O$.

2.2 Dicalcium Silicate

The dicalcium silicate phase hydrates at a slower rate than C_3S. At the same surface area of 4500 cm^2/g and W/S ratio of 0.45, the estimated amounts of C-S-H in the hydrated C_2S at 1, 3, 7 and 28 days are 4.9, 9.2, 15.2 and 51.6% respectively and the corresponding values for C_3S are 34.4, 36.6, 45.5 and 62.0%.[71] This would indicate that the strength development in the hydrating C_2S proceeds at a slower rate than that in C_3S. The C/S ratio of the C-S-H product in the hydrated C_2S is slightly higher than that formed in the hydrated C_3S.

Compared to the extensive investigations on the hydration of C_3S in the presence of $CaCl_2$, only meager work has been done on the action of $CaCl_2$ in the hydration of C_2S.[52][72]-[76] Generally all chlorides accelerate the hydration of C_2S, calcium chloride being more efficient than others at nearly all ages (Table 3).[38]

Table 3. Degree of Hydration of Dicalcium Silicate Containing Chloride Salts

Chemicals	Hydration %		
	1 Day	7 Days	28 Days
Reference	16.1	24.3	33.0
$CaCl_2$	21.6	34.1	56.1
LiCl	24.3	33.0	44.3
NaCl	20.1	33.2	53.2
KCl	19.9	27.0	44.6
$BaCl_2$	20.2	31.9	44.6
$SrCl_2$	18.9	28.3	46.2

The values for the degree of acceleration by calcium chloride on C_2S reported in the literature vary because of the differences in the nature of sample, experimental conditions, and the methods adopted for determining the degree of hydration. Table 4 shows the effect of different percentages of $CaCl_2$ on the rate of hydration of C_2S.[38] The hydration rate is increased as the amount of chloride is increased.

Table 4. Degree of Hydration of ß-C_2S with Different Amounts of Calcium Chloride

Sample	Degree of Hydration		
	1 day	7 days	28 days
0% $CaCl_2$	16.1	24.3	33.0
0.5% $CaCl_2$	21.3	29.2	47.0
2.0% $CaCl_2$	21.6	34.1	56.1
5.0% $CaCl_2$	26.8	35.9	54.9

Calcium chloride accelerates the hydration of C_2S at all water-solid ratios.[73] At 250 days, 2% $CaCl_2$ increases the hydration by 20%. At early times, the accelerating action of $CaCl_2$ in C_2S is only marginally affected compared to that observed in the hydration of C_3S. The C_2S paste containing $CaCl_2$ and hydrated to 1–3 months may show negligible amounts of $Ca(OH)_2$ compared to the paste hydrated without $CaCl_2$.[24] This would indicate that a higher C/S product is formed in the pastes hydrated with $CaCl_2$. The ratio can increase from 1.7 to 1.82 with 2% $CaCl_2$.[27] There is evidence that in the hydration of ß-C_2S, some chloride is bound rigidly.[26] Complexes such as calcium oxychloride hydrate are not formed in this system at normal concentrations of $CaCl_2$. The accelerating action of $CaCl_2$ is also observed when C_2S is hydrated at 80°C.[25] A combination of $Ca(OH)_2$ + $CaCl_2$ is reported to retard the hydration of C_2S.[10]

The porosity of a C_2S paste is increased by $CaCl_2$ from 0.168 to 0.18 ml/g.[73] The porosity values may decrease if H_2O is used instead of N_2 for measurements. At thirty-five days of hydration, a paste containing 2% $CaCl_2$ shows a 9% decrease in porosity using H_2O as an adsorbate but a 19% increase with N_2.[52]

The surface area of C_2S paste is only slightly increased by the addition of $CaCl_2$. A C_2S paste formed at a $W/S = 0.5$ shows a surface area of 62 m^2/g, and with $CaCl_2$, the value increases to 70 m^2/g.[73]

Calcium chloride does not seem to influence the morphology of the hydrated C_2S as it does that of the hydrated C_3S. The characteristic fibrous particles are observed both in $CaCl_2$-containing and $CaCl_2$-free hydrated specimens, the size being somewhat smaller in the former.[73] Some morphological differences have been reported in TEM on thin films of C_2S and C_3S + $CaCl_2$ formed by evaporation and hydration.[77] At three days, foils, fans and afwillite were formed. At six days, foils converted to a fan-type morphology and fiber bundles appeared. At fourteen days, foils disappeared and fans, fibers and afwillite persisted. Hydration of C_2S + $CaCl_2$ seemed to promote the appearance of fiber bundles and their eventual conversion to α-C_2SH. These observations are not typical of normal C_2S pastes, in which the normal W/S ratio is rather low.

Addition of $CaCl_2$ to C_2S results in an increase in the rate of strength development. An addition of 3% $CaCl_2$ increases the bending strength of C_2S by 26% at 2 months, about 34% at 3 months, and about 60% at 6 months.[78] Cone penetration measurements also show that the strength of C_2S paste increases from 0.4 kg/cm^2 (at 30 mins) to 84 kg/cm^2 (at 30 days), and the corresponding values with $CaCl_2$ are an increase from 0.08 to 160 kg/cm^2.[39] Large additions of $CaCl_2$ are, however, detrimental to strength development.

The strength development also depends on the fineness of C_2S. Figure 15 shows that, as the fineness increases, the strength also increases at any particular dosage of $CaCl_2$.[70]

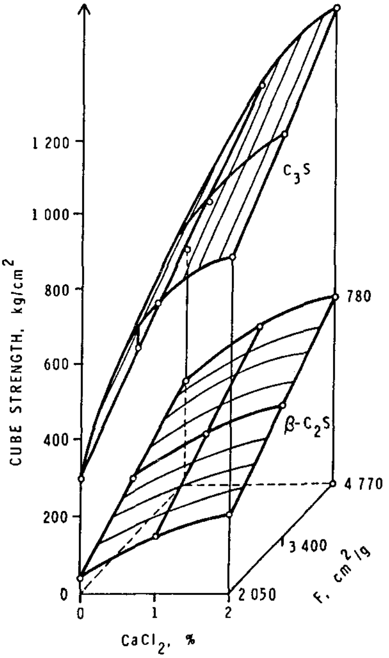


Figure 15. Effect of $CaCl_2$ on the cube strength of C_3S and C_2S pastes.

In an investigation of tensile strengths developed by ß-C_2S containing $CaCl_2$ and other salts, at 60% hydration, different values were obtained.[79] This would indicate that the nature of the products formed in the presence of these admixtures is different.

2.3 Tricalcium Aluminate

Two chloroaluminate hydrates are known: the low form $C_3A•CaCl_2•xH_2O$, and the high form $C_3A•3CaCl_2•yH_2O$. It is generally believed that the low form is the main reaction product formed under practical conditions of hydration. The low form may be prepared by mixing, at ordinary temperature, a calcium aluminate solution with lime water and $CaCl_2$.[80] The compound $C_3A•CaCl_2•xH_2O$ forms a series of solid solutions with C_4AH_{13}. The high form ($C_3A•3CaCl_2•yH_2O$) is obtained by hydrating C_3A at higher concentrations of $CaCl_2$.[81][82] The low form crystallizes as hexagonal plates and the high form as needle-shaped crystals. The basal spacing for the low form is 8.1 Å and that for the high form is 10.15 Å.[83] The Differential Thermal Analysis technique may be used to differentiate between the two forms of chloroaluminate. Endotherms at about 190°C and 350°C are caused by the monochloroaluminate and the endotherm at about 160°C is exhibited by the higher chloroaluminate.[81]

A study of the morphological and phase changes in the system containing C_3S, CaO, $CaSO_4•2H_2O$ and $CaCl_2$ was carried out by Gupta and coworkers for up to 3 months.[83][84] The nature of the products and amounts formed at different times depended on the initial proportions of the mixtures. The compounds that formed in the system included the hexagonal plates of C_2A-C_4A hydrate, cubic crystals of C_3AH_6, hexagonal plates or foils of $Ca(OH)_2$, needles of ettringite, platy form of the low sulfoaluminate hydrate, rods of gypsum, needles of trichloroaluminate hydrate, and hexagonal plates or foils of monochloride hydrate. In the C_3A-gypsum-$CaCl_2$-H_2O system substantial amounts of chloride are immobilized within an hour whereas lower amounts of chloride are immobilized by C_3S and cement after longer times[56a] (Fig. 16).

In a saturated $CaCl_2$ solution, C_3A forms needles of $C_3A•CaCl_2•30H_2O$ which convert to the platy low form of chloride complex in 24 hrs. At 3 months the product is mainly the low form. At 9% $CaCl_2$, both hexagonal C-A-H product and the low chloroaluminate are formed. At longer times, the C-A-H (hexagonal) converts to the cubic form. With 1% $CaCl_2$, hexagonal hydrate is produced initially and at 3 months the hexagonal and cubic hydrates predominate. The reaction in the system C_3A + saturated $CaCl_2$ solution is essentially completed at 14 days, suggesting that the needle-shaped chloroaluminate is not an effective barrier against C_3A hydration.[84] With 9% $CaCl_2$, foils and plates that form do not effect complete hydration of C_3A.

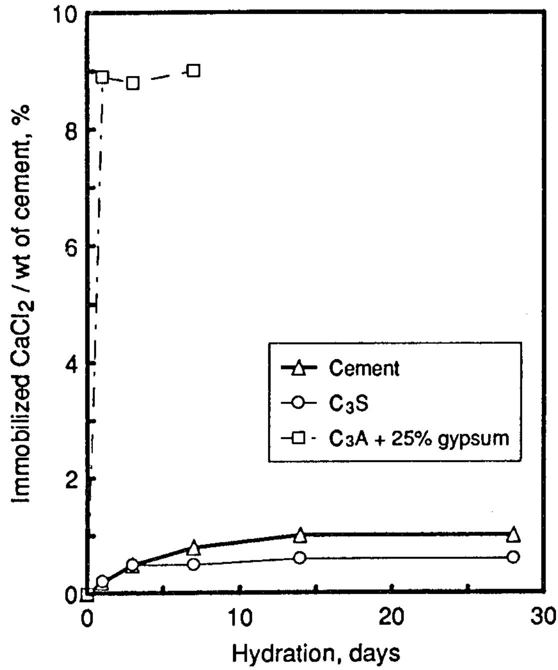


Figure 16. Relative amounts of immobilized $CaCl_2$ in various pastes. *(Reprinted with permission.)*

In the C_3A-CaO-$CaCl_2$-H_2O system in the saturated $CaCl_2$ solution, initially needles and plates of $Ca(OH)_2$ are present and at longer times plates of monochloride and needles of basic calcium chloride are identified. With 9% $CaCl_2$, initial reactions are similar to those in the C_3A-CaO-H_2O paste. The final products are cubic crystals of C_3AH_6. At 1% $CaCl_2$, the system is similar to that of the C_3A-CaO-H_2O paste.

In the system C_3A-CaO-$CaSO_4$•$2H_2O$-$CaCl_2$, with a saturated $CaCl_2$ solution, needles of high chloroaluminate and calcium oxychloride hydrate form initially. At three months, low chloroaluminate hydrate, ettringite, and calcium oxychloride hydrate are the main products. The absence of ettringite up to 14 days can be explained by the depressed solubility of gypsum in $CaCl_2$ solution.[84] In the presence of 1 or 9% $CaCl_2$ solution, no ettringite can be identified at four minutes and gypsum is almost reacted by twenty-four hours. At twenty-four hours, ettringite is formed. At three months, monochloride and monosulfate coexist.

The rate of hydration of C_3A with gypsum and $CaCl_2$ has been studied in the absence of CaO by conduction calorimetry. In Fig. 17, the conduction calorimetric curves of the mixture C_3A + 20% gypsum + 12.5% $CaCl_2$ are given, along with the identified compounds at different times.[4][23] A comparison of this curve with that obtained with C_3A + gypsum or C_3A + $CaCl_2$ would lead to the following conclusions. The reaction between C_3A and gypsum is accelerated by calcium chloride. Monochloroaluminate is formed after gypsum is consumed in the reaction with C_3A. Conversion of ettringite to monosulfoaluminate occurs only after all $CaCl_2$ has reacted.[23][41][85]-[88] The cubic aluminate hydrate (C_3AH_6) also reacts with $CaCl_2$ to form monochloroaluminate hydrate but the reaction is slower than that with C_3A as the starting material.[89]

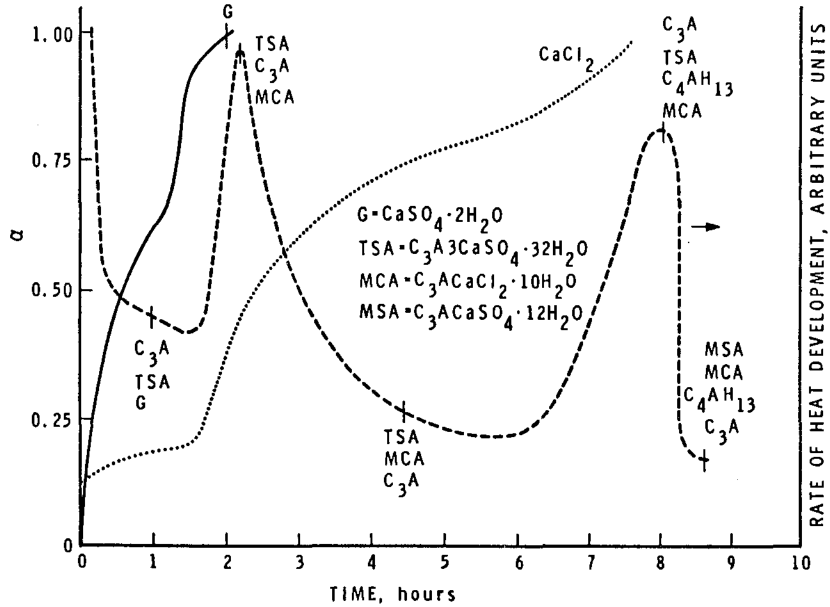


Figure 17. The rate of consumption of various components in the C_3A-gypsum-$CaCl_2$-H_2O system.

In the hydration of C_3A in the presence of $CaCl_2$ at temperatures of 75–100°C, calcium chloroaluminate is identified. The formation of this complex is retarded as the temperature is increased.[90] Higher strengths observed in the system C_3A-$CaCl_2$-H_2O containing 16% $CaCl_2$ has been attributed to the formation of the high form of chloride complex.[87] Using different amounts of gypsum and $CaCl_2$, it has been found that the acceleration of the reaction of gypsum with C_3A is accompanied by the generation of strains and consequent loss in strengths.[86]

In the system C_3S-C_3A-$CaCl_2$-H_2O, more C_4AH_{13} is formed and better strengths attained than that without $CaCl_2$.[24] The main factor may be the accelerated hydration of the C_3S phase.

In the portland cement paste containing different amounts of $CaCl_2$, the hydration of the tricalcium aluminate phase was followed as a function time.[42b] The results are summarized in Table 5. The tricalcium aluminate phase reacted to form compounds such as chloroaluminates, sulfoaluminates, and aluminate hydrates. The results show that, even at about 3 hrs, substantial amounts of the tricalcium aluminate phase have disappeared in the presence of 1% calcium chloride. The hydration of tricalcium aluminate increases with time with or without the chloride. However, at any time within the first 3 days, more hydration has taken place in the presence of the chloride. It is significant that the degree of hydration at 3 hrs for the sample having 3% $CaCl_2$ is almost equal to that at 3 days for the reference. The sequence of reactions for the tricalcium aluminate phase (containing 2%

Table 5. The Effect of Calcium Chloride on the Hydration of the Tricalcium Aluminate Component in a Cement Paste. *(Reprinted from* Cement Concrete Res., *9:38-43, I. Odler and A Maulana, © 1987, with kind permission from Elsevier Science Ltd, The Boulevard, Langford Lane, Kidlington 0X51GB.)*

Time	Calcium Chloride (%)			
	0%	0.3%	1.0%	3.0%
	% Tricalcium Aluminate Hydrated			
3 h	11	17	23	50
6 h	12	29	32	53
12 h	21	34	38	53
1 d	32	38	40	51
3 d	47	57	56	59
7 d	57	57	58	58
28 d	63	60	60	62

$CaCl_2$) in the cement paste may be described as follows. Initially tricalcium aluminate reacts with gypsum and water to form ettringite. After almost all gypsum has reacted, monochloroaluminate forms. After the formation of monochloroaluminate, the remaining C_3A forms hexagonal calcium aluminate hydrate. Subsequently, the hexagonal aluminate reacts with ettringite to form monosulfoaluminate. The final product is a solid solution of C_4AH_{13}, monosulfate hydrate, and monochloroaluminate hydrate.

2.4 The Ferrite Phase

It appears that much less work has been done on the effect of $CaCl_2$ on the hydration of the ferrite phase than on other cement minerals.[26][78][85][91][92] It is generally assumed that the sequence of reactions in the ferrite phase is similar to that of the tricalcium aluminate phase except that the reactions are slower.

The effect of $CaCl_2$ on the hydration of C_4AF does not seem to be different from that on C_3A.[85][91] In the cement paste, since tricalcium aluminate is more reactive than the ferrite phase, in the initial stage of reaction the major portion of ettringite and monochloroaluminate originate from the hydration of the aluminate phase. At later stages, the role of the aluminoferrite phase becomes important with the formation of a solid solution containing Fe(III) and Al(III). Calcium chloride accelerates the reaction between gypsum and C_4AF. The first product is trisulfoaluminoferrite TS(AF) and during its formation Cl^- is not consumed. After all SO_4^{2-} reacts with the C_4AF, monochloroaluminoferrite MC(AF) begins to form. In the presence of $CaCl_2$, the conversion of TS(AF) to MS(AF) is retarded. At additions of 20%Cl^-, in 30 mins the presence of both trichloride and ettringite is indicated. The rate of reaction of the ferrite phase with SO_4^{2-} in the presence of Cl^- depends on the composition of the ferrite phase, increasing in the order $C_2F < C_4AF < C_6A_2F$.

The rate of reaction, the sequence of reactions, and the types of products formed in the C_4AF-H_2O or C_4AF-gypsum-H_2O system at very low W/S ratios differ from those occurring when normal amounts of water are used. It can thus be expected that addition of $CaCl_2$ to such systems will influence the processes differently from what is normally observed.[93][94]

3.0 HYDRATION OF CEMENT

3.1 Hydration

The hydration of individual cement components is useful for evaluating the effect of $CaCl_2$. The kinetics of hydration may be followed by DTA, TGA, XRD, conduction calorimetry, chemical estimation, etc. The non-evaporable water content is a measure of the amount of hydrated cement formed. In cement hydrated for 6 hr, 1, 3, 7 and 28 days, the non-evaporable water content was 7.0, 10.6, 13.6, 14.3 and 15.1%, respectively, and the corresponding values with 2% $CaCl_2$ were 10.5, 14.9, 15.1, 15.6 and 16.3%. These results indicate that $CaCl_2$ accelerates the hydration of portland cement.[11]

The hydration of cement, being an exothermic reaction, produces heat and if the hydration is accelerated, heat is produced at a faster rate. This is particularly significant in the first 10–12 hrs and is of considerable importance in winter concreting. In Fig. 18, the influence of different amounts of $CaCl_2$ on the rate of heat development is shown.[4][112] The position of the peak corresponding to the maximum heat liberation decreases to lower times as the amount of added $CaCl_2$ is increased.

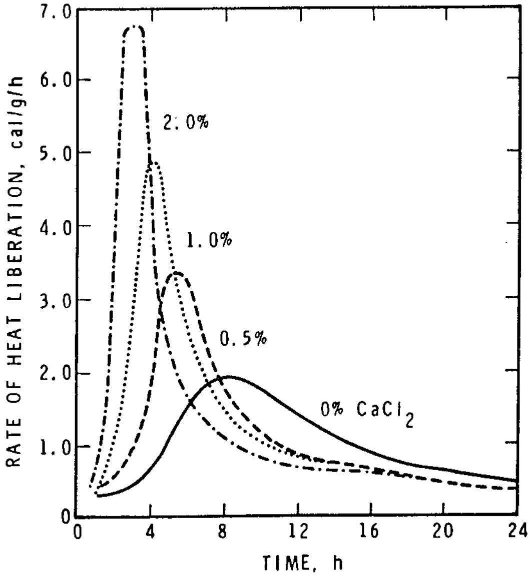


Figure 18. The effect of $CaCl_2$ upon the rate of heat development in cement.

The development of heat by the addition of calcium chloride on portland cement Type I from different plants shows significant variations, depending on the fineness and the composition of the cement (Fig. 19).

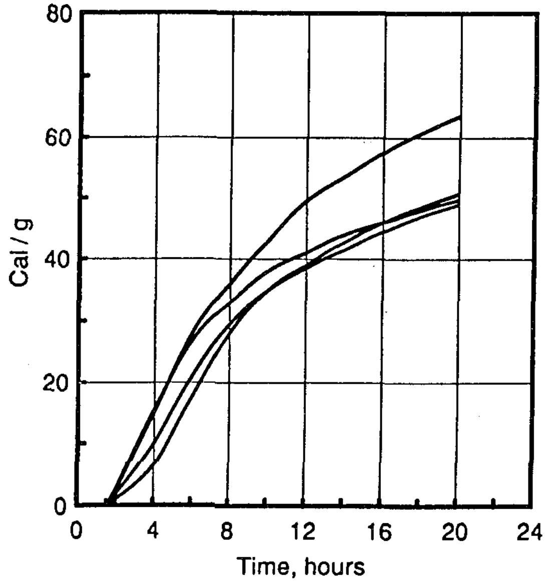


Figure 19. The effect of $CaCl_2$ on the heat development in four Type I cements.

The amount of heat generated depends on the temperature of curing. The lower the temperature of hydration, the lower is the amount of heat developed. However, if the sample contains $CaCl_2$, there is an acceleration of hydration and more heat is developed at a particular temperature. Figure 20 refers to the total heat developed at 5, 20, and 40°C for a mortar containing 20% $CaCl_2$. The heat developed due to $CaCl_2$ is especially significant at lower temperatures of curing.[4][113]

Calcium chloride also accelerates the rate of hydration of Type II, IV and V cements but only marginally that of Type III, a high early strength cement. Figure 21 illustrates the amount of heat developed in the five types of cement at various times.

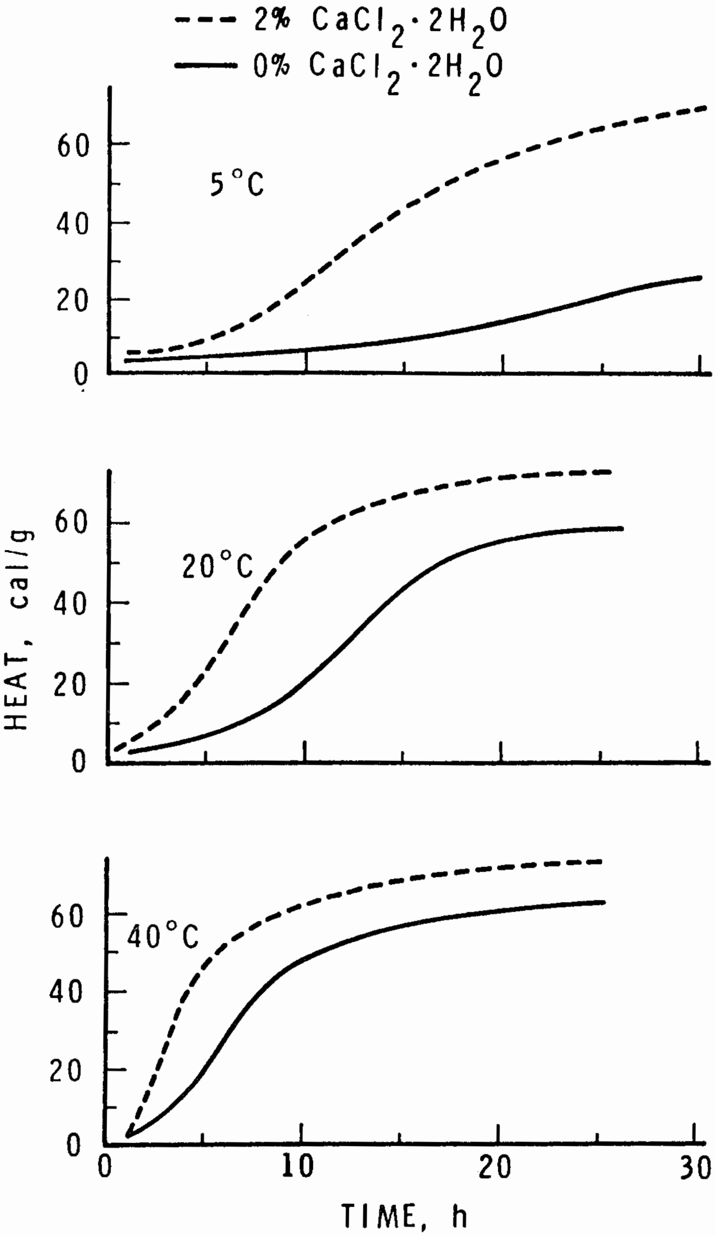


Figure 20. Influence of calcium chloride on the heat of hydration of cements at different temperatures.

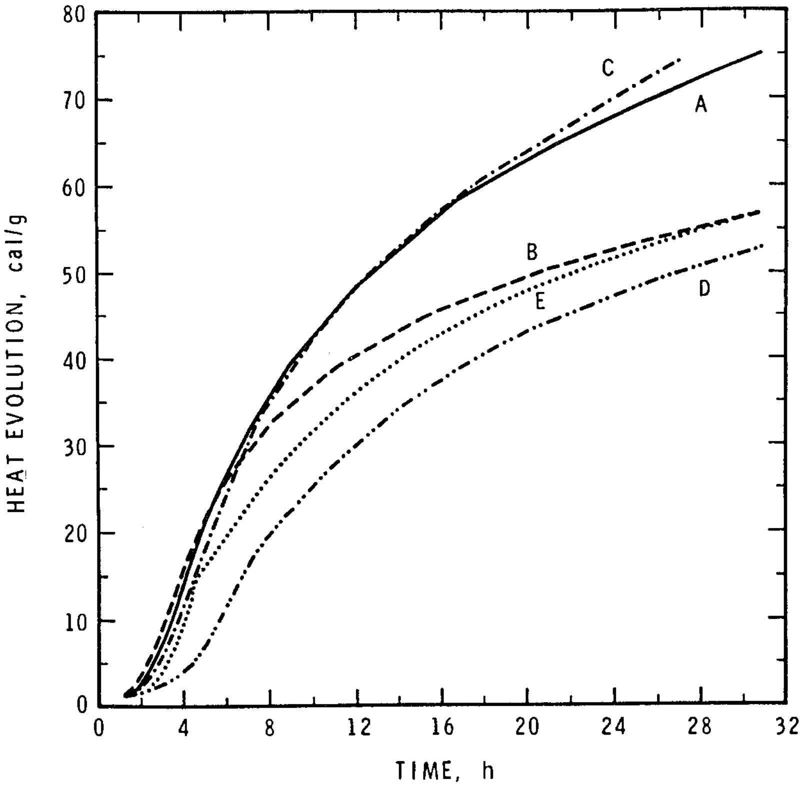


Figure 21. Influence of calcium chloride on the hydration of cements. A-Type I, B-Type II, C-Type III, D-Type IV, and E-Type V.

The hydration of cement using many multicomponent admixtures containing $CaCl_2$ as one of the ingredients has also been studied.

Portland cement binds Cl^- depending on the surface area and the composition. The amount of free Cl^- determines the corrosion potential with respect to the reinforcement. Byfors[113a] studied the bound Cl^- in cements containing admixtures such as a superplasticizer and lignosulfonate. The chloride was added as NaCl at a concentration in the range 3,000–80,000 mg/L. The amount of bound chloride was determined at 8 months of hydration (Fig. 22). The bound chloride was as high as 6%. The admixture-containing pastes increased the amount of bound chloride. This may be due to the admixtures dispersing the cement paste. The binding of chloride would perhaps be higher if calcium chloride had been used.

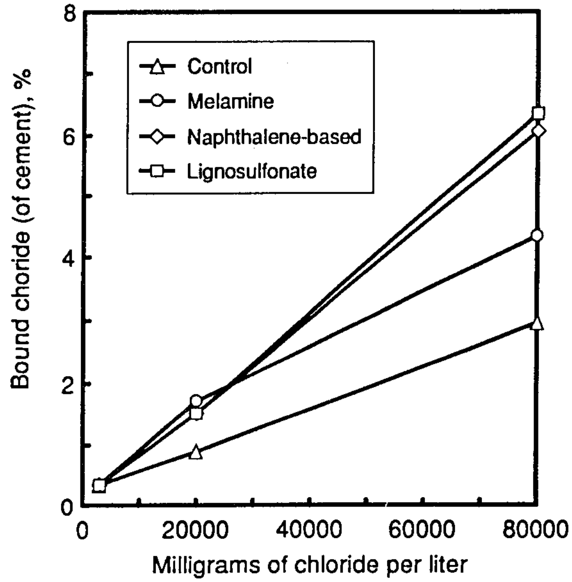


Figure 22. Amount of bound chloride in cements hydrated with chemical admixtures. N= naphthalene sulfonate, L = lignosulfonate and M = melamine.

According to Diamond, for corrosion to occur, chloride remaining in solution is not a major factor.[113b] Only modest differences in chloride concentrations were observed in the presence of NaCl and $CaCl_2$. However, the Cl^-/OH ratio was lower with the NaCl addition. The investigation of Hanson et al.[113c] has shown that 2% chloride added in the form of KCl, NaCl, and $CaCl_2$, produced bound chloride in amounts of 0.79, 0.69 and 1.18% respectively and the porosities were 42, 43 and 38% respectively. It was concluded that the main factor dictating the corrosion process is the electric resistivity of the sample. Calcium chloride, promoting a more open pore structure, may be responsible for the increased deleterious effect.

3.2 Mechanism of Hydration and Strength Development

The mechanism of the effect of calcium chloride on the hydration of C_3S is described in "Mechanism of Hydration" in Sec. 2. This has an important bearing on the overall action of $CaCl_2$ in cement hydration and strength development. Several mechanisms have been suggested as follows:

(a) Calcium chloride combines with the aluminate and ferrite chloride hydrate respectively. These accelerate the setting behavior. These complexes may also be formed in a finely divided form and provide nuclei for the hydration of silicate phases. It is known however, that hydration of C_3S by itself also accelerated by calcium chloride.

(b) The set acceleration is due to an intensification of the hydration of aluminates. The acceleration of the C_3S phase should also be considered.

(c) Calcium chloride reacts with calcium hydroxide (a reaction product of the hydration of C_3S) to form a complex such as $3CaO{\bullet}CaCl_2{\bullet}12H_2O$. Formation of such a complex has not been confirmed at normal dosages of $CaCl_2$.

(d) Nuclei of hydration may be produced by a porous C-S-H product with a low C/S ratio.

(e) The rapid set may be attributed to the crystalline shape of ettringite produced as a felt consisting of very fine needles. The accelerated formation of ettringite in the presence of calcium chloride has also to be considered.

(f) An adsorbed complex containing chloride ions forms on the hydrating C_3S. This activates the surface and accelerates the hydration. This may also occur in the acceleration of hydration of C_3A with gypsum.

(g) Calcium chloride acts as a catalyst in the hydration of C_3S. This presumes that $CaCl_2$ does not react with any of the components of cement.

(h) The C_4AH_{13} rather than the C_3AH_6 phase is preferentially produced in the presence of calcium chloride. Higher strengths are attributed to the formation of crystalline C_4AH_{13}. The role of C_3S is ignored in the theory.

(i) The coagulation of the hydrosilicate ions (possible polymerization) is responsible for the accelerated hardening. The accelerated formation of C-S-H has also been considered.

(j) Calcium chloride decreases the pH of the liquid phase in the hydration of cement and consequently increases the dissolution rate of hydrolysis of lime. The pH value may decrease from about 12.8 to 12.0 with 3% $CaCl_2$.[1] All accelerators may not decrease the pH of the system.

(k) Higher dissolution of cement components and of the hydrated phases occurs in the solution of calcium chloride. This mechanism has been elaborated by Chengju.[113d] Portland cement cured in $CaCl_2$ extracts or precipitates a substantially higher amount of $Ca(OH)_2$ than the reference (Fig. 23). It is possible that chloride combines with CH to form a basic chloride complex. This is a metastable phase and decomposes, and the sequence of more dissolution of CH proceeds to accelerate the hydration. This mechanism is related to that stated under *(c)* and *(g)*.

(l) Due to the diffusion of Cl^- ions through the initially-formed hydrates and accelerated outward diffusion of OH ions, the precipitation of CH occurs more rapidly and the decomposition of calcium silicates is accelerated.

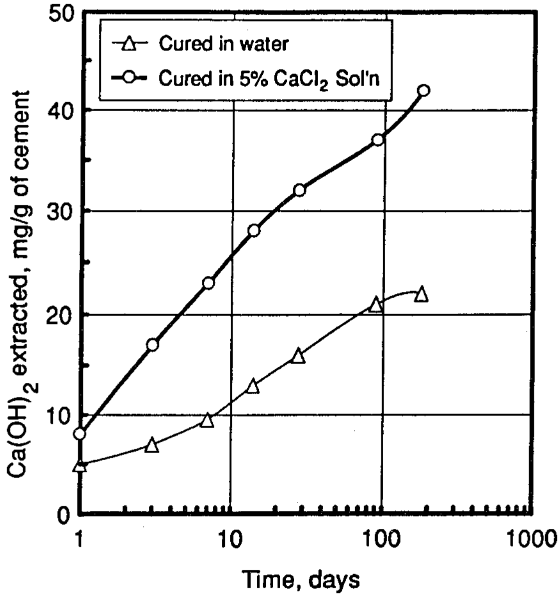


Figure 23. Extracted lime from cement paste containing calcium chloride.

None of the above theories can explain all the effects of $CaCl_2$ in concrete. It is possible that any one mechanism may be able to explain only one or some of the observations. It is likely that an overall mechanism should take into account the amount of the admixture used and the time of hydration and the experimental conditions.

3.3 Pore Structure

In an investigation on the effect of different amounts of $CaCl_2$ (0, 1, 2 and 3 1/2%) on the properties of cement pastes, Ramachandran and Feldman[60] found that the product shows a decrease in porosity as hydration progresses (Fig. 24). When cement is mixed with water, it sets into a rigid body. Water in the pores slowly reacts with the unhydrated particles forming the hydrated products and these products fill the spaces originally occupied by the water molecules as well as spaces originally held by the unhydrated particles. As the density of the hydrated cement is lower than that of the unhydrated cement, a decrease in porosity results during hydration. The decrease is steep during the first 24 hours, and at the same time there is a rapid rate of hydration. After 28 days, most samples show a 50% decrease in porosity.

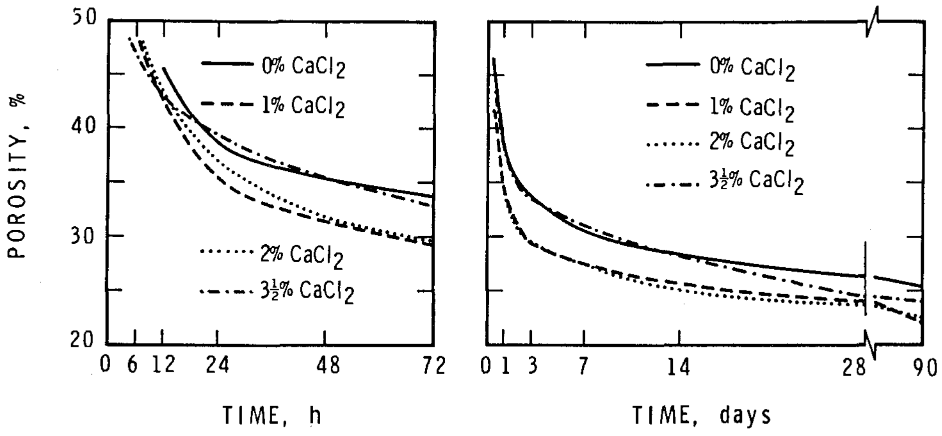


Figure 24. Porosity of cement paste containing different amounts of calcium chloride.

In Fig. 25, the porosity of cement pastes is expressed as a function of the non-evaporable water content. Porosity decreases as the degree of hydration increases. The main factor causing decrease is the filling of pores by the low density hydrated cement. The relatively higher porosity values for pastes with a W/C = 0.4 are due to the higher initial amounts of water in them. A completely hydrated cement formed at a W/C = 0.4 has an absolute density of 2.19 g/cm^3. An extrapolation of the line representing the sample made at a W/C = 0.4 to a density of 2.19 g/cm3 corresponds to a porosity of 22.5%. This is the minimum porosity that can be attained with a cement paste prepared at a W/C = 0.4 (made with or without admixture). At the same degree of hydration for samples made at a W/C ratio of 0.4, porosity decreases as follows: Cement + 3 1/2% $CaCl_2$ > Cement + 2% $CaCl_2$ > Cement + 1% $CaCl_2$ > Cement + 0% $CaCl_2$. Collepardi et al.[98] compared the porosity of cement hydrated for 7 days with and without $CaCl_2$ and found that the total porosity is higher in the paste containing $CaCl_2$. The sample hydrated with $CaCl_2$ had a higher amount of microporosity (10–50 Å). The differences in porosity obtained at the same degree of hydration indicate that the types of hydration products formed in pastes containing different amounts of $CaCl_2$ are intrinsically different in nature. It can also be concluded that in this system the differences in porosity are mainly due to the variation in the absolute densities of the hydration products.

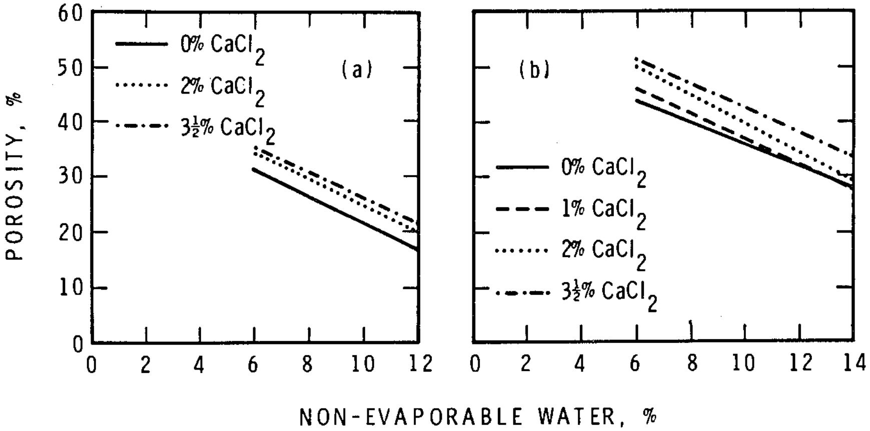


Figure 25. Porosity vs non-evaporable water relationship. *(a)* W/C = 0.25, *(b)* W/C = 0.4.

3.4 Surface Area

The addition of $CaCl_2$ increases the surface area of hydrated C_3S and hence it follows that a similar effect should also operate in portland cement paste. In the presence of $CaCl_2$, the surface area values of portland cement, pozzolanic cement, and blast furnace cement increase from initial values of 43.2, 45.4 and 45 m^2/g to 76.3, 61.0 and 198 m^2/g respectively.[99] Calcium chloride is more effective in enhancing the surface area of C_3S paste than that of portland cement paste. A part of the explanation is that $CaCl_2$ increases only marginally the surface area of the C_2S component of cement. The small increase in the surface area of pozzolanic cement is due to the negligible influence of $CaCl_2$ on the lime-pozzolana reaction. The activation of slag by $CaCl_2$ may explain its significant influence on this system.

The surface areas of various cement pastes, determined at a particular degree of hydration, were reported by Ramachandran and Feldman.[60] At a particular degree of hydration, the surface areas generally increase as the amount of $CaCl_2$ is increased (Table 6).[60] The difference is minimal if water is used as an adsorbate. The significant differences in the surface area values for the same degree of hydration suggest the existence of differences in the intrinsic properties of samples. At higher degrees of hydration, any decrease in surface area of pastes containing 2 and 3½ % $CaCl_2$ may be due to aging.

Table 6. Specific Surface Area of Cement Pastes Containing Calcium Chloride at 40% and 70% Hydration

		Degree of Hydration	
		40%	70%
Sample No	$CaCl_2$, %	Surface Area (m^2/g)	
1	0	20.5	22.1
2	1	20.3	24.3
3	2	37.9	28.7
4	3.5	37.3	32.2

3.5 Morphology

Addition of $CaCl_2$ to the hydrating cement affects the microstructural features of the paste. Without the admixture, the paste may consist of cluster of sheets mixed with fibers, the fibers being much more abundant than in C_3S pastes. By the addition of 2% $CaCl_2$, the fibrous particles are reported to be completely absent.[98] At early ages, in normal pastes with $CaCl_2$, a greater proportion consists of reticulated network.

Ramachandran and Feldman compared the microstructural features of cements containing 0, 1, 2 and 3½ % $CaCl_2$, all formed at a W/C = 0.4 and hydrated to 70%.[60] At lower degrees of hydration (corresponding to a constant non-evaporable water content of 8.2%) pastes containing 0% $CaCl_2$ showed well-defined needles representing C-S-H and ettringite formation. Columnar particles of CH, identified by energy dispersive x-ray analysis were also present. At 1% $CaCl_2$, however, thin plates of C-S-H appeared. At 2% $CaCl_2$, the structure became more consolidated and contained plates and small particles. A sponge-like mass was evident at 3½ % $CaCl_2$ addition. Specific area, density, porosity, and strength differences existing between samples could not be explained on the basis of microstructure. Some of these do not depend on microstructural features and are not easily resolved by the SEM. Also some of the features may be obscured by the deposition of a gel-like hydration product. Micrographs, however, showed that there are some morphological differences, especially at lower degrees of hydration. In hot pressed cements containing admixtures such as $CaCl_2$, triethanolamine, and citric acid, Sarkar and Roy[100] found differences in strength development but the microstructural investigation yielded no useful information for explaining the strength variations.

3.6 Strength Development

Calcium chloride increases compressive strength of cement pastes especially at earlier times.[98] The most significant effect on compressive strength occurs with portland blast furnace cement and marginally with portland-pozzolan cement.

The compressive strength of cement pastes in the presence of 2% $CaCl_2$ improves by about 50, 41, 11, 9 and 8% over the reference at 6h, 1d, 3d, 7d and 28 days respectively.[113e]

Strengths are generally compared at a particular time of curing. However, comparison of the properties at equal degrees of hydration forms a good basis to study the intrinsic property of pastes hydrated in the presence of different amounts of $CaCl_2$. This approach was adopted by Ramachandran and Feldman[60] for an examination of strength development in portland cement pastes hydrated in the presence of 0, 1, 2 and 3½ % $CaCl_2$. Figure 26 shows that at any particular degree of hydration, the sample with 3½ % $CaCl_2$ has the lowest strength; at lower degrees of hydration sample containing 0% $CaCl_2$ is the strongest, although with time, samples containing 1–2% $CaCl_2$ form stronger bodies than all others. Porosity, density, and bonding are factors that affect these results. It is thus evident that addition of $CaCl_2$ not only changes the rate of hydration but also the intrinsic nature of the hydration products.

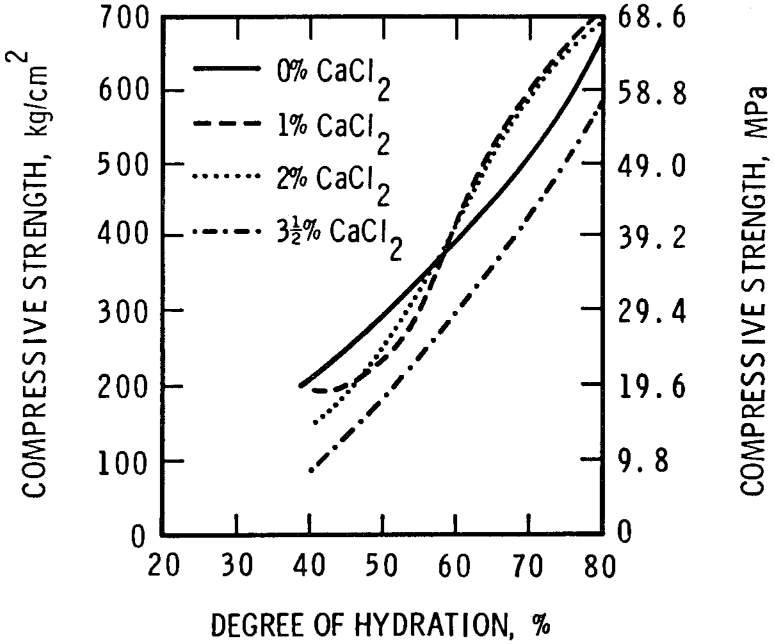


Figure 26. Strength vs non-evaporable water relationship for cement paste containing calcium chloride.

The improvement in flexural strength is generally less than that in compressive strength when $CaCl_2$ is used. At longer periods of curing, the flexural strength may even be lower than that of the control concrete. Figure 27 shows the development of compressive and flexural strengths in cement pastes containing different amounts of $CaCl_2$.[4][99]

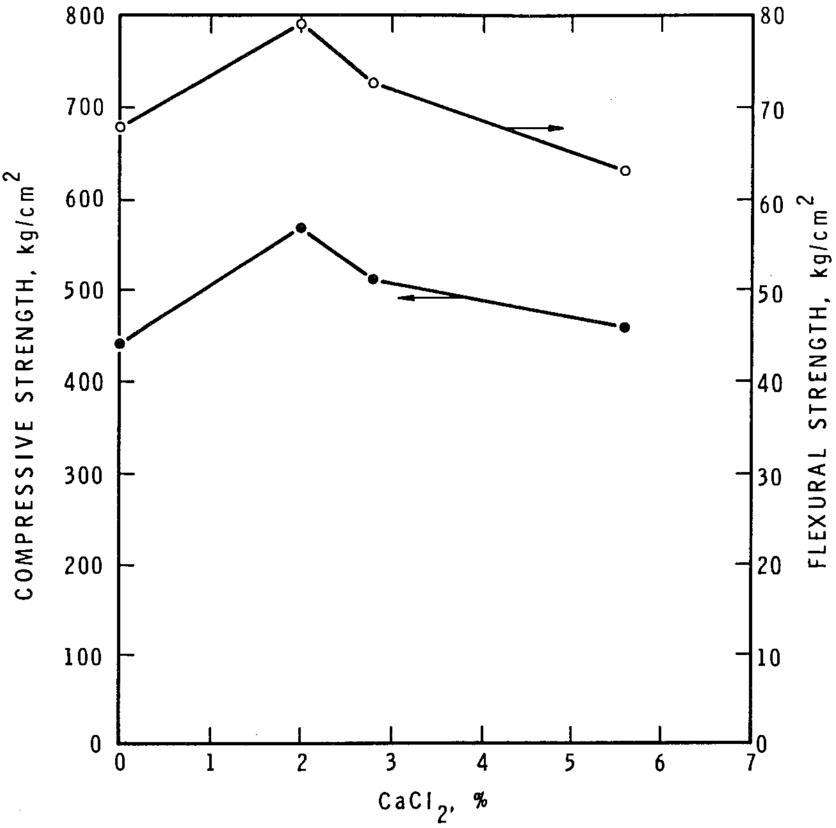


Figure 27. Development of strength in a cement paste containing calcium chloride.

4.0 PROPERTIES OF CONCRETE

4.1 Workability

Addition of calcium chloride influences various physical, chemical and mechanical properties of concrete. In the fresh concrete, the following properties are affected marginally or significantly. The properties such as workability, shrinkage, corrosion of rebar, alkali-aggregate expansivity, and efflorescence are increased, whereas bleeding, porosity, frost resistance, and sulfate resistance may be decreased.

It is generally observed that addition of $CaCl_2$ increases slightly the workability and reduces the water required to produce a given slump of concrete. In combination with an air-entraining agent, $CaCl_2$ may sometimes improve further the workability. A small increase in air content and average size of air voids may also result.

4.2 Setting Characteristics

Calcium chloride reduces significantly both the initial and final setting times of concrete. This is useful for concreting operations at low or moderate temperatures. It permits quicker finishing and earlier use of slabs. The influence of different amounts of calcium chloride on initial and final setting times of neat cement pastes is given in Fig. 28.[4] The setting times are decreased as the amount of $CaCl_2$ is increased. Excessive amounts e.g., 4–5% may cause rapid set and hence should be avoided. Even using the same type of cement but obtained from different sources shows differences in setting characteristics. There is no direct correlation between the acceleration of setting and subsequent strength development in the hardened state.

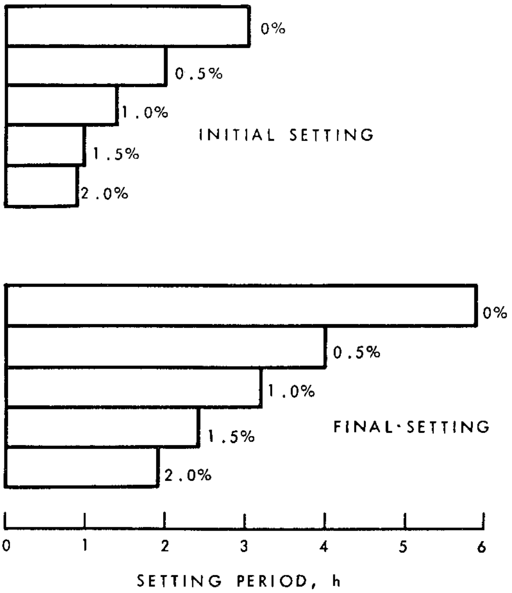


Figure 28. Initial and final setting periods of cement containing calcium chloride.

Calcium chloride is used in combination with other admixtures to obtain earlier setting. For example, lignosulfonate, a water reducer, will extend the setting time and this can be counteracted by the incorporation of $CaCl_2$.

According to some references, $CaCl_2$ in small amounts acts as a retarding admixture. According to Levitt[95] the strength ratios of mortar (strength of mortar containing $CaCl_2$ to strength of reference specimen) containing 0.0005, 0.005, 0.01, 0.05, 0.5 and 1% $CaCl_2$ are 0.8, 0.6, 0.9, 2.0, 1.8 and 2.1 respectively.

4.3 Drying Shrinkage

Although there is some disagreement on the effect of $CaCl_2$ on drying shrinkage, there is evidence that drying shrinkage of mortar or concrete is increased. Table 7 gives the drying shrinkage values for three admixtures at different times of curing. Calcium chloride addition results in a higher shrinkage at all times.[113f]

Table 7. Drying Shrinkage with Accelerators. *(Reprinted with permission, E&F.N. Spon, Ltd.)*

Samples			Days		
	7	14	28	84	168
			% Shrinkage		
Reference	0.013	0.021	0.030	0.049	0.056
$CaCl_2$, 2%	0.023	0.033	0.045	0.056	0.068
TEA, 0.033%	0.016	0.029	0.040	0.056	0.064
Ca Formate, 3%	0.015	0.025	0.036	0.054	0.056

4.4 Bleeding

Calcium chloride generally reduces both the bleeding rate and bleeding capacity. These reductions may be related partly to the increase in density and viscosity of the liquid. With 1% $CaCl_2$ addition, the bleeding rates for ASTM Type I, II and III cements were reduced from 163, 139 and 129 (x 10^6 cm/sec) to 146, 103 and 89 (x 10^6 cm/sec) respectively.[97]

4.5 Creep

Calcium chloride and triethanolamine admixtures increase the creep of concrete. Hope and Manning[101] determined the creep in concrete under wet or dry conditions in the presence of 1.5% $CaCl_2$. The percentage increase in creep for concrete containing $CaCl_2$ and loaded at 7 days and 28 days was 36% and 22% respectively.

4.6 Efflorescence

The effect of $CaCl_2$ on the efflorescence in concrete is not clearly understood. The published reports have indicated that either the efflorescence is not increased, decreased or intensified. It is also reported that the surface discoloration or mottling of concrete slabs occurs due to the presence of $CaCl_2$ admixture. It is likely that $CaCl_2$, being very soluble, is drawn to the surface and being deliquescent, will attract moisture. The blotching of the surface may be caused by the interaction of Cl^- ion with the alkali and C_4AF.

5.0 MECHANICAL PROPERTIES

5.1 Compressive Strength

It is recognized that $CaCl_2$ increases the early strength of cement paste, mortar and concrete. The actual values depend on the amount of $CaCl_2$ added, the mixing sequence, temperature, curing conditions, W/C ratios and the type of cement. Calcium chloride increases the strengths of all types of cements (Types I to V, ASTM designation). The time required for concretes to attain a strength of 13.8 MPa using 2% $CaCl_2$ is indicated in Table 8.[56] The long term effect of $CaCl_2$ on the strength development in concrete is not clearly established, some reporting higher strength while others reporting lower strength. Shideler's work suggests that at 2% $CaCl_2$ in Type II cement at different cement contents, the strengths are always higher in chloride-containing concrete up to 5 years.[111] Addition of CaO-$Al_2(SO_4)_3$ mixture may restore the strength loss in some cases.[103]

The strength development in concrete depends on the amount of initially-added $CaCl_2$. Higher amounts decrease strength. The optimum dosage suggested varies between 1 and 4%. Most practitioners however, recommend a dosage not exceeding 2% flake $CaCl_2$ or 1.5% anhydrous $CaCl_2$.

Table 8. Time Required for Concrete to Attain a Compressive Strength of 13.8 MPa Using 2% $CaCl_2$

Types of Cement	Time (days)	
	Plain Concrete	Concrete Containing Calcium Chloride
I	4	1.5
II	5	2.0
III	1	0.6
IV	10	4.0
V	11	5.5

The acceleration of strength development is also achieved at temperatures lower than the ambient temperature. Figure 29 shows the relative strengths developed in concrete cured for periods 1, 3, 7 and 28 days and at temperatures of -4.0, -4.5, 13 and 23°C.[56] Although the addition of $CaCl_2$ results in greater strengths at ambient temperatures of curing, the percentage increase in strength is particularly high at lower temperatures of curing.

The acceleration of hardening of concrete in the manufacture of precast concrete has several advantages. An accelerator such as $CaCl_2$ can be used for this purpose. In the USSR, it is claimed that precast concrete units may be obtained without heating by using large amounts of K_2CO_3 and $NaNO_2$ with $CaCl_2$.[104]

The Soviet literature contains references to the use of many complex admixtures. For example, by using nitrites and nitrates in combination with $CaCl_2$, higher strengths are reported at below freezing temperatures. Among the combination used, Mchedlov-Petrosyan et al.[105] found that maximum strength was developed with a mixture of 1.1% $CaCl_2$ and 1.2% $Ni(NO_3)_2$. The higher strengths were attributed to a more complete hydration, low basic C-S-H formation, and complex formation of the salt with the hydrating cement. Strengths are not a linear function of the degree of hydration and caution should be exercised when comparison is made of pastes containing complex admixtures. For example, at 50% hydration of cement, the strengths developed with $Ca(NO_3)_2$-$Ca(NO_2)_2$-$CaCl_2$ combination and the reference cement are, respectively, 160–230 kg/cm^2 and 100 kg/cm^2.[106]

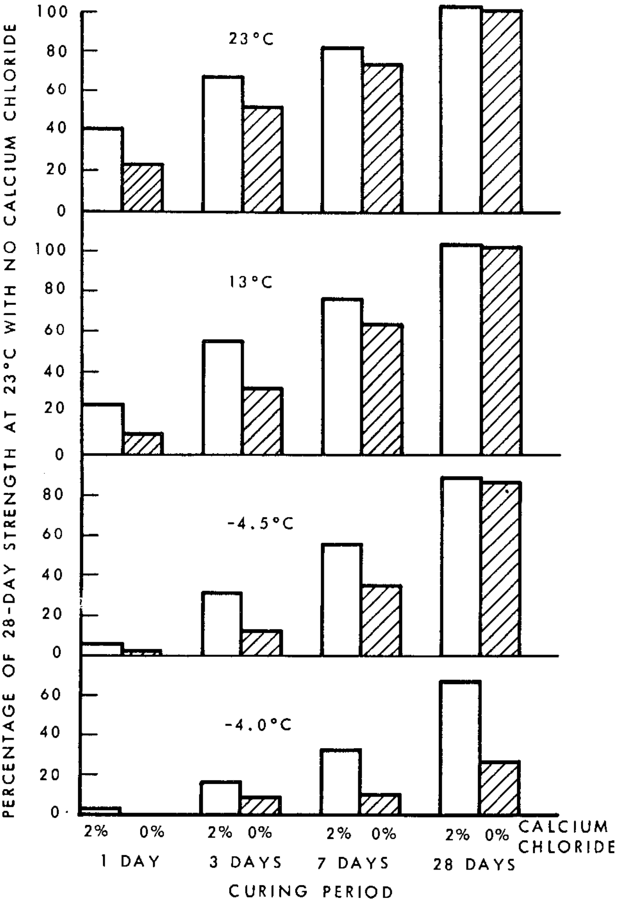


Figure 29. Effect of calcium chloride on strength development in concrete at different temperatures.

Strength development in concrete containing various other chlorides has also been investigated. Using chlorides of Ca, Ba, Mg, and Fe, Ranga Rao[107] found that 1.6% $BaCl_2$ gives 1-day strength equivalent to that obtained with 2% $CaCl_2$. However, the 28-day strength with $BaCl_2$ was lower than that obtained with $CaCl_2$. It was also found that $BaCl_2$ is not as efficient an accelerator as $CaCl_2$ at 10–15°C. It is likely that the differences in the solubility of $BaCl_2$ and $CaCl_2$ play a role in the mechanism of acceleration and strength development.

An accelerated strength test has been developed for the prediction of 28-day strength of concrete by mixing it with 3% $CaCl_2$ and curing at 70°C for 20 hrs.[108]

5.2 Flexural Strength

The effect of curing temperature on the strength development of concrete containing 2% $CaCl_2$ has been studied up to 1 year. In general, the 3-day strengths were higher for a concrete containing the admixture at temperatures -3.9, 4.4, 12.8 and 22.8°C.[109] At longer times, at -3.9, 4.4 and 12.8°C, the flexural strengths of concrete containing $CaCl_2$ decreased compared to those of plain concrete.

5.3 Tensile strength

Tensile strength of concrete is increased by the addition of $CaCl_2$. Larger amounts (2% $CaCl_2$) decrease this strength. It has been reported that chloride reduces the split-cylinder tensile strength of concrete by 11–13% with respect to the reference concrete moist-cured for 3 months.[113g]

The effect of 1.5% $CaCl_2$ on compressive strength, tensile strength, modulus of rupture, pull out strength, and modulus of elasticity are tabulated in Table 9.[113g] Generally up to 90 days, calcium chloride enhances strengths of concrete.

Table 9. Effect of Calcium Chloride on Strengths of Concrete*

Age	Compr Str.		Tens Str.		Mod. Rup.		Pull out Str.		Mod. Elas.	
Days	0	1.5	0	1.5	0	1.5	0	1.5	0	1.5
3	18.4	22.3	2.18	2.02	-	-	-	-	2.21	2.57
7	21.9	29.4	2.32	2.70	3.49	3.16	34.2	43.7	2.40	2.73
14	24.5	30.4	2.82	2.93	3.74	4.40	37.7	48.3	2.57	2.51
91	30.4	46.1	3.13	3.50	-	-	43.6	50.3	3.08	3.17

* 0=0% $CaCl_2$; 1.5= 1.5% $CaCl_2$; Compressive, tensile and modulus of rupture in MPa; modulus of elasticity = MPa X 10^3; pull out strength in kN.

5.4 Modulus of Elasticity

Modulus of elasticity is related to the compressive strength of concrete. It is reported that modulus of elasticity is increased at early ages with $CaCl_2$ but at 90 days the values are almost the same for cements containing 0% or 1–4% $CaCl_2$.[110] Typically at 1 day in concrete with 0, 1, 2, 3, and 4% $CaCl_2$, the moduli of elasticity are 2.6, 3.3, 3.6, 3.6, and 3.6 x 10^6 lbs/sq.in. respectively whereas the corresponding values at 90 days are 6.9, 6.6, 6.6, 6.5 and 6.4 x 10^6 lbs/sq.in.[110]

5.5 Abrasion Resistance

Concrete containing 2% $CaCl_2$ is more resistant to erosive and abrasive forces than plain concrete under both moist curing and drying conditions.[111] As the curing period is increased, concrete containing $CaCl_2$ exhibits a better resistance to erosion.

6.0 DURABILITY OF CONCRETE

6.1 Frost Resistance

At early ages, concrete with 2% $CaCl_2$ shows a higher resistance to freezing and thawing than that without the accelerator. At later ages $CaCl_2$ decreases the durability of concrete. According to Gonnermann[102] the resistance to scaling due to freezing and thawing is increased by an air-entraining admixture. Addition of $CaCl_2$ up to 2% does not decrease the effectiveness of air entrainment.

6.2 Alkali-Aggregate Expansion

The expansion due to alkali-aggregate reaction is further increased by the addition of $CaCl_2$. In mortars containing a cement with 1.16% Na_2O and 0.04% K_2O, addition of $CaCl_2$ may increase expansion by about 30%.[111] Investigations by Blanks and Meissner[114] showed that, in cements containing 0.18% alkali, calcium chloride increased the expansion from almost nil to about 0.7% after 2 years. When the alkali-aggregate expansion is controlled by the addition of a pozzolan, the effect of chloride is not significant.

6.3 Sulfate Resistance

Calcium chloride contributes to a lower resistance of concrete to sulfate attack. In Type I, II, and V concretes containing different amounts of cement, 2% calcium chloride increased sulfate expansion.[111] Compressive strengths are also decreased. The sulfate resistance of concrete containing $CaCl_2$ is decreased to a greater extent when it has lower cement contents. The detrimental effect of calcium chloride can be counteracted to some extent by using air-entrained concrete.

The expansion of concrete in the presence of $CaCl_2$ may be due to several reasons. Small expansion may be due to the formation of CS(HCl) compound.[115] The calcium chloroaluminate may favor the growth of calcium sulfoaluminate crystals. Ben Yair[116] found that in the presence of $CaCl_2$, sulfoaluminate needles grew from 60 microns to 300 microns in length.

In a reexamination of the effect of $CaCl_2$ on sulfate resistance of concrete, Harrison exposed concrete containing different amounts of chloride to a Na_2SO_4-$MgSO_4$ solution. The specimens were initially cured for 28 days. Mean compressive strengths after 7 years of immersion showed that even at 4% $CaCl_2$, little or no enhanced effect of sulfate attack occurred. The pessimum amount was found to be 0.4% chloride below which increased sulfate attack occurred.[113h]

6.4 Corrosion of Reinforcement

Corrosion is an electrochemical process that involves a flow of electricity. When two metals are immersed in an electrolyte, they develop different potentials. If the two metals are connected together, electrons from the anode will flow towards the cathode. The steel in concrete may achieve this condition by having two areas containing different concentrations of moisture, oxygen or dissolved substances. The presence of metallic impurities, internal stresses, and other factors also create potential differences.

The composition of the corrosion product varies greatly and is best represented by the formula $(FeO)_x\ (Fe_2O_3)_y\ (H_2O)$. Corrosion occurrence depends on the availability of oxygen, water, potential difference and electrolytes. The formation of green rust on steel is sometimes observed. There is a possibility of the formation of soluble chloro-complex product containing both Fe^{2+} and Fe^{3+}.[113i]

In an alkaline medium such as that existing in concrete, corrosion does not occur because the pH value is higher than 10. A protective layer of iron product is formed. If conditions are such that the pH decreases to lower values, the protective layer is disrupted and iron corrodes. In the presence of chloride, corrosion of steel is enhanced because of the detrimental effect of chloride on the protective film on steel. Chlorides may be added as accelerators or introduced from external sources such as when using de-icing salts. Not all chloride added initially is available in the free form. Some is bound with the cement components and immobilized.[49][117]-[123][127]

Because of the potential hazards of corrosion in conventionally reinforced concrete wet in service, a very limited amount of calcium chloride is allowed in it, but in prestressed concrete it is either totally banned or only allowed in small amounts. One of the methods to minimize or almost completely retard corrosion is to take special measures including adding a corrosion inhibitor.[128] Rosenberg[128] studied the effect of calcium nitrite as a possible inhibitor. This inhibitor at a dosage of 2% passed the requirements of the ASTM C 494 standard and also decreased corrosion. Many other inhibitors have been suggested. They include stannous chloride,[129] chromates, phosphates, hypophosphites, alkali nitrites, fluorides, benzoates, lignosulfonate, calgon, etc. It is important that these additives should not affect the physical and chemical properties of concretely adversely. According to Evans,[131] the inhibitor is beneficial if the steel is clean and chlorides are absent. It appears that an inhibitor is no substitute for good concrete practice.[129] Inhibitors should be added as an added precaution. A more detailed discussion of corrosion inhibitors forms the content of Ch. 14.

7.0 USE OF CALCIUM CHLORIDE IN OTHER CEMENTITIOUS SYSTEMS

Calcium chloride has an accelerating effect on the hydration of pozzolanic cements but its action times is less marked than that on portland cement. Jensen and Pratt exposed portland-cement–fly-ash blends to chloride solutions. The initial rate of reaction was accelerated in chloride. Some chloride was also bound by the calcium aluminate hydrates produced by the pozzolanic reaction.[153] Addition of chlorides to pozzolanic cements reduces the volume of large pores and permeability of the pastes.[123][126][127]

In portland blast furnace cements, $CaCl_2$ does not influence the strength significantly at lower temperatures although at higher temperatures it acts as an accelerator. Increases in strength of the order of 15–20% may take place under steam curing conditions. As in portland cements, the presence of $CaCl_2$ may cause corrosion of steel reinforcement in blast furnace slag cements. The accelerating effect of $CaCl_2$ may diminish as the amount of slag increases in the portland blast furnace cement.

Caution should be exercised if $CaCl_2$ has to be used in expansive cements because of the possibility of its adverse effect on the expansive characteristics and shrinkage. The effect of $CaCl_2$ should first be established before it can be used in such cements.

In small amounts, $CaCl_2$ slows the setting of high alumina cement and is regarded as a deleterious admixture for this cement. Calcium chloride reduces the strength of CA pastes. Calcium monoaluminate (CA) is a major phase in high alumina cements.

Reports on the action of $CaCl_2$ on the hydration of gypsum plaster are contradictory. Some results suggest that in small amounts $CaCl_2$ has an accelerating effect on the hydration of plaster, whereas according to others, in amounts in the range 0.25–2.0%, $CaCl_2$ has negligible effect on the setting times of plaster.

Sawdust and wood shavings have been used with portland cements to make lightweight products. Because of the presence of soluble carbohydrates in wood, excessive retardation of setting of cement may occur. Addition of $CaCl_2$ to such mixes may counteract the retarding action of the carbohydrates.

A rapid hardening cement, known as *jet set* or *regulated set* cement, consisting of $C_{11}A_7CaF_2$ has been advocated for use for special purposes. It has been shown that in this cement, $CaCl_2$ acts as a retarder.

8.0 CALCIUM CHLORIDE: PROPERTIES AND PREPARATION

8.1 Types and Production

Calcium chloride is a colorless crystalline solid both in the hydrous and anhydrous state. The commercial products may either be white or opaque. Two types of calcium chloride are available for use in concrete. Type I is a flake form with a minimum $CaCl_2$ content of 77% and Type II (pellet or other granular forms) contains a minimum of 94% $CaCl_2$. For all practical purposes, 2% flake form of calcium chloride may be taken as equivalent to 1.5% anhydrous $CaCl_2$. Calcium chloride is deliquescent. The hygroscopicity expressed as the amount of water taken up by 1 lb of flake $CaCl_2$ is 1.0, 1.6, 2.0, 2.8, 3.5, 5.0 and 8.4 lbs at a relative humidity of 36, 60, 70, 80, 85, 90, and 95% respectively.

Calcium chloride depresses the freezing point of water. The freezing point of the solution with 0.25, 0.5, 1.0, 2.0, 3.0, 5.0 and 7.0% anhydrous chloride is lowered by about 0.1, 0.2, 0.4, 0.9, 1.4, 2.3 and 3.4°C respectively. It is apparent from the above figures that in the amounts normally used in concrete calcium chloride has only a negligible effect on the freezing point of the liquid.

Two methods are used to produce calcium chloride. It can be recovered from the natural brines by removing the common salt and bromine (if required) and then treating the brine with milk of lime or magnesium hydroxide. In the Solvay process of manufacturing soda, ammonia is recovered from the waste liquor by adding milk of lime or quick lime to ammonium chloride. The resultant calcium chloride solution is clarified and the unreacted sodium chloride is then *salted out.*

8.2 Storage

Calcium chloride is supplied in moisture-proof bags, air tight drums or other appropriate means. It should be stored carefully so that it does not pick up moisture. It should be stored in a dry, well-ventilated room with a wooden or concrete floor. The bags are placed on planking about 4" off the floor (to allow air circulation) so that each tier of bags is crosswise to the previous tier. Older bags should be used first. It is a good rule to roll partly used bags down tight to the unused portion. The broken bags should be repaired with section of used bags and gummed tape and used first. If the bags are to be stored temporarily outside, they should be placed on raised planks and should be provided with a waterproof covering. Lumps that develop during storage should be discarded because they are not easily soluble in water. If the undissolved matter is used, it may produce popouts. Precautions recommended for handling include using hand trucks with nose blades large enough to project beyond the bottom bag and ensuring that the bags don't overhang. Calcium chloride is nontoxic and harmless to the skin. If it comes into contact with hand or clothing it can be removed by rinsing with water. Soap should be used only after the chloride is completely dissolved and rinsed off. Details are to be found in a publication by Allied Chemical Canada.[133]

8.3 Addition

Calcium chloride may be added either in the solution or dry form; the former method is preferred. The method of preparing and adding calcium chloride solution has been described by Allied Chemical Canada Ltd Instruction Booklet.[46] The following is taken from the ACI manual of practice.[130]

Calcium chloride should be introduced into the concrete mixture in solution form. The dihydrate and anhydrous solid forms should be dissolved in water prior to use. Preparation of a standard solution from dry calcium chloride requires that the user be aware of the per cent calcium chloride printed on the container. In dissolving the dry product, it should be added slowly to the water, rather than the water to the calcium chloride as a coating may form that is difficult to dissolve. The concentration of the solution may be verified by checking the density. The correct density should be obtained from the supplier.

Calcium chloride should not come directly into contact with cement as it may cause flash set. It is usually added to the mixing water or to the aggregates in the mixing drum as a solution. If dry calcium chloride is used, it should be added to the aggregates in the mixer drum during mixing, or to the mixed concrete just before discharge. If it is added to the mixed concrete, at least 20 revolutions of the mixer drum is recommended. When ready-mixed concrete is used, calcium chloride should be added at the plant site if the concrete is to be poured within one hour after the start of the mixing; otherwise it should be added at the pouring site, allowing approximately 1 min mixing time or 20 revolutions of the mixer.

Calcium chloride may be dispensed either by volume or be weight. The type and sophistication of dispenser to be used depends on the volume of concrete used, batch size, quality of concrete required, and extent of the use of admixture. The types of dispensers used for admixture include manual dispenser (gravity and pneumatic type) and automatic types (timed flow, pneumatic or electric). Dispensers should be regularly flushed with water and checked for accuracy from time to time. For small jobs, a graduated glass bottle or a container can be used. For medium jobs, valve systems combined with gravity feed should be used. For large jobs, fully automatic dispensers utilizing the principle of time-flow or positive displacement are used. Further details are to be found in the pamphlets published by the Calcium Chloride Institute, USA, and other publications.[4] If the calcium chloride is to be added in a dry form, the powder, free of lumps is batched and measured by volume or weight. It should not directly come into contact with cement. When it is to be measured by volume, it is necessary to calibrate a container for the type and form used. Adequate dispersion in concrete is affected if dry chloride is added during the first half of the mixing operation.

Calcium chloride may not be compatible with certain types of air-entraining and water-reducing agents. Preliminary tests should be made and if compatibility is a problem, the admixtures should be added separately.

9.0 STANDARDS AND PRACTICE

Calcium chloride and other accelerators used in concrete are covered by various standards. A short survey of international regulations covering the use of calcium chloride has been discussed by Ramachandran.[4] In this chapter, ASTM, CSA, and ACI standards dealing with the use of accelerators will be described.

9.1 ASTM (American Society for Testing and Materials)

ASTM D98-87, entitled "Standard Specification for Calcium Chloride" covers the types, chemical requirements, grading, sampling and testing, and packaging and marking of calcium chloride used for various purposes.

ASTM D345-90, on "Standard Test Methods for Sampling and Testing Calcium Chloride for Roads and Structural Applications," deals with the sampling, sieve analysis and a rapid technical method for estimating calcium chloride for roads and structural applications.

ASTM D1411-82 entitled "Standard Test Method for Water Soluble Chloride Present as Admixtures in Graded Aggregate Road Mixes" gives details on the test methods for determining water soluble Ca, Mg and Na chlorides used in admixes in the preparation of graded aggregate road materials. "Standard Test Methods for Analysis of Calcium Chloride," describes the procedures for the determination of calcium chloride, magnesium chloride, alkali chlorides and calcium hydroxide in Type I and Type II calcium chlorides.

ASTM C1102-88 is related to shotcrete admixtures and deals with the setting time determination of accelerating admixtures.

ASTM C494-92 standard describes seven types of chemical admixtures including accelerating admixtures (Type C) and water-reducing and accelerating admixtures (Type E). Types C and E may contain $CaCl_2$. Type C is an admixture that accelerates the setting and early strength development of concrete. Type E is an admixture that reduces the quantity of mixing water required to produce concrete of a given consistency and accelerates the setting and early strength development of concrete. These admixtures should conform to the requirements of Table 10.[4]

9.2 CSA (Canadian Standards Association)

CSA standard A266.2 covers chemical admixtures and A266.4 covers the guidelines for the use of admixtures. The guidelines give information on the composition, effect of admixtures on fresh and hardened concrete, applications and limitations, preparation, storage, dispensing and field evaluation. The admixture designated AC refers to chloride type admixture and type SN is an admixture that increases strength without substantially affecting the water requirement for a given consistency. Type SN may contain carbohydrates and some type of accelerator. The physical requirements of the type AC and type SN admixtures are given in Table 11.[4]

9.3 Chloride Limits

The influence of chloride on corrosion depends on many factors. It is the water soluble form (may vary between 50 and 85%) of the total chloride added to concrete that may cause corrosion. The available methods are not precise for measuring the soluble amount of chloride. Generally 2% calcium chloride has been allowed for normal concrete provided certain precautions are taken. The American Concrete Institute approach has been to limit the chloride ion content for use in concrete because it is the chloride ion that acts detrimentally as far as corrosion is concerned. Recommendations have been made in ACI Manual of Practice, Part 3, 1993 (Table 12).[134] No limits have been specified for non-reinforced concrete.

Table 10. Physical Requirements of Type C and Type E Admixtures According to ASTM C-494

Test	Physical Requirements	
	Type C	Type E
1. Water content, max., % of control	————	95
2. Time of setting, allowable deviation from control (hr:min)		
(a) Initial: at least	1:00 earlier	1:00 earlier
not more than	3:30 earlier	3:30 earlier
(b) Final: at least	1:00 earlier	1:00 earlier
3. Compressive strength, min., % of control		
3 day	125	125
7 days	100	110
28 days	100	110
6 months	90	100
1 year	90	100
4. Flexural strength, min., % of control		
3 days	110	110
7 days	100	100
28 days	90	100
5. Length change, max shrinkage		
(a) Percent of control (when length change of control is more than 0.030%)	135	135
(b) Increase over control (when length change is less than 0.030%)	0.010	0.010
6. Relative durability factor (applicable only when the admixture is to be used in air-entrained concrete which may be exposed to freezing and thawing while set)	80	80

Test C and E admixtures are also specified by the American Association of State Highway Officials(AASHO M - 194) and Corps of Engineers, USA (CE CRD-C87)

Table 11. Physical Requirements of Type AC and Type SN Admixtures (CSA 266.2 - 1978)

Property	Calculation	Type AC	Type SN
1. Water content, max	T/R x 100	100	97
2. Initial set			
(a) min hr: min	T—R	-1:00	-1:20
(b) max hr: min		-3:00	+1:20
3. Compressive Strength	T/R x 100 x 1.10		
3 days		125	120
7 days		110	120
28 days		105	120
6 months		100	100
1 year		100	100
4. Length Change		If R exceeds 0.030%, T/R shall not exceed 1.35, if R is not more than 0.030%, T-R shall not exceed 0.010%	
5. Air void spacing factor, max mm**/ ***	T	0.21	0.21
6. Relative durability factor min **/ ***	T/R x 100 x 1.05	100	100

Note: T = test values; R = reference concrete.

* Applicable only when required by the purchaser or when no previous test or service record is available.

** At the purchaser's option, either the air-void spacing factor or the relative durability factor may be used to determine acceptability.

*** Applicable only when tested in air-entrained concrete.

Table 12. ACI 318/319R-31: Maximum Chloride Ion Content for Corrosion Protection

Category of Concrete Service	Max Water Soluble Chloride Ion Content, by % wt of Cement
Prestressed concrete	0.06
Reinforced concrete which will be exposed to chlorides in service (bridge decks, parking garages, marine construction and certain industrial plants)	0.15
Reinforced concrete that will be dry or protected from moisture in service	1.00
Other reinforced construction	0.30

The CSA standard A 23.1-M 90, clause 15.1.7, specifies what amount of soluble chloride is allowed for various purposes. For prestressed concrete the limit is 0.06%. For reinforced concrete exposed to moist environment or chloride, the limit is 0.15%. For reinforced concrete exposed neither to moisture nor chlorides, the limit is 1.0%. It is also stipulated that the limits can be exceeded if the owner can be satisfied that no corrosion problems have occurred in the past in concrete structures made with similar materials and exposed to similar conditions.

In a report published in 1971 by the Greater London Council[4] the limits of chloride prescribed in twenty-four countries were analyzed. Depending on whether the concrete is reinforced, non-reinforced or prestressed, the requirements vary. For non-reinforced concrete, up to 4% $CaCl_2$ has been permitted.

10.0 ESTIMATION OF CHLORIDES

An estimation of chloride in a fresh or hardened concrete is necessary to understand the mechanism of acceleration. Also, field problems frequently require qualitative and quantitative analyses of chloride compounds (added deliberately or inadvertently) present in concrete. For example, corrosion of reinforcement in concrete may be traced to bad workmanship or to the presence of excess amounts of chloride added originally to the mix or introduced externally, such as the introduction of de-icing salts. Chloride estimation is also necessary to assess the efficacy of various treatments suggested against chloride penetration.

The most popular procedure for chloride analysis is Volhard's method (ASTM D 345-90). In the procedure developed by Berman, which is based on Volhard's method, the total quantity of chloride in concrete is determined by dissolving the sample in nitric acid, filtering and titrating with $AgNO_3$, using a chloride-selective electrode.[136] Uncertainties occur in estimation at low concentration ranges. One method to counter this is to use 0.01N $AgNO_3$ and to start with additions of 0.1 ml. The first addition may show a large increase in voltage that can be mistaken for an end point. This effect is attributed to the delayed nucleation of AgCl crystals and can be circumvented by adding a known quantity of NaCl to solution to be titrated.[137] Gravimetric analysis and x-ray fluorescence methods also give accurate values. In the CSA A23.2-4B specification, the method to determine water soluble chloride content is similar to that described in the ASTM C-114, Sec. 19, except that a boiling water extraction procedure is used instead of a nitric acid extraction.

In the ASTM D 1411-82 method for determining soluble chloride, silver nitrate is added in excess and boiled to coagulate silver chloride. To the excess silver nitrate, ferric ammonium sulfate is added and then titrated with ammonium thiocyanate solution. In the method of ASTM E 449-90 for "the standard method of analysis of calcium chloride," calcium from calcium chloride in alkaline solution is titrated with standard EDTA solution, using modified calcein II as an indicator. The color change is from green to purple. If the indicator alpha-hydroxynaphthol is used, the color change is from red to blue.

There are other methods which require less skill than the above. In the *Quantab* method, a test strip in which a column partly changes color from light brown to white can be related to the chloride concentration.[138] A rapid in-situ determination of chloride in portland cement concrete bridge decks consists of a chloride ion specific electrode.[139] In this method, the chloride-specific electrode is inserted into a borate-nitrate solution in a ¾-inch diameter hole drilled on the bridge surface.

A rapid method of measuring acid-soluble chloride has been developed by Weyers and coworkers.[113j] In this method, an acidic solution containing a defoaming (isopropyl alcohol) agent to digest the chloride is used. A stabilizing solution is added in place of a temperature correction factor for direct reading of chloride using a specific ion electrode. A spray method was described to estimate chloride that has penetrated concrete.[113k] Silver nitrate is sprayed on the fractured surface to observe the color change at the boundary. Silver forms a brown precipitate. An estimate of the Cl^- of the order of 0.15% is possible by this method.

Other non-routine techniques that can be used are neutron activation analysis, x-ray analysis attachment to the electron microscope, x-ray secondary emission spectroscopy, colorimetric technique, and atomic absorption spectrophotometry, but these are specialized equipment which require the use of skilled operators. Choice of a method should depend on accuracy, economy, speed and practicability considerations.

11.0 MISCONCEPTIONS IN THE USE OF CALCIUM CHLORIDE

Although calcium chloride has been used for more than one hundred years, there are still some misconceptions related to its use in concrete. In this chapter, some common misconceptions pertaining to the role of calcium chloride are described.

11.1 Winter Concreting

Calcium chloride is known to accelerate hardening of cement. This does not necessarily mean other methods cannot be used to accelerate the hydration of cement. Early strengths may be improved by using high early strength cement (Type III-ASTM), additional amounts of cement, or by using higher temperatures. For example, the protection recommended for safe strengths for concrete placed in cold weather (ACI 306R-88) for unexposed structures will be two days if Type I or II cement is used whereas with type III cement, accelerator, or extra cement (60 kg/m^3), the period can be reduced to one day. The corresponding periods for exposed structures are three and two days, respectively.

11.2 Accelerating Action: Definition

The definition of a chemical accelerator is not the same in different standards. The attributes of an accelerator are variously described as one accelerating initial setting, final setting, early strength development, initial rate of reaction, or causing lower final strengths. An accelerator, as the term suggests, should increase the rate of development of certain characteristic property of cement and concrete. It does not necessarily mean that it affects every one of several properties in this way simultaneously. For example, in the chemical sense, acceleration may mean an increase in the rate of reaction, in the physical sense, an increase in the rate of setting or volume change, and in the mechanical sense, an increase in the rate of development of strength. These changes may not occur at the same rate over the whole period of hydration. The same admixture may have different effects or even opposite effects depending on time, conditions of the experiment, and amount and composition of the materials.

There is general misconception that the acceleration of cement hydration will result in a corresponding gain in strength. Studies using 1, 2 and 3½ % $CaCl_2$ suggest that, during early hydration, maximum acceleration effect is achieved with 3½ % $CaCl_2$. However, no corresponding accelerated hardening occurs. In fact, at 3½ % $CaCl_2$, lowest strength results.[66]

Calcium chloride is generally termed as an accelerator for cement, but in the early literature it was considered as a retarder of setting of cement. In lower amounts, calcium chloride may act as a retarder. It is a retarder for high alumina cement, calcium alumino-fluorite cement, and slag cements. Although the addition of calcium chloride accelerates setting and hardening of cement, it does not necessarily follow that when added to individual components of cement, it acts as an accelerator. For example, calcium chloride retards the hydration of the tricalcium aluminate phase, while acting as an accelerator for the hydration of the silicate phase.

If an accelerator is defined as an admixture that increases the rate of formation of normal hydration products, then accelerating agents such as calcium fluorosilicate, alkali silicates, aluminates and carbonates which produce accelerated set of concrete would be excluded. The action of these admixtures involves formation of insoluble compounds by reaction with $Ca(OH)_2$, a product of the hydration of cement.

A determination of the accelerating effect based on the rate of hydration requires application of a proper method. The method based on the estimation of $Ca(OH)_2$ assumes that the composition of the C-S-H phase remains constant. Though applicable for the hydration of cement, it is less accurate when extended to that containing $CaCl_2$. In the presence of larger amounts of $CaCl_2$, more Ca ions enter the C-S-H, forming a product with a larger than normal C/S ratio.[68] The degree of hydration on the basis of the consumption of the anhydrous compounds of cement would be a more accurate method, but is attended with some practical limitations of accuracy. The method based on the non-evaporable water content assumes that the product of hydration of cement is substantially the same in the presence of calcium chloride as without it. This method becomes less accurate for estimating the rate of hydration of cement containing larger amounts of $CaCl_2$.

11.3 Immobilization of Calcium Chloride

The mechanism by which calcium chloride accelerates the hydration and hardening of tricalcium silicate or cement has not been established. Some of these theories imply that calcium chloride acts catalytically. In these theories, there is a tacit assumption that all added calcium chloride remains in a free state.

Application of methods, such as thermal analysis, chemical analysis and x-ray diffraction, has revealed that calcium chloride may react with the aluminate and ferrite phases and it may exist in different states in the tricalcium silicate-calcium chloride-water system. In this system, very strongly held chloride that cannot be leached even with water occurs to an extent of about 20% of the initially added chloride. Since this is not soluble in water, it would not be available for corrosion processes. These factors have to be taken into consideration for evaluating the corrosion of reinforcing steel in the presence of calcium chloride in concrete. The role of immobilized chloride and its consequences for corrosion are not clear.

11.4 Dosage Requirements

In spite of the widespread use of calcium chloride, the values referring to its dosage in concrete are often ambiguous or erroneous. This may have resulted in the use of incorrect amounts of calcium chloride and may have been one of the contributing factors to many failures of concrete. A knowledge of the actual dosage of chloride added to concrete is essential to prevent inclusion of excessive amounts that cause corrosion of reinforcement. When aggregates of marine origin are used, chloride present in them should also be taken into account for calculation purposes.

A dosage expressed in terms of a certain percentage of calcium chloride will be ambiguous because it might refer to the pure anhydrous calcium chloride or to the hydrate. By purification and desiccation, a number of solid hydrates can be prepared.

Calcium chloride is available as pellets or other granules, flakes, or in a solution form. According to the standards, the regular flake form should contain a minimum of 77% calcium chloride (anhydrous) and the pellet or other granular forms, a minimum of 94% calcium chloride. In these two types, the percentage of calcium chloride may vary depending on the purity. The use of specific language would ensure the use of the right amount. Dosage should be expressed in terms of "per cent calcium chloride dihydrate" or "per cent anhydrous calcium chloride" or by the chemical formula $CaCl_2$ or $CaCl_2 \cdot 2H_2O$, or chloride ions.

11.5 The Antifreezing Action

The freezing point of a solution is less than that of a pure solvent so the addition of calcium chloride to water should result in the depression of the freezing point of water. Consequently, it could imply that in concrete, calcium chloride admixture acts as an antifreeze. By the addition of 0.25, 0.5, 1.0, 2.0, 3.0, 5.0 and 7.0% anhydrous calcium chloride, the freezing point of water is lowered by 0.1, 0.2, 0.4, 0.9, 1.4, 2.3 and 3.4°C, respectively.[4] For example, if 2% calcium chloride (dihydrate) is added to cement at a water-cement ratio of 0.5, the concentration of dihydrate in solution would be 4%. This amount, which is equivalent to 3% anhydrous calcium chloride, would lower the freezing point by approximately 1.4°C. This shows that at normal dosages, the depression of the freezing point is negligible and hence calcium chloride does not act as an antifreeze. The real effect of calcium chloride is its ability to increase the rate of reaction in the cement-water system.

11.6 The Intrinsic Property

The use of calcium chloride in concrete technology is based on its ability to increase the rate of setting and strength development in concrete. These time-dependent properties have been studied extensively and major efforts have been directed to a comparison of the relative properties of concrete with or without calcium chloride after a particular curing time. These are very useful but from a basic and characterization point of view the comparisons should be based on some intrinsic property of the system. They could be based on equal degrees of hydration or equal porosity. A comparison of strengths at equal porosity values has revealed that among the systems magnesium oxychloride, portland cement, gypsum and magnesium hydroxide, it appears that magnesium hydroxide forms the strongest body at a porosity of about 30%.[140]

The changes in properties of concrete in the presence of calcium chloride may just be due to the degree of hydration or to the change in the intrinsic structure of the cement paste. Results have been obtained on the effect of different amounts of $CaCl_2$ (0–3½ %) on the intrinsic properties of hydrated cement at constant degrees of hydration.[60] At common degrees of hydration, porosity, surface area, strength, absolute density, and microstructural features reveal differences. These results indicate that the intrinsic characteristics of cement paste are changed by the addition of $CaCl_2$. This may explain some of the discrepancies related to the influence of $CaCl_2$ on the properties of concrete. For example, a concrete containing calcium chloride shows a higher shrinkage than plain concrete, especially at early periods of hydration. The larger shrinkage at earlier periods can be attributed mainly to a higher surface area of the product as a consequence of a larger degree of hydration. With increasing hydration, the difference in shrinkage becomes smaller but still shrinkage in the paste containing $CaCl_2$ is higher because at a constant degree of hydration the paste containing $CaCl_2$ exhibits a higher surface area than that not containing it.

11.7 Chloride-Free Concrete

Many specifications require that certain types of concrete should contain no chloride. This is a requirement which is very restrictive and almost impossible to achieve because the concrete-making materials: cement, water, aggregate, and admixture, may contain small amounts of chloride.

Cement contains such a negligible amount of chloride that it is practically undetected by ordinary methods of analysis and hence can be neglected as a source of chloride. The mix water, however, may contain chloride in the amount of about 0.0005%, and at a W/C = 0.5, this amounts to about 0.0025% chloride by weight of cement. There is also a possibility of the presence of chloride even in the so-called chloride-free admixtures. Such an admixture containing about 1000 ppm chloride would supply an equivalent of about 0.001% $CaCl_2 \cdot 2H_2O$ by weight of cement to concrete.[56]

As concrete contains a large amount of aggregate, even small amounts of chloride inclusion would add up to significant overall percentage. Normally aggregates contain negligible amounts of chloride. A chloride content of 0.1% in the aggregate will reflect as 1.2–2% flake calcium chloride by weight of cement.[56] Standard specifications should recognize these possibilities and accordingly specify the minimum limits of chlorides that can be tolerated in concrete.

12.0 NON-CHLORIDE ACCELERATORS

One of the limitations to the wider use of calcium chloride in reinforced concrete is that, if present in larger amounts, it promotes corrosion of the reinforcement unless suitable precautions are taken. There is, hence, a continuing attempt to find an alternative to calcium chloride, one equally effective and economical but without its limitations. A number of organic and inorganic compounds including aluminates, sulfates, formates, thiosulfates, nitrates, silicates, alkali hydroxides, carbonates, halides, nitrites, calcium salts of acetic acid, propionic acid, butyric acid, oxalic acid and lactic acid, urea, glyoxal, triethanolamine, and formaldehyde have been suggested. However, practical experience and research on these admixtures are limited, and most of them in combinations with other chemicals are described in the patent literature and are dealt in Ch. 17.

12.1 Triethanolamine (TEA)

Triethanolamine of formula $N(C_2H_4OH)_3$ is an oily water-soluble liquid having a fishy odor and is produced by reacting ammonia with ethylene oxide. Normally it is used in combination with other chemicals in admixture formulations. Its first use was reported in 1936 and the formulation contained TEA interground with calcium lignosulfonate to increase early strengths.[140a]

Ramachandran followed the hydration of C_3A (with and without gypsum) containing triethanolamine.[141] It was found that TEA accelerated the hydration of C_3A to the hexagonal aluminate hydrate and its conversion to the cubic aluminate hydrate. The formation of ettringite was also accelerated in the C_3A-gypsum-H_2O system.

In a study of the effect of 0, 0.1, 0.5 and 1.0% triethanolamine on the hydration of C_3S and C_2S, Ramachandran concluded that there was an initial retardation of hydration.[142] At 1 day acceleration of hydration took place and thus TEA can be construed as a delayed accelerator. Figure 30 shows the conduction calorimetric curves of C_3S containing up to 1.0% triethanolamine and hydrated for about 35 hrs. The induction period is prolonged in the presence of triethanolamine. Additions of triethanolamine promoted the formation of C-S-H with higher a C/S ratio, increased the formation of noncrystalline $Ca(OH)_2$ and enhanced the surface area of the hydrated silicate product. Similar observations were also made in the hydration of C_2S. The mechanism of the action of triethanolamine on the individual cement compounds has not been established. It is possible that the protective layer formed on the surface of the hydrating phase is affected.[143]

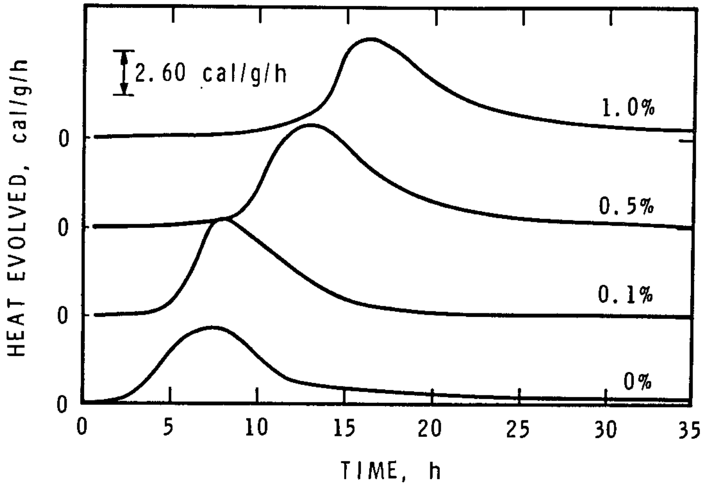


Figure 30. Conduction calorimetric curves of $3CaO•SiO_2$ with different amounts of added triethanolamine.

The retarding effect on tricalcium silicate hydration is almost completely eliminated in the presence of C_3A or NC_3A + gypsum. Adsorption of TEA on ettringite may remove the admixture to facilitate the hydration of tricalcium silicate. In Fig. 31, it is shown that the amount of TEA in solution in contact with ettringite decreases with time.[140b] Another possibility is that TEA chelates metallic ions in the highly alkaline medium. It can be speculated the Fe^{+3} in cement, precipitating during the hydration of cement, coats the silicates and aluminates and slows down the reaction.[140c]

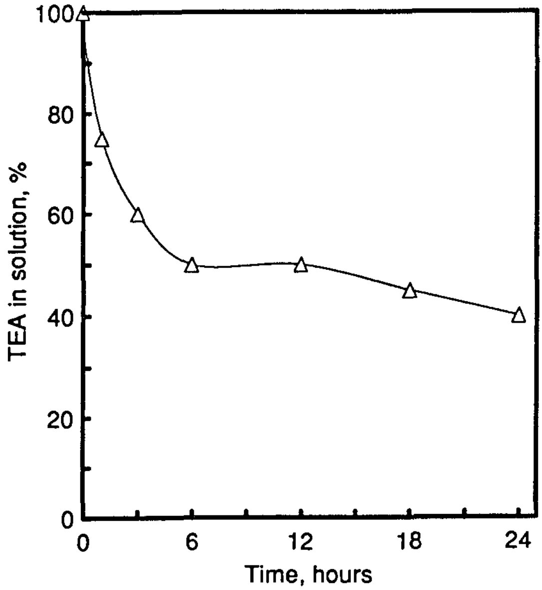


Figure 31. Adsorption of TEA by ettringite.

Amine salts are used in combination with other salts to improve setting and strength development. In a study of such a mixture containing an amine and chloride, it was found that the rate of hydration of C_2S was accelerated significantly (Fig. 32) especially after 7 days.[140d]

The mono- and diethanolamines also affect the hydration of tricalcium silicate similar to triethanolamine.

When added to cement, triethanolamine decreases its strength at all ages. Figure 33 shows the strength development in cement pastes containing 0, 0.1, 0.25, 0.35, 0.5 and 1% triethanolamine.[144] Strength decreases as the amount of triethanolamine is increased. Complex factors that may cause low strengths are: formation of C-S-H with higher C/S ratio, retardation of C_3S hydration, rapid initial setting followed by large heat development, and a more porous structure.

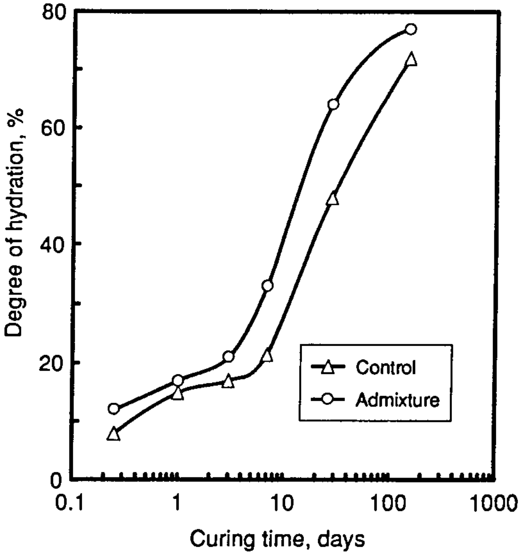


Figure 32. The hydration of dicalcium silicate in the presence of TEA-calcium chloride admixture.

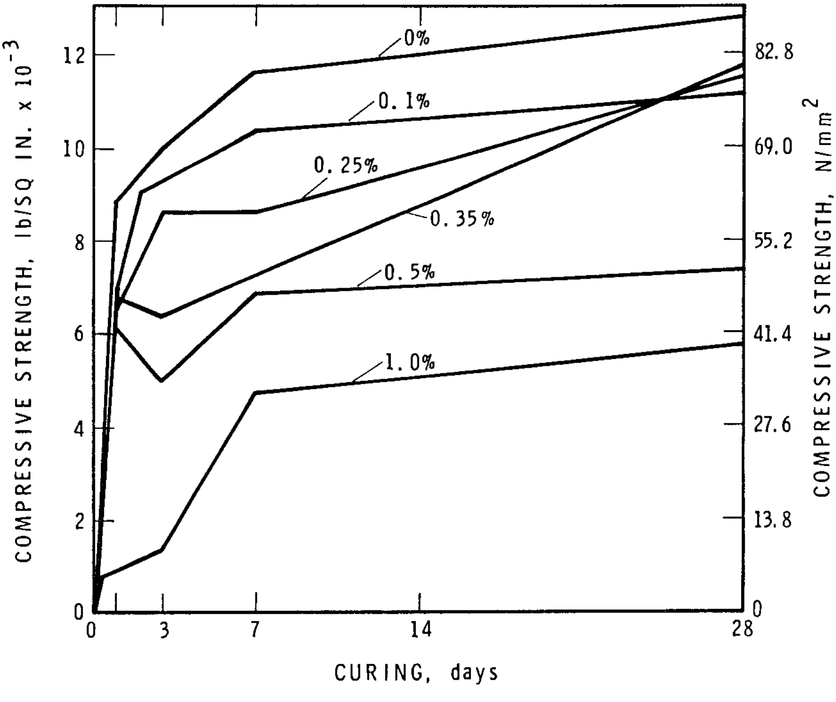


Figure 33. Compressive strengths of cement pastes containing triethanolamine.

The initial and final setting characteristics of portland cement treated with 0 - 0.5% triethanolamine are shown in Table 13.[144] With up to 0.05% triethanolamine the initial setting time is retarded slightly and there is an accompanying slight extension in the induction period of the hydration of C_3S. At 0.1 and 0.5% triethanolamine, however, rapid setting occurs. The rapid setting may be associated with the accelerated formation of ettringite.

Table 13. Initial and Final Setting Characteristics of Cement Mortars with Added TEA

No	Per Cent TEA	Initial Setting Time	Final Setting Time
1	0	4.3 hr	8.3 hr
2	0.01	4.7 hr	8.1 hr
3	0.025	4.9 hr	8.1 hr
4	0.05	4.8 hr	8.4 hr
5	0.1	~ 2 min	24 hr
6	0.5	~ 6 min	–

The drying shrinkage is increased in the presence of triethanolamine. For example, the drying shrinkage of a reference sample at 7, 14 and 28 days is 0.013, 0.020 and 0.031% and corresponding values with triethanolamine are 0.016, 0.029 and 0.040%.[145] Table 14 shows that the drying shrinkage of concrete containing TEA is higher than the reference concrete at all dosages and times of drying.[140e] Creep is increased by the addition of triethanolamine in concrete specimens loaded after 7 days of curing whereas no difference occurs for specimens loaded at 28 days.[101] Triethanolamine is also known to increase the creep caused by lignosulfonate addition to concrete.[146][147]

Amine salts are used in combination with other chemicals. Kuroda et al.[140f] tested the effect of a formulation containing calcium nitrite, calcium rhodonate, and TEA. Both initial and final setting times were accelerated by this admixture combination at 5 and 20°C. The compressive strength of concrete was increased at these temperatures (Fig. 34).

Table 14. Drying Shrinkage in Concrete Treated With TEA

TEA,%	Drying Shrinkage, Microstrain					
	Drying Period, Days					
	7	14	28	56	84	168
0	110	170	250	340	400	480
0.02	130	200	290	400	460	550
0.033	140	210	320	430	480	560
0.50	230	360	490	560	590	640

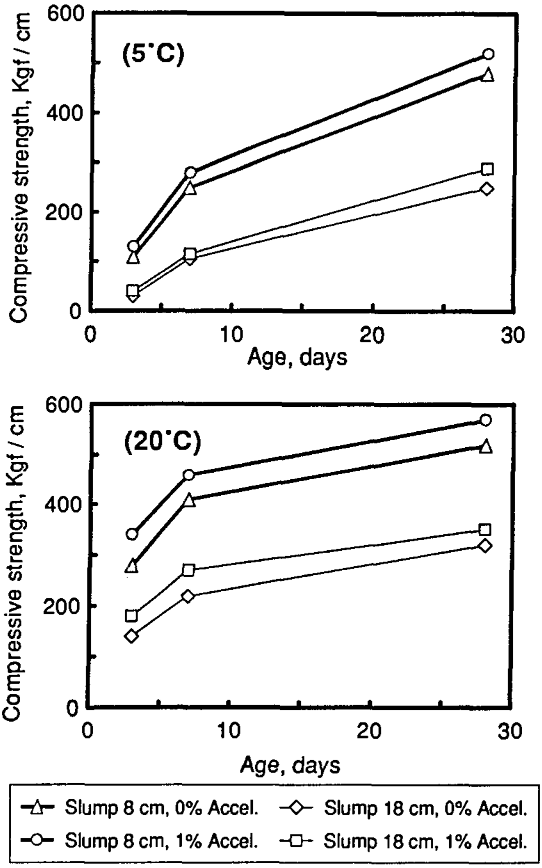


Figure 34. Development of compressive strength using Ca nitrite-rhodonate-TEA admixture. *(Reprinted with permission.)*

Although it has been shown that TEA decreases the strength of portland cement systems, it acts differently with blast furnace cements. In a mortar containing 30% portland cement and 70% slag, at 7 days with 0.5% TEA, the strength increased by about 40%. The total porosity of the paste was lower in the presence of TEA. The TEA promoted acceleration of hydration by increasing the rate of reaction of gypsum with slag in the presence of lime.[140g]

The estimation of TEA, both in the aqueous phase during hydration and in the hardened concrete, has been carried out. In the method suggested by Yilmaz and others,[140h] TEA in solution is converted to TEA-Fe^{+3} complex by adding NaOH and 10% Fe^{+3} solution. Polarographic techniques were used to determine TEA. It could also be determined by atomic absorption spectrophotometer. The method developed by Muszynski[140i] is as follows. The TEA is extracted with 75% methyl ethyl ketone, 14% ethanol, and 11% water using a Soxhlet extraction procedure. The extracted material is dried and redissolved and subjected to high pressure liquid chromatography, which yields ultraviolet detection traces unique for the TEA. The UV traces show major peaks at 148s, 168s and 222s.

12.2 Formates

Calcium formate of formula $Ca(HCOO)_2$, is a by-product in the manufacture of polyhydric alcohol, pentaerthritol. It is a powder and has a low solubility of about 15% in water at room temperature. It is a popular non-chloride chemical that is advocated in practice. Many non-chloride accelerating admixture formulations contain formates. Calcium formate is an accelerator for the hydration of C_3S; at equal concentration however, $CaCl_2$ is more effective in accelerating the hydration of C_3S (Fig. 35).[148]

The rate of hydration of tricalcium silicate in the presence of different amounts calcium formate (0.5–6.0%) has been reported by Singh and Abha.[140j] The degree of hydration obtained with different amounts of calcium formate at different times is tabulated in Table 15. Calcium formate accelerates the tricalcium silicate hydration but beyond 2% addition, especially with respect to the effect at 24 hrs, is not significant. It is speculated that in the presence of formate the protective layer on the silicate surface is ruptured resulting in an acceleratory effect.

The hydration of C_2S is also accelerated by calcium formate. The increase in compressive strength of formate-treated dicalcium silicate samples in relation to the reference sample is evidence of the acceleratory effect (Fig. 36).[140k]

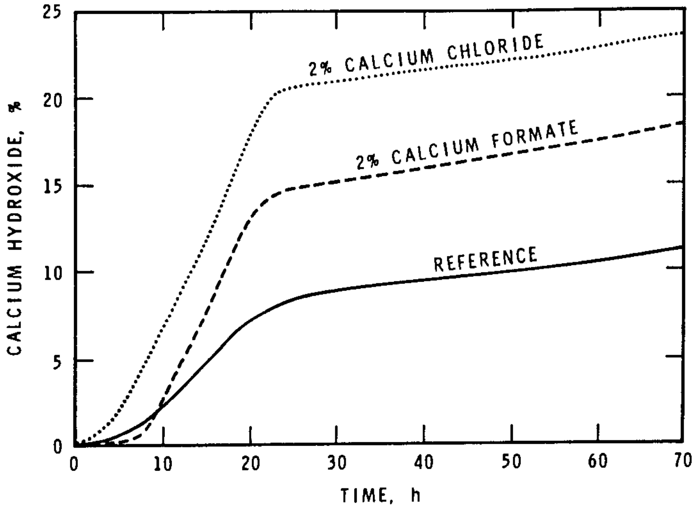


Figure 35. Influence of accelerators on the hydration of tricalcium silicate.

Table 15. Degree of Hydration of Tricalcium Silicate in the Presence of Calcium Formate. *(Reprinted from* Cement Concrete Res., *13:619-625, N.B. Singh and K. Abha, © 1983, with kind permission from Elsevier Science Ltd, The Boulevard, Langford Lane, Kidlington 0X51GB.)*

% Ca Formate	Time (Hrs)	% Degree of Hydration
0	2	11.03
	4	12.73
	8	39.36
	24	59.95
0.5	8	46.08
	24	59.95
1.0	8	52.85
	24	69.78
2.0	2	17.76
	4	45.24
	8	66.08
	24	80.33
4.0	2	17.80
	4	42.71
	24	82.88
6.0	2	18.39
	4	44.82
	24	82.71

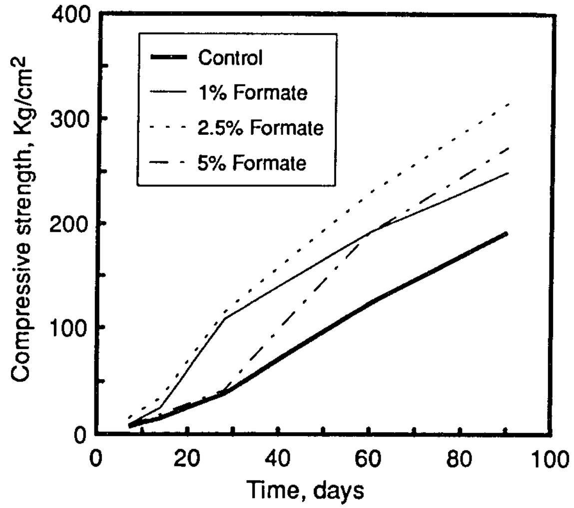


Figure 36. Influence of calcium formate on the strength development in C_2S mortars. *(Reprinted with permission.)*

In the hydration of portland cement, although initially larger amounts of heat are developed in the presence of Ca formate, at later ages the heat may be slightly lower or equal to that of the reference material. The curves for the amount of heat developed using equimolar concentrations of $CaCl_2$ and Ca formate are shown in Fig. 37. It is also evident that at 24 hrs the total heat produced in the presence of Ca formate is less than that produced in the reference cement. In the early hydration periods, Bensted found that cement produces more ettringite in the presence of Ca formate than in the presence of $CaCl_2$.[149] However, the amount of C-S-H was higher in the presence of $CaCl_2$.

Calcium formate accelerates the hydration of all types of cement. Fig. 38 gives the relative amounts of heat produced by adding 0.18 molar calcium chloride, calcium nitrite and calcium formate to Type V cement. Calcium chloride is the best accelerator followed by calcium formate.

Calcium formate accelerates the setting time of concrete but, comparatively, a higher dosage is required to impart the same level of acceleration as that by $CaCl_2$. Table 16 compares the initial and final setting times of cement containing 2% $CaCl_2$ and Ca formate.[149] The effectiveness of Ca formate is known to be valid for setting times at different temperatures. Fig. 39 shows the effect of Ca formate in reducing the setting times of concrete at temperatures 40, 70 and 100°F.[140c]

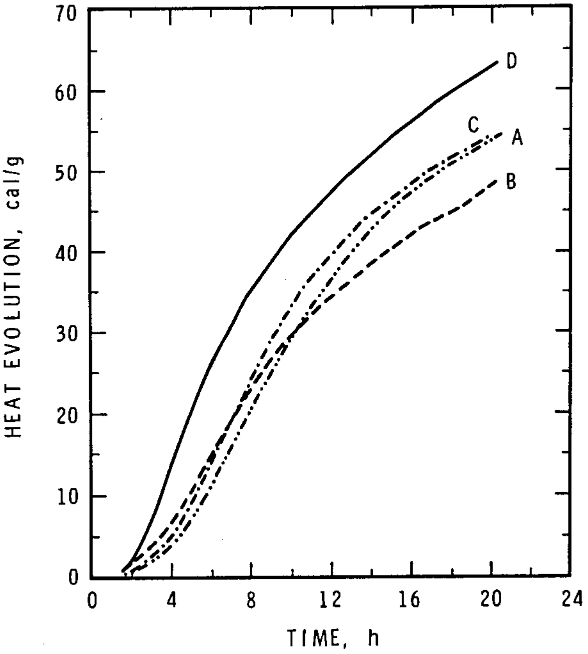


Figure 37. Heat evolution in cement treated with accelerators.

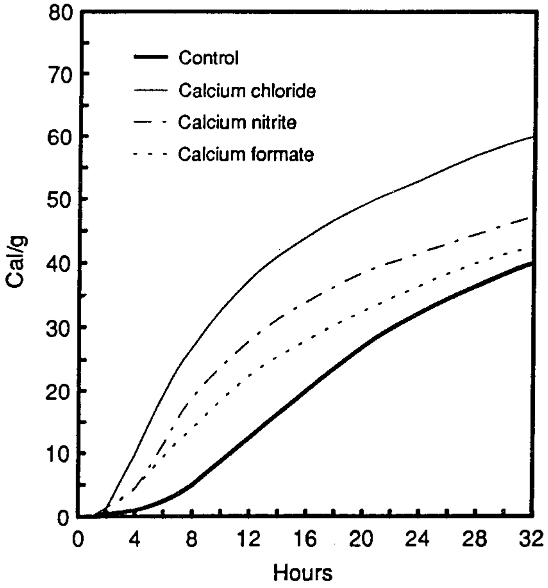


Figure 38. Effect of some accelerators on the hydration of Type V cement.

Table 16. Setting Characteristics of Portland Cement Containing Calcium Chloride or Calcium Formate (2%)

Admixture	Initial Setting (minutes)	Final Setting (minutes)
None	185	225
Calcium chloride	65	75
Calcium formate	80	90

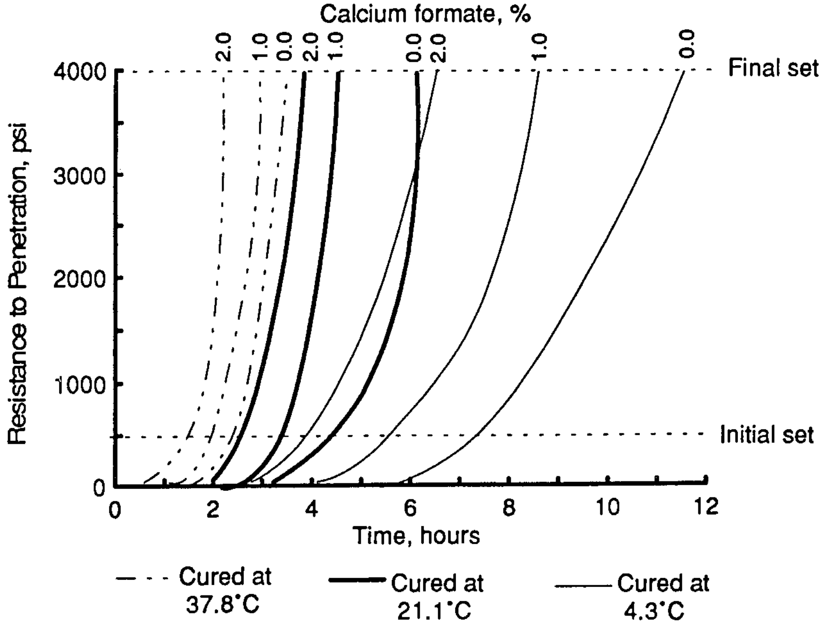


Figure 39. Effect of calcium formate on setting times at different temperatures. *(Reprinted by permission of Chapman & Hall.)*

The strength of a Ca formate containing cement, mortar or concrete may depend on the cement composition.[95] Geber[140] found that the early and later strengths in mortar depended on the C_3A/SO_3 ratio of the cement. The compressive strength increase over the control at C_3A/SO_3 ratios (at 1 day and 2% Ca formate) of 2.44, 3.32, 4.34, 5.00 and 7.22 were 3, -14, 25, 88 and 70% respectively. It is suggested that to derive the effectiveness of formate, C_3A/SO_3 ratios higher than 4 are preferred.

It is generally reported that Ca formate increases the early strength of concrete. In Fig. 40 the results on the effect of 2% and 4% Ca formate indicate that the strengths are increased in the first 24 hrs.[143] At lower dosages, the strength development may not be very significant. In combination with sodium nitrite, Ca formate accelerates the early strength development in cement to a significant extent. In comparison with the reference specimen without an admixture, the combination admixture increases strengths by 125, 70, 47 and 23% at 18 hrs, 1 day, 3 days and 7 days respectively.[1]

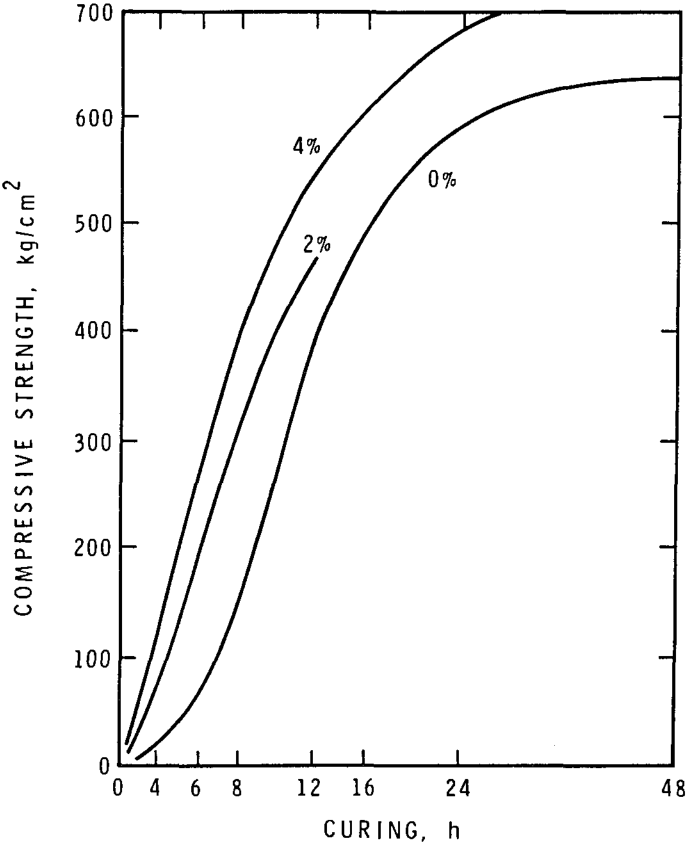


Figure 40. Influence of calcium formate on early strength of concrete.

An extensive study of the strength development in mortars containing Ca formate, Ca formate + Na formate and calcium chloride was carried out by Geber.[140l] Some of the data are tabulated in Table 17. All the samples were made at a w/c ratio of 0.47. Higher amounts of Ca formate are not particularly effective in increasing early strengths. Inclusion of Na formate is detrimental to strength development. Calcium chloride at 2% dosage promotes earlier strengths better than 2–6% Ca formate.

Table 17. Compressive Strengths of Mortars Containing Accelerators

Admixture	Dosage	Strength (lbs/sq in)					
		18h	1d	3d	7d	14d	28d
None	-	1680	2020	3360	4220	5010	5500
Ca Formate	2%	1260	1740	3960	5460	6480	7230
Ca Formate	4%	1520	2110	4520	6080	6900	7590
Ca Formate	6%	1320	1960	4440	6940	7440	8190
Ca Formate+Na Formate	2% + 2%	1120	1660	3540	4600	5310	5820
Ca Chloride	2%	2740	3170	5680	6540	7140	7580

Only limited data is available on the effect of Ca formate on shrinkage, creep, and long term durability of concrete. Shrinkage tends to be more with Ca formate admixture. In comparison with the blank which has a shrinkage of 0.013, 0.020 and 0.031% at 7, 14 and 28 days of curing, use of 3% Ca formate leads to values of 0.015, 0.025 and 0.036% respectively.[145]

Some attempts have been made to determine and estimate the amount of calcium formate in concrete. In the method of Muszynski,[140i] the solvent consisted of methyl ethyl ketone, alcohol and water and the mixture was extracted using a Soxhlet apparatus. The identification of formate was accomplished applying high pressure chromatography. In the UV trace, formate gave three peaks at 142s, 148s and 154s.

There are some considerations that have to be taken into account in using calcium formate. In addition to the differences between the cost of calcium chloride and calcium formate, there are other factors. Calcium formate has a limited solubility of about 14% in water. If added as a powder, it creates some dispensing problems. Although sodium formate is more soluble than calcium formate and acts as an accelerator, its addition would increase the sodium content and is not conducive to the durability due to alkali-aggregate expansivity. The effect of calcium formate depends on the composition of the cement. For cement with a C_3A/SO_3 ratio higher than 4, there is a good potential for accelerated strength.

12.3 Other Non-Chloride Accelerators

Many other non-chloride accelerators have been suggested which are based on organic and inorganic compounds. Valenti and Sabatelli studied the effect of alkali carbonates Na_2CO_3, K_2CO_3 and Li_2CO_3 on setting times and strengths of cements. At lower dosages, sodium and potassium carbonates retarded the setting times of cement[150] but at higher dosages (> 0.1%) they accelerated the setting. Lithium carbonate acted as an accelerator of setting at all concentrations studied. At concentrations especially higher than 0.1%, the admixture generally increased the compressive strength at 28 days. Addition of Na_2CO_3 is reported to change the intrinsic property of the hydrated cement. Total porosity and pore size distribution values of hydrated cement with or without Na_2CO_3 are not the same. In the presence of Na_2CO_3, smaller pores of radius 10–100 Å are decreased and pores of radius > 150 Å are increased slightly.[151] The reduction in the pores may be due to the precipitation of $CaCO_3$.

Calcium nitrate, calcium nitrite and calcium thiosulfate are also suggested as accelerators. Calcium nitrite accelerates the hydration of cement as evident from the increased amounts of heat developed in its presence (Fig. 38). Calcium nitrite also increases the strength and accelerates the setting times. Table 18 compares the setting times of concrete containing $CaCl_2$ and $Ca(NO_2)_2$.[128] Table 19 shows the strength development in concrete containing 2, 3, 4 and 5% calcium nitrite.[128] Improvement is less significant at dosages greater than 4%. Calcium thiosulfate increases the strength development of concrete at early ages. For example, at 1 day compared to a compressive strength of 15.8 km/cm^2 for a reference mortar, that containing 1, 2, 3, 5 and 6.5% CaS_2O_3 shows values of 17.1, 18.1, 18.8, 20.1 and 21.2 kg/cm^2 respectively.[103] Sodium thiosulfate also accelerates the setting time but the compressive strengths are slightly reduced with respect to the reference concrete at dosages of 0.5 and 1.0%.[152] Depending on the dosage of $NaNO_2$, Rosskopf et al. found that acceleration of setting varied between 0.5 an 2.3 hrs. At dosages of 0.1–

1.0% $NaNO_2$ the compressive strength of concrete at 7 days was equal or slightly lower than that of the reference concrete.[152] They also found that formaldehyde and paraformaldehyde in small amounts (0.01–0.25%) reduced the setting time from 9.5 to 6.3 hrs.

Table 18. Setting Times of Concrete Containing Calcium Chloride and Calcium Nitrite

Cement Brand	Admixture	Setting Time (hr: min)	
		Initial	Final
A		8:45	12:21
A	Calcium Chloride	4:20	7:30
A	Calcium Nitrite	6:00	10:20
B			8:38
B	Calcium Chloride	3:16	5:00
B	Calcium Nitrite	5:24	9:04

Table 19. Effect of Calcium Nitrite on Strength Development

Admixture %	Compressive Strength (lbs/sq in)		
	1 Day	7 Days	28 Days
	1299	3401	5032
2	1615	4538	5732
3	1959	4964	5907
4	2294	5337	6383
5	2367	5324	6493

The relative acceleratory effects of calcium chloride, calcium nitrate and sodium thiocyanate on cement have been studied.[153a] Figure 41 represents the heat developed when 1% of these admixtures is used. The total heat is higher in the presence of all accelerators. Calcium chloride addition results in the maximum amount of heat. Sodium thiocyanate accelerates better than calcium nitrate. Calcium nitrate works well at early stages but sodium thiocyanate is more effective at later ages.

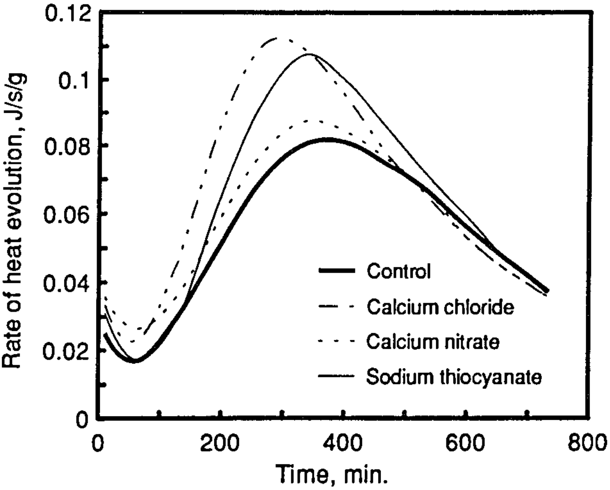


Figure 41. The effect of some accelerators on heat development. *(Reprinted with permission.)*

Sodium molybdate is known to be a corrosive inhibitor. The rate of hydration of portland cement is accelerated by molybdate at 5 and 20°C. However, strengths at later ages are decreased. This chemical is more expensive than others.[154] Molybdenum trioxide also acts as an accelerator at dosages of 5–10%.[155]

Generally the alpha hydroxy carboxylic acids are regarded as retarders, but lactic acid behaves differently.[156] In dosages of 0.1 to 0.4% it reduces both the initial and final setting times of cement. The compressive strength at 28 days is higher than the reference by about 10–15%.

A new accelerator formulation consisting of inorganic salts and organic compounds (one of these being a sulfonate dispersant) is claimed to be effective at low temperatures of -7°C as well at a higher temperature of 35°C. It accelerates setting, increases early and ultimate strengths, decreases shrinkage and does not initiate corrosion.[157] In Table 20, setting times and strengths of the reference concrete are compared with that containing the above admixture. The admixture develops better strengths than the reference and can be used in cold weather concreting.

Table 20. Setting Time and Strength Development in a Newly Formulated Admixture

Admixture	Setting Times (Hrs)		Strength (MPa)			
	Initial	Final	1 d	3 d	28 d	1 yr
Air Entrained (Reference)	10.67	14.58	1.6	11.7	26.2	36.9
Air Entrained (Accelerator)	6.15	11.50	2.8	9.0	30.8	43.1
Non-Air Entrained + Accelerator	5.50	11.50	3.6	8.7	34.2	46.3

In cements, incorporation of calcium carbonate is permitted in some countries. In Canada the maximum limit is set at 5%. Calcium carbonate is not an inert filler. It is known to react with calcium aluminate. In a study of the hydration of tricalcium silicate in the presence of finely divided calcium carbonate, Ramachandran observed that the carbonate acted as an accelerator. In Fig. 42, the conduction calorimetric curves clearly show the accelerating influence of calcium carbonate. There was evidence of formation of a complex of the carbonate with the hydrated silicate[158] Ushiyama et al.[159] examined the effect of carbonates of Na, K, Li, Cs and bicarbonates of Na, K and Li on the hydration of alite. Although small amounts retarded the hydration, larger amounts acted as accelerators.

Alkalis such as NaOH, and Na salts of carbonate, aluminate and silicate are known to accelerate the hydration of cement and cause early stiffening. In the hydration of tricalcium silicate with NaOH, there was an acceleratory effect even up to 28 days. After seven days however, the strength of the reference was higher than that containing NaOH[160] (Fig. 43). There was no difference between the total porosities. Although weaker, the NaOH-treated sample had a larger amount of finer pores. There was marked difference in morphologies. Whereas the reference contained interlocking fibers and stacked type of massive calcium hydroxide, the alkali-treated sample developed a reticular and thin platy structure. Evidence was also obtained for the incorporation of Na in the hydrated product.

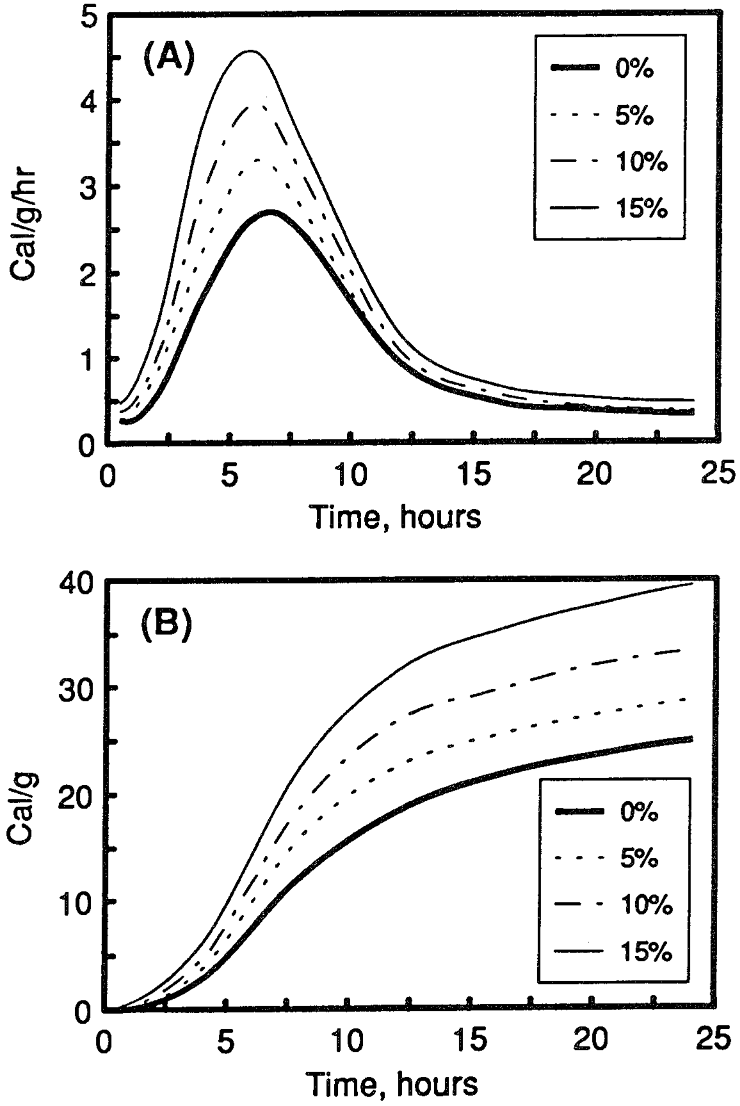


Figure 42. Conduction calorimetric curves of tricalcium silicate in the presence of calcium carbonate.

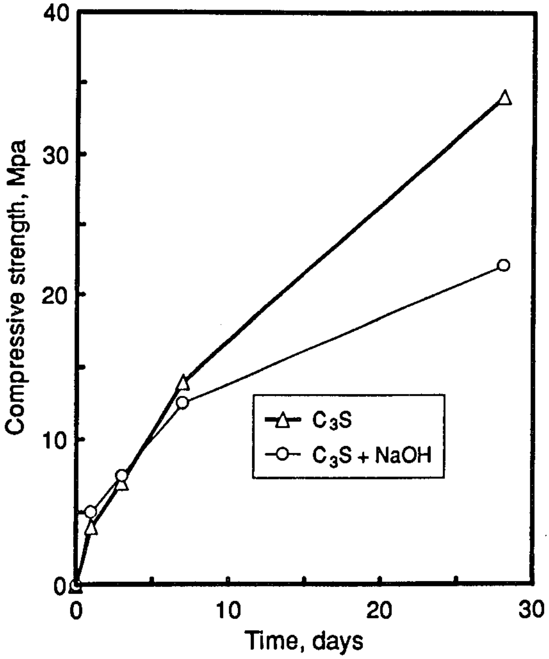


Figure 43. Strength development in tricalcium paste containing sodium hydroxide.

Volatilized silica, obtained as a by-product in the metallic silicon or ferrosilicon industry, is known as silica fume. It has been advocated for incorporation into cement to obtain high strength. It acts as a pozzolan and is also known to accelerate the hydration of tricalcium silicate. Therefore it can be treated as an accelerator. The details of its action are described in Ch. 10.

There has been continued interest in developing an organic-based accelerator. Ramachandran and coworkers studied the effect of o, m and p-nitrobenzoic acids on the hydration of tricalcium silicate.[161] The m and p nitrobenzoic acids acted as accelerators (Fig. 44). The acceleratory effect was attributed to the complex formation between the organic compound and the C-S-H phase on the surface of the tricalcium silicate phase.

Some work has been carried out using a finely ground portland cement hydrate at a dosage of 2% as a *seeding agent.*[130] It is claimed that 2% of seeding is equivalent to 2% $CaCl_2$ in its accelerating effect.

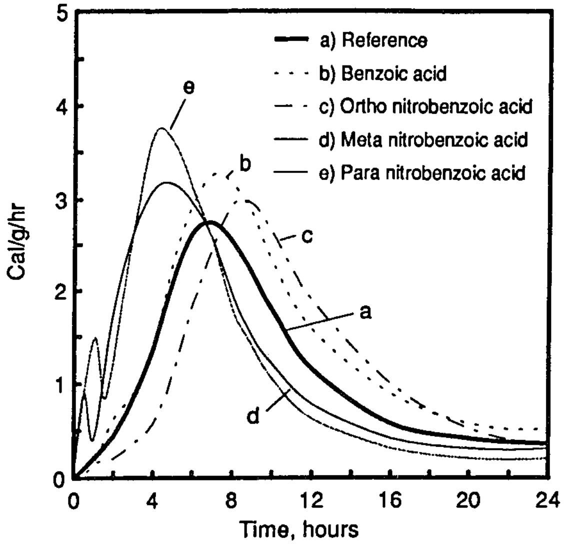


Figure 44. Conduction calorimetric curves of tricalcium silicate hydrated in the presence of nitrobenzoic acids.

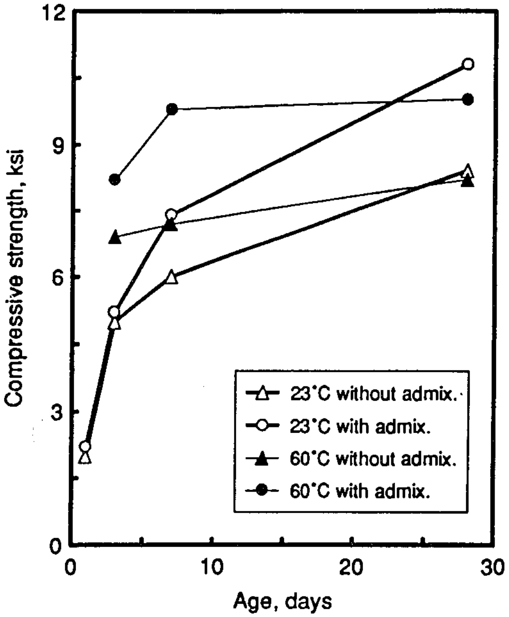


Figure 45. Effect of an accelerator on strengths at two temperatures. *(Reprinted with permission.)*

The effect of a chloride-free admixture, a water soluble organic compound, on mortar and concrete has been described by Popovics.[162] The accelerator reduces the setting times by 150% and is compatible with epoxies and superplasticizers. Higher strengths are obtained using Type I, III and V cements. The admixture is even more effective at higher than normal temperatures of curing. In Fig. 45, the effect of temperature of curing on strength development in concrete using Type II cement is plotted. At both 23 and 60°C, the strength of concrete containing the accelerator is higher than that of the reference. This increase is more pronounced at 60°C.

It appears from the published reports that in spite of intensive efforts, no single chemical has been found to perform as well as calcium chloride in terms of accelerating the hydration of cement, when used at equal dosages.

12.4 Commercial Accelerators

Some of the accelerators that are manufactured/supplied in North America are described below. The Dow Chemical Co. supplies calcium chloride as an accelerator. It meets the ASTM D 98 specification. Dowflake (77–80% calcium chloride), Peladow (90% calcium chloride) and Liquidow (30–42% calcium chloride solution) are products that are available. The complete details about the application of calcium chloride are to be found in Secs. 4 to 11.

The Master Builders manufacture Canchem HE-202 and Pozzutech 20. The Conchem admixture is supplied in the liquid form which accelerates the set time and meets the ASTM C 494 requirements for Type C accelerator. It improves pumped concrete, shotcrete (wet mix) and conventionally placed concrete. It does not entrain air and does not contain intentionally added chloride. It is normally used at a dosage of 8–64 fl ozs per 100 lbs (0.5–4 liters per 100 kg) of cement. At a larger dosage, the early and ultimate strengths of concrete are increased. The Pozzutech 20 is a low temperature accelerating admixture that can be used all year round. It is a non-chloride liquid admixture. It is effective in reducing the freeezable water and provides early protection against freezing at subzero temperatures. It meets the performance requirements of ASTM C-494 specification for Type C accelerating admixture and Type E water-reducing and accelerating admixtures. For subzero temperature applications, 6–90 fl ozs per 100 lb (3910–5860 mL per 100 kg) of cement are recommended. It is also necessary that concrete containing Pozzutech 20 admixture should be sealed to prevent ingress of additional water to hardened concrete. A surface sealer should be applied as soon as concrete reaches initial set or after finishing is completed. Concrete should also be protected against wind to avoid wind chill effects on the surface. Pozzutech is supplied in 55 US gallon (208 L) drums. It should be stored at 5°F (-15°C) or above. Pressurized air should not be used for agitation.

W. R. Grace and Co. manufactures two products, namely, Daraset (noncorrosive, non-chloride) or Daraccel, a water-reducing set-accelerating admixture. Early strength or acceleration is accomplished with Daraset. It meets the ASTM C 494 Type C specification. One gallon of Daraset weighs about 11 lbs. Typical addition levels range from 10–80 fl ozs per 100 lbs of cement, but as high as 150 fl ozs per 100 lbs of cement can be used. It is compatible with many air entraining agents and water reducers. It is supplied in 55-gallon drums. Daraccel is a liquid admixture containing calcium chloride and other admixtures to increase settting times and strength development. It is specifically designed for cold weather concreting. It is a water-reducing accelerator complying with ASTM C 494 requirements for Type E admixture for use with Type I and II cements. It is used at an addition level of 8–40 fl ozs per 100 lbs of cement. It is compatible with commercially available air-entraining agents. Mixing it with air entraining agents or other admixtures prior to use is not recommended. It does not entrain air and is recommended for use when ambient temperature is 50°F or lower.

Axim Concrete Technologies manufactures a product called Catexol 1000 R.H.E. (non-chloride accelerating admixture) and Catexol 900 H.E. (accelerating and water-reducing admixture). Catexol 1000 is recommended where acceleration of setting, reduced bleeding and segregation, greater impermeability, durability and strengths are desired. It is specifically effective in concrete containing pozzolans. It is normally used in dosage rates of 1000–2000 mL per 100 kg of cement. Catexol 900 is designed to accelerate setting of concrete, especially that of fly ash, and provides high early and ultimate strengths. By the use of this admixture, increased workability, finishability, pumping, strength and durability, and reduced segregation and permeability are achieved. It is not recommended for prestressed concrete or other applications where the use of chlorides would be undesirable. The recommended dosage is 1000–2000 mL/100 kg cement. It is compatible with other admixtures, but they should be added separately. It meets requirements of the ASTM C 494 Type C and E admixtures and CSA A266.2 and AC types of admixtures.

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6

Water Reducers/ Retarders

Mario M. Collepardi

1.0 GENERAL CONSIDERATIONS

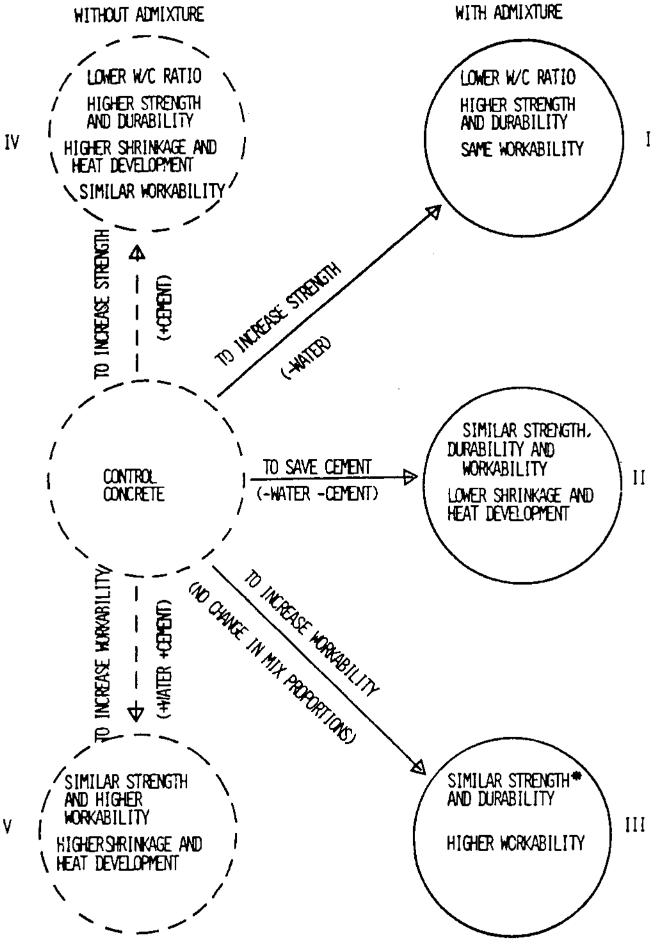
Most water reducers as well as most retarders are organic, water soluble products and many formulations of these admixtures are based on the same raw materials, such as lignosulfonates, hydroxycarboxylic acids, carbohydrates, etc. For this reason, these two admixtures are examined together in this chapter.

A water reducer can be defined as an admixture that reduces the amount of mixing water for concrete for a given workability. It improves the properties of hardened concrete and, in particular, increases strength and durability. Usually, according to standards (Sec. 6) the reduction of mixing water by the use of these admixtures must be at least 5%. However, commercial water reducers can reduce mixing water up to 10 to 15%.

There is another mode of use of these admixtures, involving reduction of both water and cement, so that workability and strength of concrete containing admixtures are similar to those of the control concrete. Admixtures could thus act as cement reducers. Besides allowing cement saving, these admixtures are capable of reducing the heat of hydration, a property that is useful for concreting in hot climates or massive structures.

If water reducers are added without modifying mix proportions, concrete workability improves; in this case they act as plasticizers. This is particularly useful for placing concrete in areas of high steel content that require a more workable concrete.

The three types of uses of water reducers are schematically shown in Fig. 1 and are based on a similar comparison by Rixom.[1]



(*) REALLY A LITTLE LOWER STRENGTH AT EARLIER AGES AND A LITTLE HIGHER STRENGTH AT LONGER AGES SHOULD BE EXPECTED, EXCEPT WHEN AN ACCELERATING WATER-REDUCER IS USED: IN THIS CASE STRENGTH IS HIGHER AT EARLIER AND LONGER AGES.

Figure 1. Schematic diagram of the effect of water reducers on fresh and hardened concrete.

The decision to use water reducers depends on the comparative savings that result from using less cement to attain the same performance (II in Fig. 1). Such an approach should also be applied when strength increase (I and IV in Fig. 1) or improved workability (III and V in Fig. 1) is desired.

An admixture that lengthens setting time and workability time is known as *set retarder* or *retarding admixture.* This is particularly useful for concreting under high-temperature conditions. Ice, which can be added into the mixer to decrease the temperature, is more expensive than a retarding admixture and may not be readily available at the job site.

1.1 Category

In fully compacted mixes, the properties of hardened concrete, especially strength and durability, improve as the water-cement ratio (w/c) decreases and the degree of hydration (α) of cement increases.

Generally, for a given performance of fresh or hardened concrete, the cost of admixture is lower than that of the cost of cement variation, provided that the content of cement of the control concrete is higher than about 200 kg/m^3 (330 lb/yd^3). Conversely, for leaner concretes, use of higher cement content is generally more economical than the use of water reducing admixture.[2]

The influence of a water reducer on strength development depends on the reduction of the w/c ratio and its effect on α. A *normal* water reducer should be defined as a water reducing agent that does not substantially modify α. If a water reducer increases or lowers α at early ages, it should be termed as an *accelerating* or *retarding* water reducer respectively.

Figure 2 compares the compressive strength, as a function of time, of concretes containing the three above-mentioned types of water reducers with that of a less workable control concrete. The same w/c ratio is used in all the concretes (N, A, R and control mixes in Table 1), so the differences in strength are mainly due to the influence of the admixtures on α. In general, these differences are not significant, except at early ages when a retarding and water-reducing admixture is used. In Table 1, N = normal, A = accelerating, and R = retarding water reducers.

Conversely, when water reducers are used at the same workability as that of the reference concrete (N′, A′, R′ and control mix in Table 1) to decrease the w/c ratio, considerable variations in strength are observed (Fig. 3). The accelerating water reducers increase strength particularly during the first week, while the retarding types show their influence mainly during the first three days. These effects are exploited in the production of concrete in cold and hot weather conditions respectively.

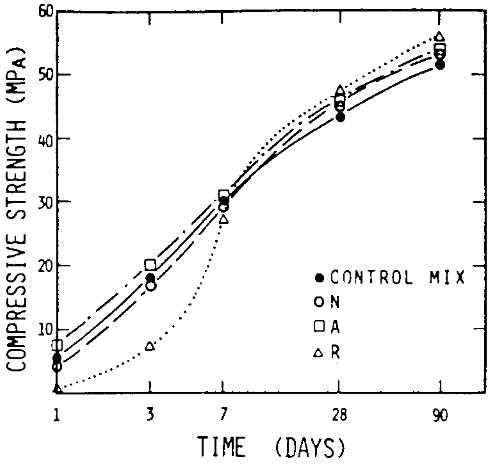


Figure 2. Effect of different types of water reducers on the compressive strength at the same water-cement ratio as the control concrete (N = normal water reducer, A = accelerating water reducer, and R = retarding water reducer).

Table 1. Typical Characteristics of Concretes at 20°C Without and With Commercial Water Reducers

Mix*	Control	N	A	R	N′	A′	R′
w/c	0.55	0.55	0.55	0.55	0.49	0.51	0.49
Water reducer							
ASTM Type	—	A	E	D	A	E	D
% by wt of cement	—	0.2	0.8	0.3	0.2	0.8	0.3
Setting time** (hr:min)							
Initial	3:30	4:20	3:55	6:35	3:50	3:05	5:15
Final	7:05	8:55	7:10	10:20	7:55	6:10	8:55

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* Type 1 cement content 300 kg/m^3 (505 lb/yd^3). Compressive strengths are shown in Figs. 2 and 3.

** Mortar has been wet-screened from concrete mix or No. 4 sieve.

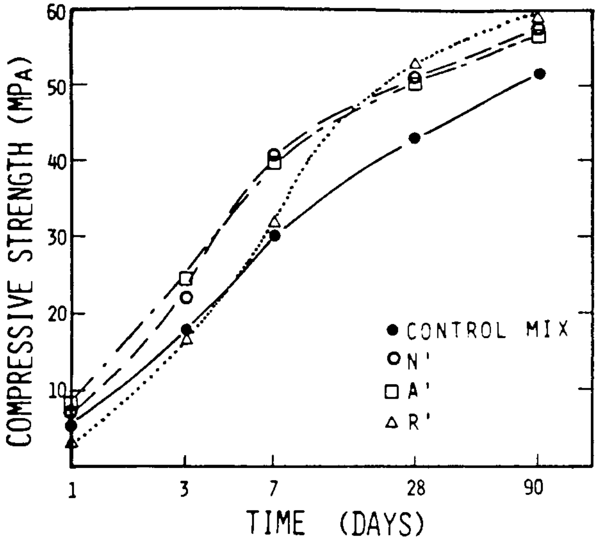


Figure 3. Effect of different types of water reducers on the compressive strength at the same workability as the control concrete (N′ = normal water reducer, A′ = accelerating water reducer, and R′ = retarding water reducer).

The setting times depend on the type of water reducer used (Table 1). In general, all water reducers tend to extend setting times with respect to the control concrete. This is due to the lower hydration rate of cement during the first hours in the presence of a water reducer. Accelerating admixtures slightly accelerate or do not modify setting times, therefore the word *accelerating* should be employed to indicate early strength development, in place of *setting times. Retarding* water reducers, on the other hand, extend setting times more significantly than other types.

Retarding admixtures are often treated under the same category as that of "water-reducing and retarding admixtures." This is because the main components used for retarders are also present in water-reducing and retarding admixtures (Sec. 1.2). As a result, many retarders reduce mixing water and many water reducers retard the setting of concrete. Also, standard requirements for the initial setting times of these admixtures are the same, whereas there are some differences in water requirement and compressive strength (Sec. 6). Table 2 shows the typical effect of a commercial retarder on setting times and strength of a concrete mix.

Table 2. Typical Characteristics of Concrete without and with a Commercial Retarder. (Cement content = 300 kg/m^3; retarder dosage = 0.3% by weight of cement; slump = 65 ± 5 mm.)

Mix	Control Mix			Mix With Retarder*		
Temperature, °C (°F):	5° (41°)	20° (68°)	35° (95°)	5° (41°)	20° (68°)	35° (95°)
w/c ratio	0.58	0.60	0.61	0.56	0.57	0.58
Setting Time** (hr:min):						
Initial	11:05	5:05	3:30	13:30 (+22%)	6:10 (+21%)	4:30 (+24%)
Final	16:55	7:50	6:20	19:05 (+13%)	8:55 (+14%)	7:15 (+15%)
Compressive Strength (N/mm^2):						
at 3 days	8.2	15.5	18.3	7.4	16.1	19,1
at 28 days	35.0	35.3	34.1	40.7	43.3	41.2

* Figures in brackets indicate the percentage increasein the setting time caused by the admixture in comparison with the reference mix.

** Mortar has been wet-screened from concrete mix using No. 4 sieve.

1.2 Chemical Composition and Manufacture of Water Reducers/ Retarders

There are a number of formulations described in patents concerning water reducers or retarders. Usually the main components of these formulations are water soluble organic compounds. The earliest known published reference to the use of water reducers, in the thirties, refers to certain polymers of condensed naphthalene sulfonic acids for use in small amounts of about 0.1% by weight of cement.[3] These polymers were never used as plasticizers or water reducers on a large scale until the seventies when they were rediscovered (with some changes in the degree of polymerization and in the dosage), for use as superplasticizers or high-range water reducers (Ch. 7).

The main compounds used in the manufacture of water reducers can be divided into four groups. The first one contains Ca, Na or NH_4 salts of lignosulfonic acids. The second group contains the hydroxycarboxylic acids generally as Na, NH_4 or triethanolamine salts. The carbohydrates belong to the third group. The last group comprises other compounds. All the water reducing admixtures are generally offered by the suppliers as an aqueous solution with a specific gravity in the range of 1.10 to 1.30 g/ml. Table 3 shows a list of some commercial water reducers and retarders which are available in America, Europe, Japan and Middle-East.

Table 3. Examples of Commercial Water Reducers and Retarders

Brand Name	Supplier	Active Ingredients	Effect	Dosage (ml/kg)
Catexol 900 HE	Axim	Synthetic products and chlorides	Acceleration and water reduction	10–20
Catexol 1000 N	Axim	Synthetic products	Water reduction	10–20
Catexol 1000 RX	Axim	Synthetic products	Set-retardation and water reduction	1.6–3.2
Conchem 25 R	Master Builders		Set-retardation and water reduction	2.5–4
Daraccel	W. R. Grace	Lignosulfonate and calcium chloride	Acceleration and water reduction	5.20–26
Mapeplast N10	Mapei	Lignosulfonate	Set-retardation and water reduction	2–5
Mapeplast N30	Mapei	Naphthalene polymer and lignosulfonate	Water reduction	3–6
Paric T	Fujisawa	Hydroxycarboxylic acid	Set-retardation and water reduction	2–3
Paric 1	Fujisawa	Salt of hydrocarboxylic acid	Water reduction	2
Plastiment	Sika Chemical Corp	Salt of hydrocarboxylic acid and retardation	Water reduction	1.3–2.6
Plastocrete	Sika Chemical Corp	Salt of hydrocarboxylic acid	Water reduction	1.3–2.6
Pozzolith 100 N	Master Builders	Hydroxylated polymers	Water reduction	1.95–3.25
Pozzolith 100 XR	Master Builders	Hydroxylated polymers	Set-retardation and water reduction	1.3–2.6
WRDA-HC	W. R. Grace	Salt of hydrocarboxylic acid	Water reduction	1.95
WRDA-79	W. R. Grace	Lignosulfonate	Set-retardation and water reduction	3.25–5.20

Lignosulfonates. Lignosulfonates are still the most widely used raw material in the production of water reducing admixtures,[4]-[6] though their use as water reducers was discovered in the thirties.

The lignosulfonate molecule may have an average molecular weight of approximately 20,000 to 30,000 with the molecular weight distribution varying from a few hundreds to 100,000.[1][7] The lignosulfonate molecule is very complex and may be visualized as a polymer of a substituted phenyl propane unit with hydroxyl (OH), methoxyl (OCH_3), phenyl ring (C_6H_5) and sulfonic acid (SO_3H) groups (Fig. 4).

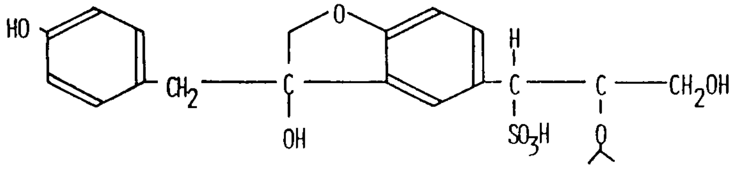


Figure 4. Structural unit of a lignosulfonate molecule.

Lignosulfonate is obtained as a waste liquor during the process for the production of papermaking pulp from wood whose composition includes about 20–30% of lignin. It contains a complex mixture of sulfonation products of lignin, decomposition products of cellulose and lignin, various carbohydrates, and free sulfurous acid and sulfates.

The composition of lignosulfonates can vary widely depending on the successive processes of neutralization, precipitation, and fermentation, which the by-product[8] undergoes, as well as on the type and age of wood used as a raw material.[1]

Table 4 shows typical analysis of lignosulfonate admixtures in a powder form.[9]-[11]

Commercial lignosulfonates used in water reducing admixture formulations contain up to 30% carbohydrates (reducing sugars). A typical analysis of untreated sulfite lye[12] may show the following percentages of sugars based on total sugar content: mannose—18%; glucose—15%; xylose—15%; galactose—10%; arabinose—6%; fructose—under 2%; unaccounted sugars—4%. In two commercial lignosulfonate-based water reducing admixtures the following percentages of wood sugars have been found: pentoses (including xylose and arabinose) 70–74% and hexoses (including mannose, rhamnose, and galactose) 26–30%. Both the type and concentration of the sugars contained in the untreated sulfite lye or commercial admixtures depend on the source and degree of fermentation. In general, the microorganisms used in the fermentation tend to consume more hexoses than pentoses, which therefore will be present in a high percentage in refined lignosulfonates. Desugarized lignosulfonates, used as water reducers, can be obtained by suitable processing techniques. Oxidation of sugars to sugar acids, during the pulp digestion process when lignosulfonates are formed, leads to the formation of sugar acids, such as xylonic, galactonic or gluconic acids in commercial lignosulfonates.[13]

Table 4. Typical Analysis (%) of Commercial Calcium and Sodium Lignosulfonate in the Form of Powder[9]-[14]

	Ca-lignosulfonates			Na-lignosulfonates	
Reference	(9)	(10)	(11)	-	-
Moisture	5	10.2	3.6	6-0	7.2
Ash	17	16.8	18.2	18.1	16.3
CaO (in ash)	9	21.0	8.3	0.1	0.2
Sulfonate	3.2	-	3.4	-	-
Reducing bodies	4.5	12.5	4.0	4.1	3.7
Total sulfur (as SO_3)	11.8	9.0	12.3	11.2	7.5
Total nitrogen (as protein)	-	0.2	-	-	-
Methoxyl	7.2	-	-	-	-
pH of a 50% solution	6.4	-	6.2	6.8	6- 9

In the lignosulfonate salts used as admixtures, a metal or ammonium cation replaces hydrogen in the sulfonic group. Calcium and sodium salts are the most widely used cations in water reducer formulations. Electrical conductivity results have shown that lignosulfonates are ionized to an extent of 20 to 30% only and that the degree of ionization in solution is higher for the sodium salt than for the calcium lignosulfonate.[7] This could explain the observation that a higher concentration of calcium salt is required to obtain the same reduction in mixing water compared to sodium salt.[1] Calcium lignosulfonate is, however, cheaper than sodium lignosulfonate.

Lignosulfonate by itself is generally used as a retarder or a water-reducing and retarding admixture. Generally, in the formulation of "normal" water reducers or water-reducing and accelerating admixtures, the retarding action of the lignosulfonate on concrete setting and early strength is counteracted by the addition of an accelerating admixture such as triethanolamine that shortens the setting time, and calcium chloride, formate or other salts that accelerate setting and early hardening.

In general, lignosulfonate based water reducing admixtures entrain a certain volume of air in concrete. This could be considered as a desirable effect when air entrainment is required to increase frost resistance, or to improve cohesion in lean mixes or in concrete containing coarse sand. It is, however, more desirable to mix the water reducer with an air-entraining agent, adding them separately until the needed volume of air is obtained. This would depend on the maximum size of the coarse aggregate, mixing conditions and the type of cement and sand.

In order to reduce air entrainment in concrete, a certain mount of defoaming agent is added in the production of commercial lignosulfonate-based water reducing admixtures. Tributylphosphate, dibutyl phthalate, borate esters, and silicone derivatives in the amount of about 1% of lignosulfonate can be used for this purpose.[14]

Because of the relatively low cost of lignosulfonates, there has been continued interest in utilizing these products even in the field of superplasticizers. Modified lignosulfonates, obtained by special treatments such as ultrafiltration,[5] desugarization,[15] or sulfonation,[16] can compete with melamine sulfonate and naphthalene sulfonate admixtures (Ch. 7).

Hydroxycarboxylic Acids. Salts of organic hydroxycarboxylic acids were developed as water-reducing agents or retarders in the fifties. Though their use has increased significantly, they are not used to the same extent as lignosulfonates.

As the name implies, the hydroxycarboxylic acids have several hydroxyl (OH) groups and either one or two terminal carboxylic acids (COOH) groups attached to a relatively short carbon chain.

Figure 5 illustrates some typical hydroxycarboxylic acids which can be used as retarding or water reducing admixtures. Gluconic acid[8][17] is perhaps the most widely used admixture. Citric, tartaric, mucic, malic,[18] salicylic,[19] heptonic,[20] saccharic,[21] and tannic[22] acids can also be used for the same purpose.

They are generally used as an aqueous solution (30%) of sodium salts and seldom as salts of ammonia or triethanolamine. Usually they are synthesized chemically and have a very high degree of purity as they are used as raw materials by pharmaceutical and food industries. Nevertheless some aliphatic hydroxycarboxylic acids can also be produced from the fermentation or oxidation of carbohydrates and for this reason they are also called sugar acids.

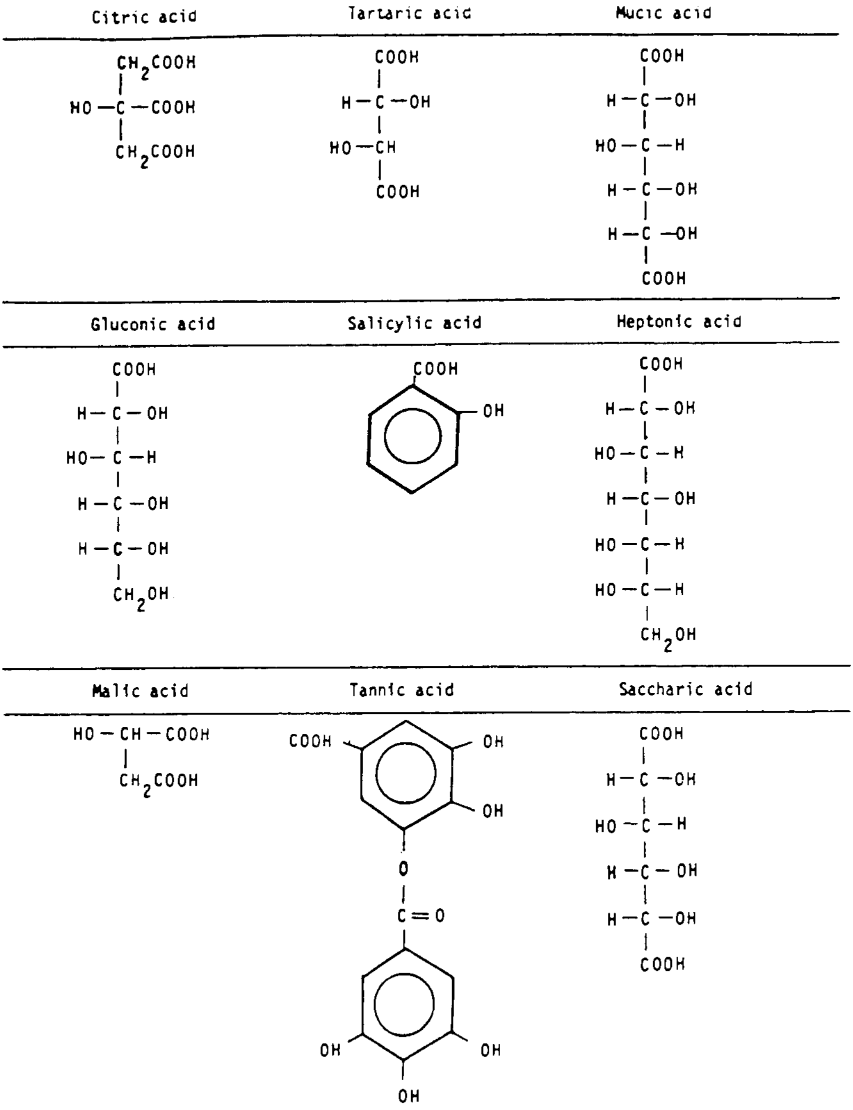


Figure 5. Typical hydroxycarboxylic acids used in water-reducers and retarders.

Hydroxycarboxylic acids can be used alone as retarders or water-reducing and retarding admixtures. For use as normal and accelerating water reducers they must be mixed with an accelerator as in lignosulfonate based water reducing admixtures (see *Lignosulfonates* in this section).

Carbohydrates. They include natural compounds, such as glucose and sucrose, or hydroxylated polymers obtained by partial hydrolysis of polysaccharides, such as those contained in corn starch, to form polymers with a low molecular weight, and containing from 3 to 25 glycoside units[23] (Fig. 6).

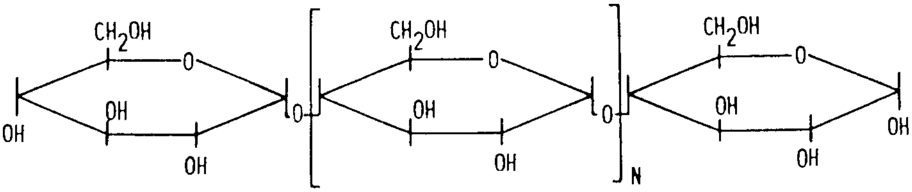


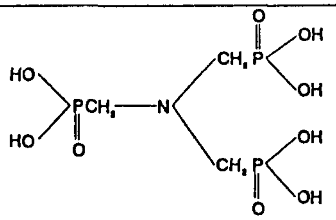
Figure 6. Hydroxylated polymers based on glycoside units.

In the production of normal or accelerating water reducers, carbohydrates must also be mixed with small amounts of triethanolamine and calcium chloride or other salts to counteract the retarding effect (see *Lignosulfonates* in this section).

Phosphonates. Phosphonates (Fig. 7) have been used as extended or super retarders for special applications.[24]-[26] Use of super retarders has been proposed to improve the construction joints.[27] Overnight or weekend stabilization of both returned plastic concrete and truck wash water for reuse as part of the mix batched the next day is another important application.[4][28]

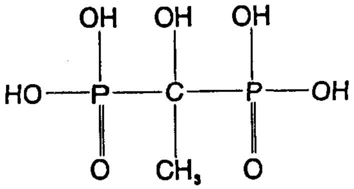
Other Organic Compounds. Several patents claim that other organic compounds could function as water-reducing admixtures. Ramachandran[4] has summarized papers and *Chemical Abstracts* on recent developments in concrete admixture formulations including those concerning water-reducers and retarders. According to this review, many formulations of water reducers are based on acrylate and methacrylate polymers to reduce slump loss, improve workability, and increase strength. Examples are polymers of alkoxylated monomers and copolymerizable acid functional monomers. Some are polymers of maleic acid an anhydride that have been copolymerized with a variety of monomers and blended with other materials. Copolymers containing ethylene, pentene or isopropene-2 methyl butene-pentene can also be used as water reducers. Other copolymers have also been synthesized for use as water reducers. They are: acetone-formaldehyde-sodium sulfite, 1:11-allyloxy-2, 3 dihydroxy propane-maleic anhydride copolymer containing 4-6 carbon olefin and maleic anhydride, and a composition containing saturated beta dicarboxylic acid and C_6 olefin. Several waste materials may be used for developing water reducers. They include digested product of cellulosics, sulfite yeast mash based product, wastes from fish oil processing, corn cobs, straw, and sunflower heads treated with sulfuric acid and sodium hydroxide and residues from the manufacture of dibutyl phthalate. A good plasticizer can be obtained using the alkaline wastes from caprolactam manufacture, lime, and sodium sulfate. Other novel combinations include magnesium methacrylate, dihydroxyethyl methacrylate, methylene bis-acrylamide, ammonium persulfate, and dimethylaminopropionitrile, a mixture containing sulfonated phenol, boric acid, potassium carbonate and ozocerite emulsion, ethylene oxide-ethylene imine oxide copolymer, salts of di- and polycarboxylic acids polymerized with various olefins and unsaturated non-cyclic and alicyclic hydrocarbons. According to the Ramachandran's review, a patent refers to a retarder containing humic acid and sulfonic acid groups, and another containing amino acids or their alkali metal salt or alkaline earth metal salts that imparted good fluidity and strength characteristics to concrete. Urea has been suggested as a good retarder whereas extended set retarders can be produced by a mixture of phenol carboxylates with an alkali such as NaOH or saccharides. The setting times vary between two and ten days. Other retarders include phenol polymer pretreated with formaldehyde and monomethyl urea, hydroxylated polyacrylamide homopolymer or copolymer (0.01%), and waste syrups from pentaerythritol.

Inorganic Compounds. In addition to the organic products, some inorganic compounds may act as retarding agents. Borates, phosphates, and salts of Pb, Zn, Cu, As, and Sb are retarders for the portland cement hydration,[30] however, they are not usually utilized commercially as they are more expensive than the organic compounds and only slightly soluble in the aqueous phase close to the neutral pH. Toxicological effects of waste waters containing these admixtures has also to be considered.



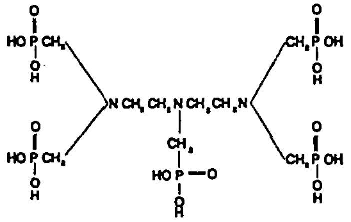
Aminotri(methylenephosphonic acid)

ATMP



1-Hydroxyethylidene-1,1-diphosphonic acid

HEDP



Diethylenetriaminepenta(methylenephosphonic acid)

DTPMP

Figure 7. The molecular structures, chemical names and abbreviations of the phosphonic acid compounds.[24]

2.0 PREPARATION AND USE OF WATER REDUCERS/ RETARDERS

Water reducers and retarders are generally used as neutral or slightly alkaline aqueous solutions. They are usually supplied in plastic containers (3–25 liters), steel drums (210 liters, approx. 45 gallons), portable (1000 liters) or bulk storage tanks (2000–3000 liters) commonly constructed of mild steel or heavy polypropylene with a steel frame.

2.1 Dispensing

Accurate, reliable and preferably automatic dispensers should be used particularly in ready mixed concrete or precast batching plants. Typical variation in the amounts is 1 to 5%. Materials like mild steel which are not corroded by water reducers are generally used. In the case of water-reducing admixtures containing a certain amount of chloride, special steel or heavy polypropylene could be required as construction materials. These dispensers are automatically fed by a pump unit either at the storage drum or storage tank.

In fully automatic dispensers, at the batching console, cement is allowed to feed into the mixer, an electrical signal is transmitted to the dispenser relay and immediately, or after a certain period of time, the required volume of admixture is automatically introduced into the mixing water or directly into the mixer. In semiautomatic dispensers an operator must open an outlet valve to allow the introduction of the admixture. In this case the time of addition can be controlled by the operator.

When admixtures are only occasionally utilized or in small applications, hand pump dispensers can be used. The pump, generally constructed to fit into the drum store hole, delivers a certain volume of water reducers or retarders directly to the mixer. Alternatively, the actual volume of admixture pumped from the dispenser must be measured by filling a container of standard volume.

2.2 Addition Procedure

Water reducers should be incorporated into the concrete mix in such a way that the most rapid and uniform dispersion of the admixture throughout the fresh mix is obtained. This can be achieved by discharging the admixture into the gauging water which subsequently is added to cement and aggregates, previously dry mixed. However, such a procedure generally does not give the best performance in terms of water reduction or increase in workability.

Maximum benefit is derived by adding the admixture just at the end of the mixing time of aggregates, cement and total gauging water. However, this procedure presents some practical difficulties in obtaining prefixed constant workability of the mix and the uniform dispersion of the admixture, particularly when large and frequent concrete mix batches have to be prepared.

A reasonable compromise between good technical performance and practical use of water reducer can be obtained by the following procedure. After an initial mixing period of 15 to 30 seconds of aggregates, cement and a portion (approximately 50%) of the mixing water, the admixture dissolved in a part (approximately 25%) of the gauging water is introduced into the mix, and finally the remainder of the gauging water is added until the required workability is obtained.

In Table 5 some comparative results are reported to show the differences in the performances achieved, following the three above-mentioned procedures for the addition of a commercial water reducer. Reduction in the water-cement ratio changes from about 8%, when 0.30% of admixture is immediately added, to approximately 12%, when the same percentage of water reducer is added at the end of the mixing period, or to 10% when the same amount of admixture is introduced with a part of the gauging water after an initial mixing period of 30 secs. The addition procedure also affects setting time and compressive strength. Longer setting times and a slightly lower early (1 day) compressive strength are obtained with the delayed addition, whereas later (3 to 28 days) compressive strength is increased because of the higher reduction in mixing water. The influence of the method of addition of the water reducer can also be assessed in terms of different dosages used to achieve approximately the same performance. Table 5 shows that similar performances for both setting times and compressive strength can be obtained by using 0.25% or 0.20% of the admixture on immediate or delayed addition respectively.

Table 5. Comparative Performances of a Normal (ASTM type A) Commercial Water Reducer Using Different Addition Procedures

Procedure for addition of water reducer	Plain Mix	Immediate addition with the total gauging water	Delayed addition at the end of the mixing	Delayed addition with part of the gauging water after an initial mixing period of 30 s.	
Percent of water reducer by weight of cement	-	0.25	0.25	0.25	0.20
Water-cement ratio	0.60	0.56	0.53	0.54	0.55
Setting times* (hr:min)					
Initial	2:20	2:50	3:30	3.05	2.45
Final	6:45	7:05	8:10	7:30	7:10
Compressive Strength (N/mm^2) at:					
1 day	4.1	6.2	6.0	5.4	6..0
3 days	9.7	17.1	17.4	17.4	16..9
7 days	20.2	28.6	29.7	29.2	27.9
28 days	35.1	39.7	42.3	41.0	39.3

*Mortar has been screened from concrete mix on No. 4 sieve.

2.3 Storage and Shelf Life

As water retarders and retarders are usually aqueous solutions, protection from severe frost is normally required in order to avoid separation or solidification. The approximate minimum storage temperature is -3°C (27°F) for lignosulfonate based water reducers and -5°C (23°F) for admixtures containing hydroxycarboxylic acids or hydroxylated polymers. Still lower temperatures, up to -10°C, can be allowed for water-reducing and accelerating admixtures, depending on the nature and amount of electrolyte generally used to produce these types of water reducers. In case water reducing admixtures freeze, they must be heated at 10 to 20°C (50 to 68°F) to thaw and agitated well to produce a homogeneous liquid.

High temperatures that occur in hot weather or tropical areas, can adversely affect the shelf life of water reducers or retarders even though their effectiveness may not be modified. As the main components of these admixtures are generally organic compounds, they can support bacterial and fungal growth unless a certain amount of antibacterial and antifungal materials, like sodium pentachloride-phenate or sodium salt of tetra-alkyl ammonium, is present in the admixture. In admixtures not containing an antibacterial addition a gas may be produced in the form of carbon dioxide and water vapor, causing a potentially dangerous increase in pressure in the closed storage drum. Therefore, in tropical climates, water reducers or retarders may have to be mixed with antibacterial products.

Considering the above limits, the shelf-life of water reducers or retarders can be assumed to be very long and sometimes practically infinite. In some cases water reducers have been tested after a storage of 10 years at about 20°C and their effectiveness was found to be the same as that of similar unexposed admixtures. The only difference can be a small separation of solid products in the water-reducing admixtures prepared from unrefined lignosulfonate.

2.4 Precautions

Water reducers, like all other admixtures, should be used according to the dosage range recommended by the supplier. Typical suggested dosages of water reducers or retarders are in the range of 200 to 400 ml per 100 kg of cement (about 3 to 6 fl oz/bag). However, some trial concrete mixes should be made to find out the optimum dosage of the admixture for the specific conditions and raw materials. Particularly when temperature is not within the normal room temperature range, 10 to 30°C (50 to 85°F), some preliminary tests should be carried out with different dosages of water reducer for the maximum benefit.

In some exceptional cases it may be possible that an overdosage (2 to 3 times the normal dosage suggested by the supplier) is inadvertently used. A very long retardation in setting time as well as decrease of early compressive strength can be expected in such cases, particularly in cold weather. Concrete could remain in the plastic state also for several days. However, with double the normal dosage, compressive strengths after 2 days are somewhat higher than those obtained with a normal dosage.[30] With more than the triple of the normal dosage, compressive strengths at later ages (28–90 days) are generally higher than those of the control mix, provided that the severe overdosage does not cause abnormal air entrainment.[30] Hence, in a concrete mix containing an overdosage of water reducer, if early strengths are not affected there is no risk of low strength at longer ages, provided an abnormal air entrainment has been avoided.

2.5 Hazards

Safety aspects for water reducers, as for other types of admixture, should be provided by the supplier. Water reducers or retarders are in general mildly alkaline, and contact with skin and particularly with eyes must be avoided. In case of contact both skin and eyes should immediately be washed with water or a dilute aqueous boric acid solution and at the same time medical attention may be warranted. Oral ingestion must be avoided. Precautions regarding toxicity and measures to be taken in the event of ingestion should be provided by the supplier.

Spillage of water reducers or retarders makes floors slippery and these should immediately be washed with water.

Water reducers or retarders in aqueous solutions are neither combustible nor inflammable. The solid which remains after evaporation is generally an organic product that can be combustible.

3.0 EFFECT OF WATER REDUCERS/RETARDERS ON THE HYDRATION OF CEMENT COMPOUNDS AND CEMENT

The effect of water reducers/retarders on the hydration of cement compounds and cement has been extensively studied. Most work is devoted to the influence of pure lignosulfonate or lignosulfonate-based admixtures.

3.1 Hydration of Cement Compounds

Most investigations concern the influence of lignosulfonate on the hydration of C_3A and C_3S. Water-reducing agents other than lignosulfonate are discussed separately in this section.

Influence of Lignosulfonate on the Hydration of C_3A. Although C_3A is present only as a small percentage in portland cement, it affects setting and early hydration of cement significantly. This explains why most work has been devoted to the influence of water reducers on C_3A hydration.

Tricalcium aluminate is known to produce a mixture of two metastable hexagonal phases (C_4AH_{13} and C_2AH_8) before the final conversion to the stable cubic phase (C_3AH_6) according to Eqs. 1 and 2.

Eq. (1) $$2C_3A + 21H \rightarrow C_4AH_{13} + C_2AH_8$$

Eq. (2) $$C_4AH_{13} + C_2AH_8 \rightarrow 2C_3AH_6 + 9H$$

The transformation rate from hexagonal to cubic hydrate depends on the temperature, water-solid ratio, and the type of C_3A. Addition of lignosulfonate retards both C_3A hydration and conversion of hexagonal hydrates to cubic phase.[10][31]-[44] The higher the amount of lignosulfonate, the more effective is the retarding action. The retardation effects in the hydration of C_3A in the presence of small amounts (0–5%) of lignosulfonate are illustrated in Table 6. The influence of lignosulfonate on the DTA thermograms for C_3A hydration products is shown in Fig. 8. The hexagonal hydrates shows two prominent endothermal effects, the first below 150–200°C and the second at 200–280°C. The cubic phase shows two endothermal effects at about 300–350°C and 500–550°C. In the absence of lignosulfonate, C_3AH_6 appears at 6 hours and is the main phase at 7 days. In the sample containing lignosulfonate, C_3AH_6 is very evident only at 14 days and appears as the main phase at 6 months (Fig. 8). Similar results are shown in Table 6. It can be concluded that the hexagonal hydrates are stabilized by lignosulfonate. Chatterji and Jeffery,[32] and Chatterji[10] have explained the absence of C_3AH_6 at early ages by the depressed reactivity of C_3A in the presence of lignosulfonate admixtures (Table 6).

Table 6. Effect of Calcium Lignosulfonate (CLS) or Sugar-Free Sodium Lignosulfonate (NLS) on C_3A Hydration[10]

COMPOUNDS	$C_3A + H_2O$			C_3A + 0.2% CLS			C_3A + 0.4% CLS			C_3A + 5% CLS			C_3A + 0.4% NLS		
	1 day	14 days	3 mo	1 day	14 days	3 mo	1 day	14 days	3 mo	1 day	14 days	3 mo	1 day	14 days	3 mo
C_3A	8	2	0	8	6	1	8	6	2	10	9	8	7	5	2
C_2AH_8	1	tr	tr	1	1	tr	1	2	1	tr	0.5	1	1	1	tr
C_4AH_x	1	2	2	1	2	3	1	2	2	tr	0.5	1	2	2	2
C_3AH_6	tr	6	8	0	1	6	0	tr	5	0	0	0	0	2	6

Numerals represent the relative amounts of C_3A and C_3A hydration products

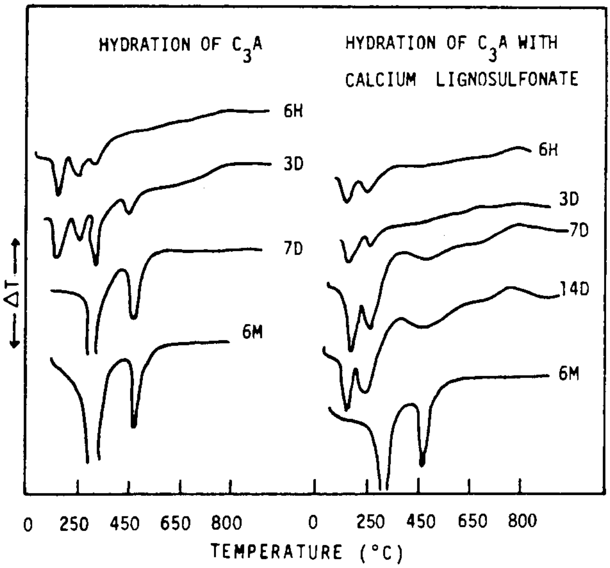


Figure 8. Influence of calcium lignosulfonate on C_3A hydration.[35] *(© Elsevier Science Publishers, reprinted with permission.)*

Although it is generally recognized that lignosulfonate is an efficient retarder of the C_3A hydration, there is disagreement on the role of sugar and sugar acids in commercial lignosulfonates. Ramachandran[36] found that sugar-free sodium or calcium lignosulfonates are at least as efficient retarders of the hydration reactions in C_3A as commercial lignosulfonates. This would mean that pure lignosulfonate has *per se* the same retarding effect as the sugars present in commercial lignosulfonate. According to Chatterji[10] pure sodium lignosulfonate is an inferior retarder compared to a commercial calcium lignosulfonate (Table 6). It is concluded that the reducing sugars are the main active ingredients of commercial calcium lignosulfonate. Milestone[13] separated two commercial lignosulfonates into various components and concluded that the retardation of C_3A hydration is caused by sugar acids. Mouton[45] and Milestone[13] have detected sugar acids, such as xylonic and gluconic acids, in commercial lignosulfonates. The disagreement may be due to differences in the methods adopted for separation, variability of the materials, molecular weight differences and hydration procedures.

Complex effects result when C_3A is treated with a large excess of lignosulfonate (10–100%). According to Ramachandran and Feldman,[34] at a calcium lignosulfonate addition of 10–30%, there is evidence of a complex formed between hydrated C_3A and lignosulfonate. It yields a thermogram different from that of calcium lignosulfonate or aluminate hydrates. The scanning electron microscope reveals this product to be a honeycombed structure formed of twisted ribbonlike material. At an even higher concentration of calcium lignosulfonate (50–100%), a gelatinous material precipitates out. The electron microscope examination of the gel-like material shows a fluffy mass typical of a noncrystalline material. Using surface area, chemical analysis, DTA and XRD, Ramachandran and Feldman[34] concluded that this gel-like material appears to be a basic calcium lignosulfonate with incorporated Al^{3+}.

The retarding effect results of sugar-free sodium lignosulfonate (NLS) on the hydration of C_3A and C_3A-Na_2O solid solution, in the presence of $Ca(OH)_2$, illustrated in Fig. 9 are based on XRD. The y-axis refers to the relative amounts of the unhydrated phase present. The effect of lignosulfonate on the hydration of C_3A–Na_2O solid solution appears to be less significant than that on the hydration of pure C_3A.[41][42] This may mean that the retarding effect of lignosulfonate depends on the alkali content of portland cement. There is evidence that lignosulfonate admixtures are less effective as water-reducing agents for concrete containing cements with a high C_3A or alkali content.[1] Ramachandran et al.[46] suggest that high alkali contents in Portland cement may interact with lignosulfonate and destroy its plasticizing ability.

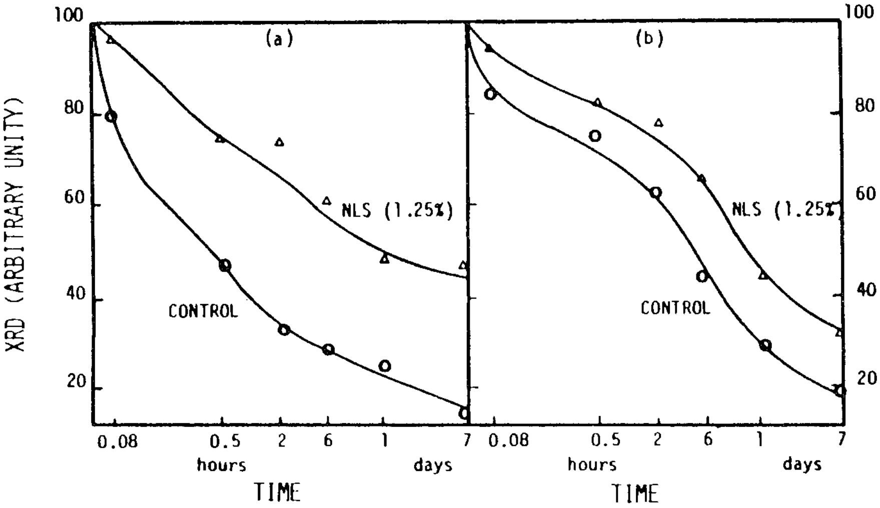


Figure 9. Influence of sugar-free sodium lignosulfonate (NLS) on the hydration of *(a)* C_3A and *(b)* C_3A-Na_2O solid solution.[42]

A simultaneous addition of sodium carbonate and lignosulfonate completely blocks the C_3A hydration with an induction period proportional to the percentage of admixtures.[40][41] The combination of sodium carbonate (1.25%) and sodium lignosulfonate (1.25%) is more effective than sodium lignosulfonate (1.25%) for the hydration of C_3A in the presence of $Ca(OH)_2$, (Fig. 10). The intensity of the DTG peaks in the temperature range 100–300°C can be used to study the retardation effects. Similar results have been obtained using calorimetric techniques on the hydration of pure C_3A.[47] It was found that the heat evolution is decreased significantly in the presence of lignosulfonate (1%) both in combination with or without Na_2CO_3 (2%), the decrease being much more severe with the combination. In this study on initial blocking of the C_3A, hydration was not observed in contrast to the results of Collepardi et al.,[40][41] who used other techniques, such as XRD, DTA and DTG.

No induction period is observed in the hydration of C_3A–Na_2O solid solution in the presence of both lignosulfonate and sodium carbonate (Fig. 11). The plasticizing effect of the sodium carbonate-lignosulfonate mixture is much more pronounced on the C_3A paste than on the C_3A–Na_2O solid solution paste.[41][42] It seems that alkalis present in portland clinker play a role that is different from those present in chemical admixtures.

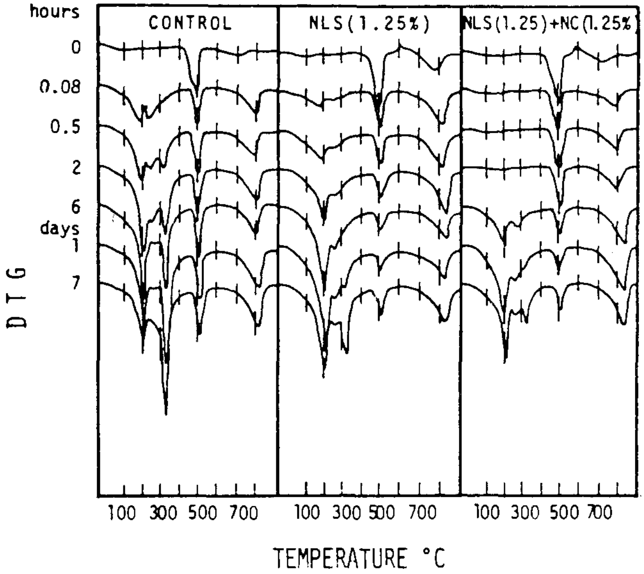


Figure 10. Influence of sodium lignosulfonate (NLS), or sodium lignosulfonate + sodium carbonate (NC) on the hydration of C_3A in the presence of $Ca(OH)_2$ by DTG.[42] *(© Pergamon Press, reprinted with permission.)*

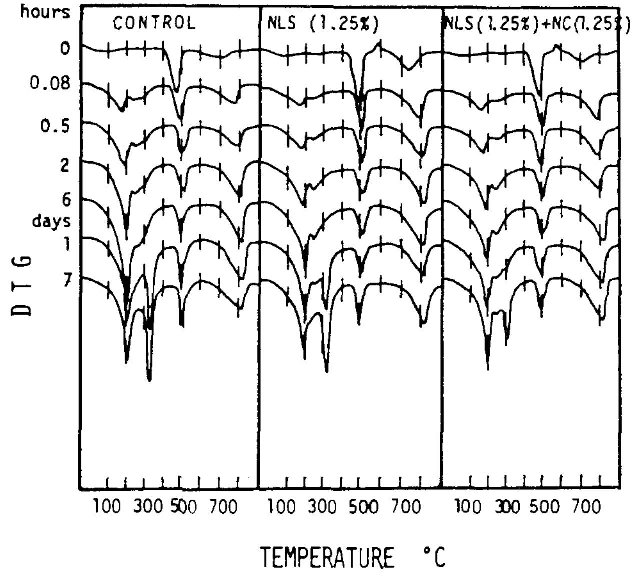


Figure 11. Influence of sodium lignosulfonate (NLS), or sodium lignosulfonate + sodium carbonate (NC) on the hydration of C_3A-Na_2O solid solution ($N_{0.25}C_{2.75}A$) in the presence of $Ca(OH)_2$ by DTG.[41] *(© Pergamon Press, reprinted with permission.)*

As only small amounts of lignosulfonate can affect the water-reducing and retarding properties of concrete, it has been assumed that the phenomenon of adsorption of this admixture on portland clinker compounds and/or their hydration products play an important role.[7][48] A considerable amount of work has been carried out[9][34][35][48] to study the adsorption of lignosulfonate on C_3A, hexagonal hydrates and cubic phase. In an aqueous medium the hydration of C_3A cannot be avoided, and therefore in the C_3A-lignosulfonate-water system it is not possible to determine a true adsorption isotherm. Consequently, the adsorption of lignosulfonate on C_3A has been examined using dimethyl sulfoxide (DMSO) as a non-aqueous solvent. Adsorption of lignosulfonate on hexagonal hydrates and cubic phase has been studied in water as well as in DMSO.[34]

Ramachandran and Feldman[34] studied the adsorption isotherm of calcium lignosulfonate on mixes of C_4AH_{13} and C_2AH_8 dispersed in water (Fig. 12). The isotherm shows a rapid increase in adsorption as the equilibrium concentration increases, but it tapers off between the equilibrium concentration of 0.5 and 1.5 g/l corresponding to 10 per cent adsorption. Between 1.5 and 3.0 g/l there is again a steep increase in the adsorption. The scanning desorption isotherms from different points do not follow the adsorption isotherm, and therefore show complete irreversibility up to 10% adsorption, indicating the formation of an interlayer complex. At higher values, desorption isotherms show only partial reversibility. Massazza and coworkers[49] found that the adsorption isotherm of sodium lignosulfonate on pure C_4AH_{13} dispersed in lime water shows maximum adsorption of about 5% at an equilibrium concentration of approximately 3 g/l.

Specific surface area measurements,[34] XRD[9][10] and DTA[9][34][35] results seem to indicate that an interlayer complex between lignosulfonate and C_4AH_{13} is formed. This might restrict the free movement of the interlayer ions for conversion to the cubic hydrate.[39]

Adsorption-desorption isotherms for the C_3AH_6-calcium lignosulfonate system in water have been carried out by Ramachandran and Feldman.[34] After a rapid initial adsorption the amount is approximately constant at about 2%. The scanning isotherms show complete irreversible adsorption.[34] Electron micrographs, XRD and DTA do not show any significant difference caused by the addition of lignosulfonate to C_3AH_6. The increase in surface area and the irreversibility of adsorption indicate that lignosulfonate is chemisorbed on the C_3AH_6 surface causing dispersion of the cubic phase.[34] Massazza et al.,[49] also studied adsorption isotherm for C_3AH_6 treated with lignosulfonate dissolved in lime water.

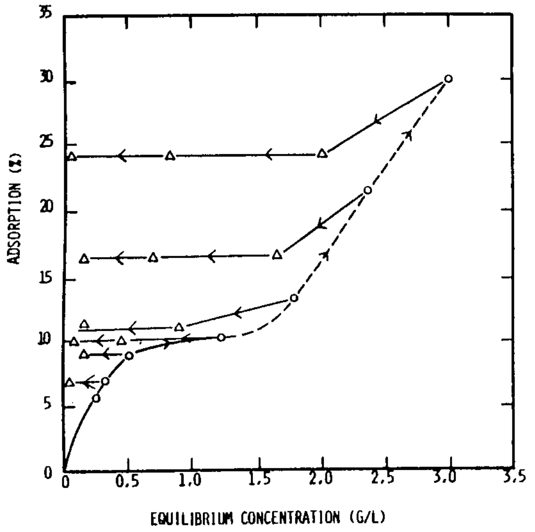


Figure 12. Adsorption-desorption isotherm of calcium lignosulfonate on the hexagonal calcium aluminate hydrates in aqueous medium.[34]

Ramachandran and Feldman[9] also studied the adsorption-desorption isotherms of calcium-lignosulfonate on the hexagonal hydrates in a non-aqueous solvent dimethyl sulfoxide (DMSO). There is a rapid increase in the amount of adsorption and a tapering of at about 2.2%. The scanning isotherms showed irreversibility even at lower concentration indicating that lignosulfonate formed complex with the hexagonal phase.[9] Massazza et al.[49] found analogous adsorption isotherms for C_4AH_{13} in a solution of sodium lignosulfonate in DMSO + 8% H_2O. According to Ramachandran[39] the amount of adsorption of lignosulfonate in an aqueous medium is much higher than in DMSO because the higher dipole moment of H_2O molecules allows them to enter the interlayer position of the hexagonal phase along with lignosulfonate.

In a non-aqueous medium, no significant adsorption of lignosulfonate occurs on C_3A[9] or C_3AH_6.[9][49] This can be due to the lower specific surface areas of C_3A and C_3AH_6, the nature of the surface, and the absence of interlayer spaces.[39]

Adsorption-desorption experiments show that in a non-aqueous solvent, such as DMSO, the relative amount of lignosulfonate on the hexagonal hydrates (C_4AH_{13} and C_2AH_8) is much higher than that on the cubic phase (C_3AH_6) or anhydrous C_3A. On the other hand, in an aqueous environment the reported adsorption values of lignosulfonate on C_3A are much higher than those for aluminate hydrates. They are in range between 15 and 450 per cent,[34][51]-[56] depending on the experimental conditions, such as the concentration of lignosulfonate, the time of contact, temperature, etc. However, in these studies, concerning the adsorption of lignosulfonate on anhydrous cement compounds, the applicability of the term *adsorption,* may be questionable. Therefore, Ramachandran and Feldman[34] suggest that the tendency of attributing the retarding effect of lignosulfonate to adsorption on C_3A should be altered in favor of the concept that the consumption of lignosulfonate, by the hydrating C_3A, is responsible for the retardation.

The adsorption of lignosulfonate on hydrating C_3A is severely reduced in the presence of Na_2CO_3. Jawed et al.[47] found that the lignosulfonate concentration in the liquid phase of a C_3A paste (w/s = 0.5), decreased from 20,000 ppm to 900 ppm in 15 min of hydration, whereas in the presence of Na_2CO_3 (40,000 ppm) the concentration of lignosulfonate decreased from 20,000 ppm to 7200 ppm in the same period of time. The increased lignosulfonate concentration in the liquid phase, due to the presence of Na_2CO_3, is accompanied by a great increase in the fluidity of the paste. They assumed that an ionic complex between lignosulfonate and CO_3^{2-} is formed, and it is more anionic than lignosulfonate and hence a more effective dispersant. This hypothesis seems to be supported by the work of Pauri et al.,[40][41] who found that the reduction in zeta potential of the C_3A-H_2O system is much higher in the presence of the lignosulfonate-Na_2CO_3 combination than in the presence of lignosulfonate alone (Fig. 13).

The change in zeta potential is assumed to be an important phenomenon to explain the dispersion of cement particles caused by electrical repulsion caused by adsorption of water reducers on cement particles. Zeta potential measurements have been carried out on hydrating C_3A[37][40][41] and pure C_4AH_{13} and C_3AH_6[49] with and without addition of lignosulfonate. Pauri et al.[40][41] found that 1 g of C_3A mixed for 5 min with 100 ml of saturated lime water produces about + 40 mV. Addition of sugar-free sodium lignosulfonate to the C_3A-lime water system reduces zeta potential to about -20 mV (Fig. 12). Massazza et al.[49] found that a small addition of sodium lignosulfonate to lime water causes a sharp potential decrease from -9.1 mV to about -18 mV for C_4AH_{13}, and from -8.7 mV to about -12 mV for C_3AH_6. The general mechanisms of retardation are also described in *Influence of Water Reducers/Retarders Other than Lignosulfonate on the Hydration of C_3A,* later in this section.

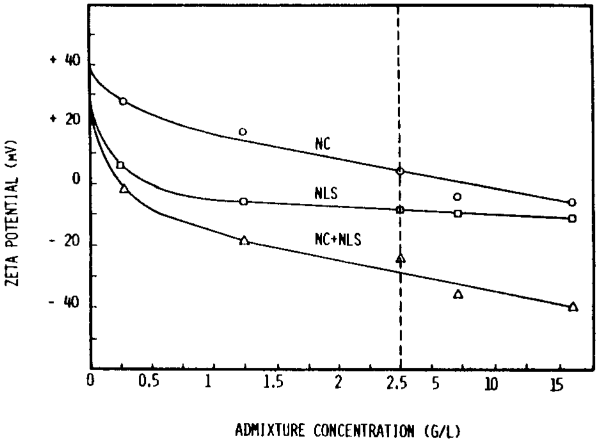


Figure 13. Zeta potential of hydrating C_3A as a function of admixture (NC = Na_2CO_3, NLS = sodium lignosulfonate) concentration in the liquid phase.[40] *(© Pergamon Press, reprinted with permission.)*

The morphological changes in the hydrated calcium aluminate hydrates in the presence of lignosulfonate may vary. Some authors[31][55]-[57] observed an acicular crystal formation in the presence of lignosulfonate, whereas others could not find any such crystal formation.[10][34] Chatterji[10] found no crystalline products during the first four minutes of hydration. At later ages he observed some crumpled foil-like products and finally very thin platelike hydration products. He also found that, if lignosulfonate solutions were stored over a period of time, some unidentified acicular precipitate formed. Thus the nature of the acicular crystals is still uncertain.

Influence of Lignosulfonate on the Hydration of C_3A Containing Gypsum. According to Seligmann and Greening,[58] for composition corresponding to the sulfate-alumina ratios found in portland cements, C_3A hydration occurs in three successive stages when excess lime is present.

Stage I. Some of the C_3A reacts with water and gypsum, producing ettringite according to Eq. (3).

Eq. (3) $C_3A + 3CaSO_4{\bullet}2H + 26H \rightarrow C_3A{\bullet}3CaSO_4{\bullet}H_{32}$

Stage II. When gypsum has been consumed, the conversion of ettringite to monosulfate occurs according to Eq. (4).

Eq. (4) $2C_3A + C_3A{\cdot}3CaSO_4{\cdot}H_{32} + 4H \rightarrow 3(C_3A{\cdot}CaSO_4{\cdot}H_{12})$

Stage III. The remainder of the C_3A reacts with lime and monosulfate to form a solid solution according to Eq. (5), and the rest reacts with lime and water to form C_4AH_{19} according to Eq. (6).

Eq. (5) $xC_3A + xCa(OH)_2 + (1 - x)[C_3A{\cdot}CaSO_4{\cdot}H_{12}] + 12xH_2O \rightarrow C_3A{\cdot}xCa(OH)_2{\cdot}(1 - x)CaSO_4{\cdot}H_{12}$

Eq. (6) $C_3A + CH + 18H \rightarrow C_4AH_{19}$

Seligmann and Greening using XRD analysis found that the addition of calcium lignosulfonate to the C_3A-gypsum-lime-water system resulted in a very little, if any, acceleration of the initial reaction between C_3A and gypsum in Stage I. A marked retardation of all hydrations occurred in stages II and III. Similar results have been obtained by Young[31] using DTA techniques. Ettringite is recognized within a few minutes in the paste containing lignosulfonate. The conversion of ettringite to monosulfate takes 3 days in the presence of lignosulfonate and 3 hours in the absence of this admixture.

Chatterji,[10] and Massazza and Costa[38] studied the influence of lignosulfonate on the hydration of C_3A in the presence of gypsum. The XRD results, reported in Table 7, indicate that lignosulfonate slightly retards the reaction between C_3A and gypsum.[10] The retarding effect on the C_3A hydration seems to be more pronounced in the absence of gypsum (Table 6). Much more marked retardation occurs in the conversion of ettringite to monosulfate.[10] Ettringite disappears after 1 day in the absence of lignosulfonate, whereas it is still present at 14 days—3 months in the presence of 0.2–0.4% or 5% lignosulfonate (Table 7). Massazza et al., using TG, XRD, DSC and conduction calorimeter techniques, confirmed that in the presence of lignosulfonate there is a slight retardation of the reaction between C_3A and gypsum, but a more significant retardation in the transformation of ettringite into monosulfate.[38] Figure 14 shows the heat evolution curves for C_3A-gypsum pastes with and without lignosulfonate. The curves exhibit two peaks: the first (not shown in Fig. 14) is due to the rapid reaction of C_3A with water and gypsum, and the second, which appears after gypsum is exhausted, indicates the conversion of ettringite to monosulfate. Lignosulfonate addition affects intensity and position of the second but not that of the first peak.[38]

Table 7. Hydration of C_3A + $CaSO_4•2H_2O$ Mixture without and with Calcium Lignosulfonate (CLS) for Different Periods[10]

COMPOUNDS	C_3A + gypsum			C_3A + gyp. + 0.2% CLS			C_3A + gyp. + 0.4% CLS			C_3A + gyp. + 5% CLS		
	1 day	14 days	3 months	1 day	14 days	3 months	1 day	14 days	3 months	1 day	14 days	3 months
C_3A	6	3	2	7	6	3	7	6	4	7	6	5
Gypsum	2	0	0	2	1	0	2	1	0	2	2	1.5
C_2AH_8		tr	1	0	0	I	0	0	tr	-	-	-
C_4AH_x		1	1	0	0	1	0	0	2	-	-	-
Ettringite	2	0	0	1	2	0	1	2	0	1	1	2–5
Monosulfate	tr	6	6	tr	1	5	tr	1	4	tr	tr	1

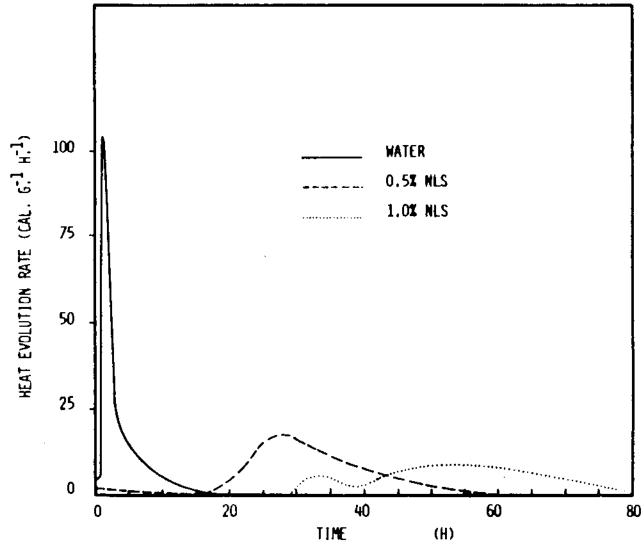


Figure 14. Heat evolution curves of pastes of 100 parts C_3A + 20 parts of gypsum + 120 parts of water or aqueous sodium lignosulfonate (NLS).[38]

Thermoluminescence technique was used to study the role of the crystal defects in C_3A that constitute preferential sites for the hydration of C_3A.[59] There was no evidence that these defects play a significant role in the hydration of C_3A with gypsum either in the presence or absence of lignosulfonate.[38]

Adsorption of sodium lignosulfonate on ettringite and monosulfate in DMSO + 8% H_2O has been studied by Massazza and Costa.[38] At the equilibrium concentration of 9 g/l, ettringite and monosulfate adsorb 5.9% and 4.3% lignosulfonate respectively. Thus it seems that sulfonate hydrates adsorb much more lignosulfonate than C_3AH_{13} under the same experimental conditions[48] (see preceding section). Massazza and Costa found that adsorption on monosulfate is accompanied by a considerable variation of the lattice distances,[38] and Chatterji[10] reported that the basal lines of calcium aluminate hydrates and monosulfate, obtained by hydration of C_3A in the presence of gypsum and lignosulfonate, are broader.

Lignosulfonate modifies the morphology of both ettringite and hexagonal hydrates (including monosulfate) when gypsum is depleted by reaction with C_3A.[31][33][38][60]

In C_3A pastes containing 10% gypsum and 5% lime, very large and thick needles of ettringite are identified by SEM.[31] After eight days of hydration these needles are converted to hexagonal plates. In the presence of commercial lignosulfonate, the large needles are changed to very small acicula.[31] Massazza and Costa studied the morphology of C_3A pastes containing 20% gypsum with and without lignosulfonate.[38] After 30 minutes of hydration the morphology of ettringite appears to be considerably affected by sugar-free sodium lignosulfonate. Figure 15 shows the presence of large fibrous crystals of ettringite produced in the absence of lignosulfonate and forming a sort of tridimensional branching which join the different grains. Figure 16 refers to the paste containing lignosulfonate and indicates that the size of ettringite crystals becomes considerably smaller. This agrees with the observation of Gupta et al.,[60] who found that the thickness of the hydration products of C_3A with gypsum and lime decreases with the increase in concentration of calcium lignosulfonate. Ettringite crystals appear as a fine felt on C_3A and gypsum particles without any interlocks among the grains forming the paste.[38] According to Massazza and Costa the plasticizing action of lignosulfonate can be attributed, at least partly, to the two following effects, both caused by the finer structure of ettringite crystals protecting C_3A grains from the action of water more efficiently.

1. A slower rate of formation of ettringite and therefore a reduction in the demand of mixing water.

2. A decrease in the interlocking of the ettringite bridges connecting the solid particles and a consequent improvement in the rheological behavior.[38]

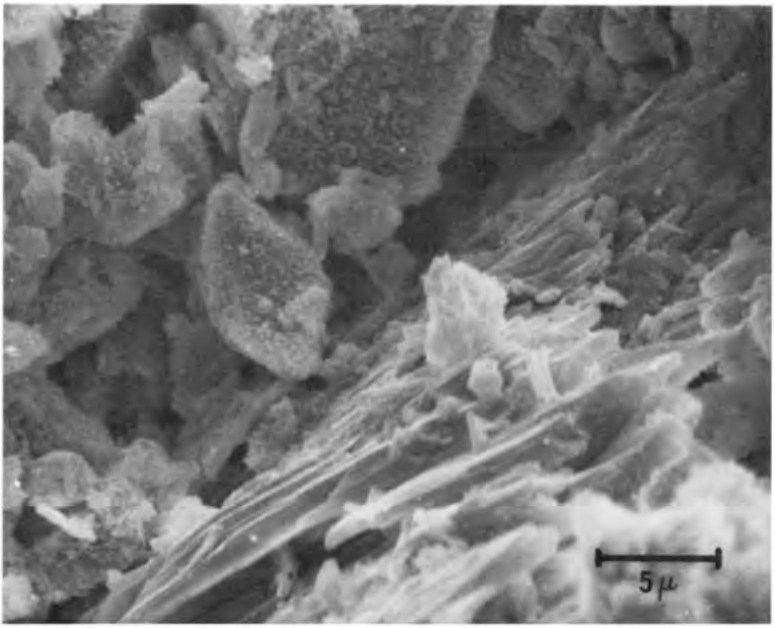


Figure 15. Large ettringite needles in pastes of C_3A + 20% gypsum hydrated for 30 minutes with water.[38]

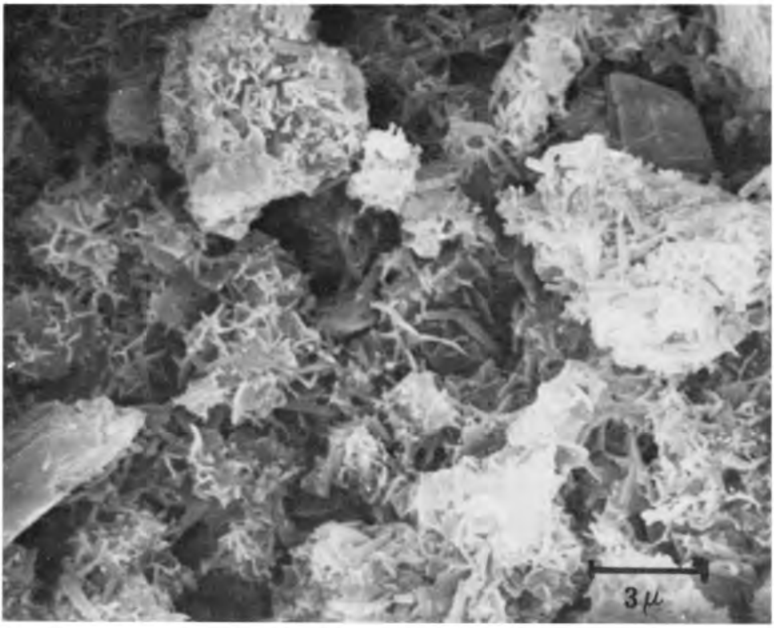


Figure 16. Ettringite needles in pastes of C_3A + 20% gypsum hydrated for 30 minutes with 1% lignosulfonate in water.[38]

The influence of lignosulfonate on the hydration of the C_3A-Na_2O solid solution has been determined by examining the rate of release of the alkali into excess water by hydrating equimolar mixtures of sodium calcium aluminate and lime with enough gypsum to give SO_3/Al_2O_3 ratio of 0.5.[58] As a source of lime, one mole of $Ca(OH)_2$ or C_3S per mole of sodium calcium aluminate has been used. Table 8 shows the chemical analysis (Na_2O and SO_3) of the liquid phase after 10 min and after 17 hr of hydration. The rate of alkali release into water was found to be equivalent to the rate of hydration of the aluminate phase itself. Comparison of mixes A and B indicates the retarding effect of $Ca(OH)_2$. Comparison of mixtures B and C indicates the early mild retarding effect of lignosulfonate and the marked retarding effect at longer hydration times. The higher sulfate concentration indicates that conversion of ettringite to monosulfate is not completed. Substitution of C_3S for $Ca(OH)_2$ in the presence of lignosulfonate (mixtures C and E) results in a more rapid alkali release and therefore a very early acceleration of stage I hydration. As lignosulfonate strongly retards C_3S hydration (see *Influence of Water Reducers/Retarders on the Hydration of C_3S* later in this section), release of $Ca(OH)_2$ from C_3S is inhibited, whereas the highly alkaline solution decreases the solubility of any $Ca(OH)_2$ present.

Table 8. Influence of Lignosulfonate (CLS) on the Hydration of $Na_2O{\bullet}C_3A$ Solid Solution in the Presence of Gypsum and Calcium Hydroxide[58] *(© Transportation Research Board, National Council, Washington, D.C., reprinted with permission.)*

Mix No.	Source of CH	Admixture Present	Analysis of Liquid Phase (%)			
			at 10 min		at 17 hr	
			Na_2O	SO_3	Na_2O	SO_3
A	None	None	0.48	0.19	-	-
B	CH	None	0.27	0.26	0.94	0.02
C	CH	CLS	0.23	0.20	0.37	0.34
D	C_3S	None	0.27	0.34	0.87	0.01
E	C_3S	CLS	0.38	0.46	1.13	0.03

Influence of Water Reducers/Retarders Other than Lignosulfonate on the Hydration of C_3A. Organic water reducers other than lignosulfonate include two groups of chemical products such as hydroxy acids[61][62] and carbohydrates.[62] All these products retard both the C_3A hydration and conversion of hexagonal hydrates to the cubic phase.

Several theories have been proposed to explain the retarding effect of organic water reducers, including lignosulfonate, on the hydration of C_3A. These have been summarized by Young.[63][64] These theories are based on adsorption, precipitation or complex formation.

Adsorption. For organic water reducers, the retarding effect on the hydration of C_3A seems to be linked with their adsorption onto the surface and into the structure of the metastable hexagonal phases that are initially formed.[65] Evidence of an interlayered organic hexagonal complex has been given by Milestone who found a DTA exotherm centered at 400°C in a C_3A paste containing 1% of either calcium gluconate, gluconic acid or glucose.[66] Dosch[67] showed that organic molecules can enter between the layers of C_4AH_x and form complexes with Van der Waals or hydrogen bonding mechanisms and exist as homopolar bonded interlayer complexes.

Adsorption of salicylic acid from ethanol on anhydrous C_3A is quite low, but it is quite high on the hydration products of C_3A.[19] On the other hand, adsorption of salicylic acid, as well as lignosulfonate, onto C_3A in an aqueous medium decreases for prehydrated C_3A.[54] Therefore Hansen's original theory[48] that retardation is due to adsorption of organic compounds by the anhydrous compounds, should be altered in favor of the idea that organic admixtures are consumed by hydrating portland cement compounds, such as hydrating C_3A.[34]

Steinour[68] suggested that the retarding effect is due to the hydrogen bonding of the hydroxyl groups. Taplin[29] found that many retarding agents contain the α-hydroxyl carbonyl group. Bruere[69] also found that retarding sugars either contain the α-hydroxyl carbonyl group or they are able to form it in an alkaline medium. He found that trehalose does not contain the α-hydroxyl group nor does it form this group in the aqueous phase in contact with cement. Therefore, it was concluded that trehalose does not act as a retarding agent in portland cement pastes.[69] However, Daugherty and Kowalewsky[70] found that trehalose strongly retards C_3A paste hydration. According to them, the carboxyl and α-hydroxyl carbonyl groups themselves do not retard the C_3A hydration significantly. Mandelic acid which contains an α-hydroxyl carbonyl group is an accelerator of the C_3A hydration. It was concluded that organic compounds with two or more hydroxyl groups retard the C_3A hydration considerably.[70]

Sorption of organic water reducers has the effect of inhibiting both the crystal growth of the hexagonal hydrates and retarding their conversion to the cubic phase. Therefore, very stable and impermeable sheaths of hexagonal hydrates are assumed to form around C_3A and to prevent further access of water. According to Young[63][64] the retarding effect of organic water-reducing agents correlates reasonably with the total number of hydroxyl, carboxylic acid and carbonyl groups in the molecule. Therefore products such as glucose, gluconic acid and glucurone are particularly effective for retarding C_3A hydration.[66]

Precipitation. The precipitation of insoluble hydration products onto anhydrous surfaces as responsible for retardation was proposed by Suzuki and Nishi.[71] According to them, the insoluble salts produced by organic retarders reacting with calcium ions should retard the rate of hydration of C_3A, as well as that of other portland cement compounds, by forming a barrier to access by water. A good correlation between solubility and retarding behavior of carboxylic acids is not always possible.[63][64] For example, the solubility of the calcium salt of oxalic acid is 5×10^{-6} M, but it is not a retarder, whereas the solubility of gluconic acid is 8×10^{-3} M, and it retards the C_3A hydration.[66][72]

Complex Formation. Taplin[29] proposed that organic water reducers containing one or more oxy-functional groups, such as OH-C-C = O in which oxygen atoms are able to approach each other, can chelate to calcium, aluminum, iron or silicon ions in solution.[63][70][73] Complexing of ions in solution may therefore play an important role in the mechanism of retardation.

According to Daugherty and Kowalewski,[70] α-hydroxyl carbonyl group itself is not necessary for retardation. A simple organic compound containing a carboxyl group and one or no hydroxyl group does not retard the hydration of C_3A. Organic products with two or more hydroxyl groups retard the C_3A hydration.[70] It seems that organic products with a carboxylic group and at least two hydroxyl groups, as in glyceric[70] or gluconic[66] groups, are good retarders.

Although calcium ions can coordinate hydroxy acids and dibasic acids, these complexes are not quite stable. No correlation exists between stability constants and retarding effect of organic compounds.[63] Because of low stability constants, existence of low concentrations of organic retarders and high levels of calcium ions in the aqueous phase, equilibria of calcium ions do not change substantially. Consequently complexing of calcium ions in solution may not be a significant factor for retardation.[63]

Complexing effects might be more significant for aluminate and ferrite ions because of their lower concentration in solution. Analyses of the aqueous phase in the hydration of cement[71][74] indicate that, in the presence of sugar, a higher concentration of aluminate and ferrite ions results. Addition of 1% organic compound, such as sucrose, succinic and tartaric acids to C_3A increases the concentration of CaO and Al_2O_3 in solution on first contact with water.[63] Evidence of a complex between alumina and salicylic acid has been obtained by Diamond.[75]

Casu et al.[76] found that the optical rotation of reducing carbohydrates, such as glucose and maltose, suddenly decreases after a few minutes of contact with C_3A. Concurrently the carbohydrates precipitate from their solutions. Interaction with C_3A was prevented by using a non-reducing monosaccharide obtained by blocking the hemiacetal group by a methyl group.[76] By means of optical rotation measurements, IR and H-NMR spectra, Casu et al. obtained evidence that complexes in solution are formed by treating C_3A with the aldonates, such as gluconate and maltobionate, of corresponding carbohydrates, glucose and maltose respectively.[76] After a few minutes these complexes precipitated on the remaining grains of C_3A as the optical rotation decreased. Rendleman and Hodge[77] showed that aluminate ions form strong complexes with carbohydrates.

According to Casu et al. all the hydroxyl groups of aldonates are involved in the complex formation. However, the carboxylate, which in the aldonates replaces a hydroxyl group of the original carbohydrates, is a better coordinating group. Since sodium aluminate also forms a similar complex, Casu et al. assumed that the complex formed with C_3A involves the aluminate group rather than calcium. However, it is difficult to explain how anions such as aluminate, could coordinate to negatively charged molecules, such as gluconate.

Soluble complexes of aluminate ions with organic products might explain the initial increase in reactivity observed for the C_3A hydration in the presence of small amounts of sugars[58][70] and could also cause the accelerating effect of a small addition of sugars and the initial rapid stiffening that have been observed occasionally in portland cement pastes.[64][70] This could be explained by the dissolution of C_3A before the characteristic hydration barriers are set up.

Therefore, it seems that the retarding effect of organic products may be a balance between a potential rapid hydration, promoted by aluminate complexing, and the subsequent retardation caused by the stabilization of the hexagonal phase, by adsorption of organic molecules onto the surface of hydrating C_3A, and by the formation of a protective layer.

Young[65] has reported that organic water-reducing admixtures, such as glucose, lactic, gluconic and malonic acids, retard the conversion of the hexagonal phase to C_3AH_6 by stabilizing the hexagonal phase. After 1 day at 60°C and 75% RH, C_4AH_{13} is completely converted to C_3AH_6 and

$Ca(OH)_2$ whereas only partial transformation occurs at 33% RH. When C_4AH_{13} is kept in contact with an aqueous solution of glucose, the conversion at 60°C is inhibited even at 100% RH.[65] After the treatment with the organic admixture there is an increase in the basal spacing, typical of interlayer compounds. The effect of glucose and other organic products on C_3A pastes is the same as that on pure C_3AH_{13}.[65] Regourd et al., found that 1% sucrose retards the C_3A hydration by inhibiting the formation of C_3AH_6 and producing ill-crystallized C_3AH_{13}.[78]

The formation of an interlayered complex in the presence of calcium or sodium gluconate is also confirmed by a DTA endotherm peak at 80°C.[66][72] This peak cannot be assigned to C_3AH_{19}, because under the drying conditions used it would transform to C_4AH_{13}.

Based on the work of various investigators it would appear that the initial retarding effect of the most common water-reducing admixtures should be in the following decreasing order: sugar acids (such as gluconic acid) > carbohydrate (such as glucose and sucrose) > and lignosulfonate.[10][43][66] Figure 17 shows comparative results on the hydration of C_3A at 20°C in the presence of 0.3% sugar-free sodium lignosulfonate, sodium gluconate or glucose, confirming the relative effects of these compounds.[79]

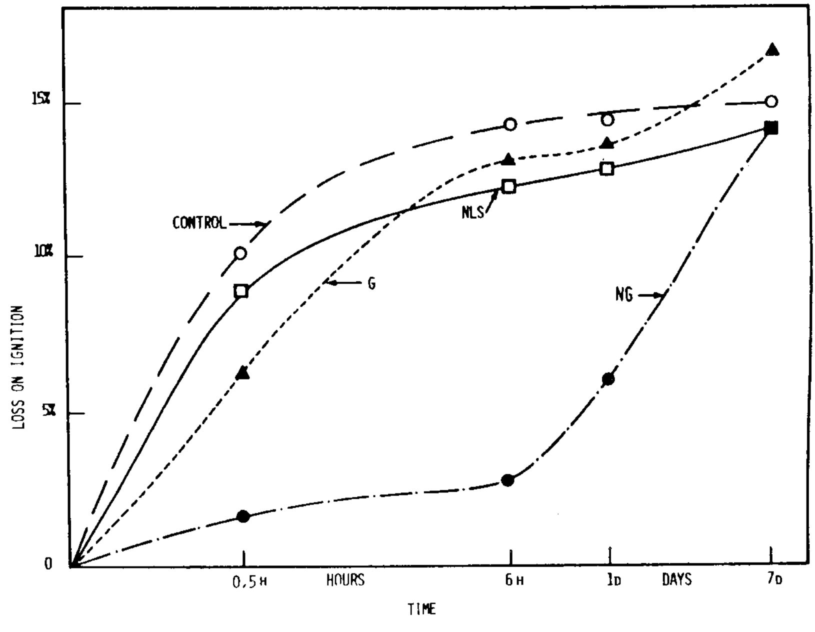


Figure 17. Loss on ignition (600°C) of hydrated C_3A with and without sugar-free sodium lignosulfonate (NLS), sodium gluconate (NG) and glucose (G).[79]

Influence of Water Reducers/Retarders Other than Lignosulfonate on the Hydration of C_3A Containing Gypsum. Information on the effect of water-reducing agents on the $C_3A\text{-}CaSO_4{\bullet}2H_2O\text{-}H_2O$ system, is meager although important from the viewpoint of abnormal set of concretes (see *Influence of Water Reducers/Retarders Other than Lignosulfonate on Portland Cement Hydration* later in this section).

The ettringite morphology can be modified by sugars.[64][65] Ettringite forms a columnar structure with the sulfate ions and most water molecules are located in the intercolumnar area.[80] The possibility exists that organic molecules can enter the intercolumnar region by stabilizing ettringite with respect to monosulfate. This is confirmed by the fact that conversion of ettringite to monosulfate is retarded by sugars.[58][73]

Experiments have indicated that the Stage I hydration time for ettringite formation, according to Eq. 3., depends on how sugar is added. This period is 17 hours in the absence of sucrose for a system containing C_3A and $CaSO_4{\bullet}2H_2O$ with a mole ratio of SO_3/Al_2O_3 of 0.5 and a water-solid ratio of 2. Addition of 0.7% sucrose to this system changes the Stage I hydration time from 17 to 1.5 or 60 hours depending on whether the addition is immediate or delayed respectively. This demonstrates that it is not always possible to classify an admixture as a retarder, an accelerator or a neutral type for the hydration of cements or cement compounds. Besides composition and concentration levels,[35][70] the way the addition is carried out determines its effect. On addition of sucrose with the mixing water to C_3A + gypsum mixture, C_3A sorbs 99% within seven minutes, producing a surface that does not permit the formation of the characteristically thin and relatively impermeable layer of ettringite on the C_3A grains.[58] Therefore, the hydration of C_3A in the presence of gypsum could continue to a greater extent before a sufficient amount of ettringite is produced to cause the usual retardation. In portland cement mixes, at low water-cement ratios the relatively large amount of ettringite formed under these conditions would act as a binder causing sometimes an initial stiffening. If C_3A is allowed to hydrate in the presence of gypsum for a few minutes before sucrose is added, sorption of sugar is decreased.[58] Consequently, the greater concentration of the sugar in the liquid phase retards all C_3A hydration stages. This could explain why a delayed addition of the admixture to portland cement mixes results in decreased sorption with the elimination of early acceleration.[81]

Influence of Water Reducers/Retarders on the Hydration of C_4AF. The hydration products of C_4AF with or without gypsum are very similar to those of C_3A and are isomorphous with C_2AH_8, C_4AH_{13}, C_3AH_6, $C_3A{\bullet}CaSO_4{\bullet}H_{12}$ and $C_3A{\bullet}3CaSO_4{\bullet}H_{32}$ with F partly replacing A.[75] The C_4AF hydration rates are markedly lower than those of C_3A (Secs. 1–6).[57]

The C_4AF phase sorbs much lower amounts of admixtures as compared to those sorbed by C_3A.[53][58]

Soluble complexes are also formed between hydrating C_3AF and sodium gluconate. However, these complexes are associated with a smaller variation in optical rotation values and are formed over a longer period compared to those involving C_3A.[76]

Collepardi et al.[83] examined the effect of sugar-free sodium lignosulfonate or a mixture of sodium carbonate and lignosulfonate on the paste hydration of C_4AF. No substantial change in the type of hydrated products is caused by the presence of 0.625% lignosulfonate during the initial hydration up to 9 hours. At longer ages (1–7 days) lignosulfonate causes a transformation of the hexagonal hydrates, $C_2(A,F)H_8$ and $C_4(A,F)H_{13}$, to the cubic phase, $C_3(A,F)H_6$. In the presence of a larger dosage of lignosulfonate (2.5%) the formation of $C_3(A,F)H_6$ is retarded even up to 7 days. The hydrated products being amorphous can be detected by DTG or DTA and not by XRD.[43] In Fig. 18, the influence of sugar free lignosulfonate on the C_4AF hydration rate is shown. At a lower dosage (0.625%), lignosulfonate appears to be a slight accelerator, whereas at a higher dosage (2.5%) it retards the C_4AF hydration.[83] On the other hand, Lorprayoon and Rossington[43] found that even in the presence of a low amount of lignosulfonate (0.125%), hydration was retarded. They used commercial calcium lignosulfonate containing sugar and carried out hydration at a high water solid ratio of 20.

Lorprayoon and Rossington[43] also found that salicylic acid is a slightly more effective retarder than lignosulfonate for C_4AF hydration. Both admixtures cause a small increase in the specific area and inhibit the transformation of the amorphous hexagonal hydrates into the cubic phase.

The addition of a mixture of sodium carbonate and lignosulfonate blocks the C_4AF hydration;[83] the higher the percentage, the longer the induction period (Fig. 19). In addition, a strong reduction in the zeta potential of about -45 mV results. The strong retarding action and the dispersing effect, caused by the mutual repulsion due to negative values of zeta potential, may explain the liquefying effect of these admixtures.

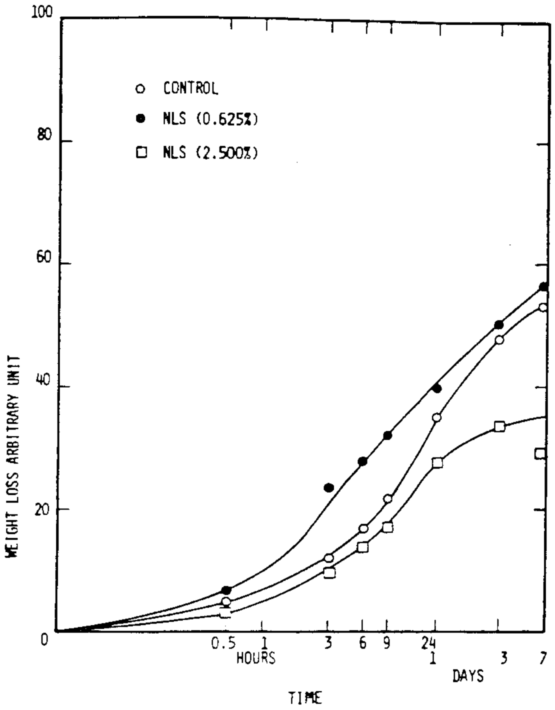


Figure 18. Influence of sugar-free sodium lignosulfonate (NLS) on C_4AF hydration.[83] *(© Pergamon Press, reprinted with permission.)*

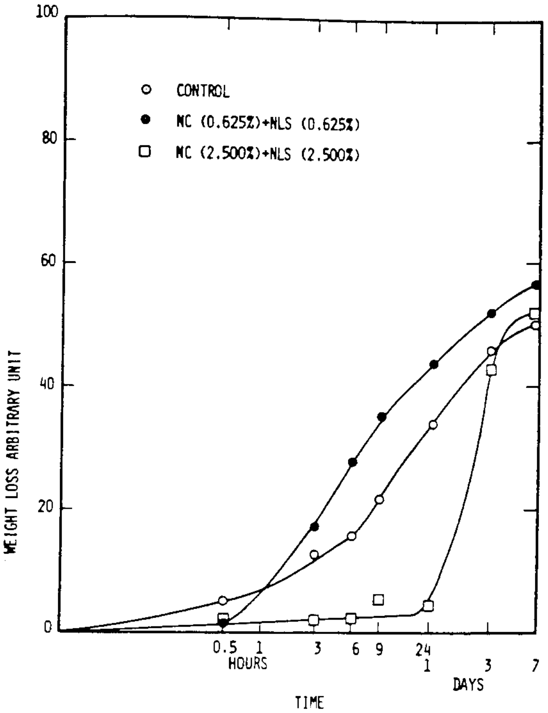


Figure 19. Influence of sodium carbonate (NC) sugar-free sodium lignosulfonate (NLS) mixture on C_4AF hydration.[83] *(© Pergamon Press, reprinted with permission.)*

Influence of Water Reducers/Retarders on the Hydration of C_3S. Tricalcium silicate hydrates to form a mixture of calcium hydroxide and calcium-silicate hydrate (C-S-H gel). The reaction can be represented approximately by Eq. 7. Details of the reaction are discussed in Ch. 1.

Eq. (7) $$C_3S + H_2O \rightarrow \text{C-S-H} + CH$$

The DTA and DTG thermograms of C_3S pastes exhibit two endothermal peaks at about 150 and 500°C, assigned to C-S-H and CH respectively. Another peak at about 800°C due to $CaCO_3$ occurs if CO_2 is not excluded during hydration.

The DTG curves (Fig. 20) indicate that in the presence of 0.3% sugar-free sodium lignosulfonate, the hydration of C_3S is completely inhibited for at least 14 days.[84] Ramachandran,[36] using conduction calorimetric techniques, found that, at 0.3% addition, commercial calcium lignosulfonate and sugar-free sodium or calcium lignosulfonate increase the so-called *induction period* from about 7 hours to 20–40 hours and found a lower hydration rate in the subsequent acceleratory period.[85] However, no inhibition of the C_3S hydration was found. The differences in the materials, conditions of hydration and techniques of measurements may explain this discrepancy. Milestone,[86] Young,[87] and Ramachandran[36][88] found that, in the presence of 0.5% to 0.8% commercial or sugar-free lignosulfonate, the C_3S paste hydration is stopped almost indefinitely. Seligmann and Greening,[58] and Milestone[86] concluded that the additions of small amounts of different types of calcium lignosulfonate admixtures (0.5%) to C_3S pastes retard the setting indefinitely, although some of these contained appreciable amounts of $CaCl_2$ and only small amounts of sugar and sugar acids. X-ray diffraction examination showed no indication of calcium hydroxide formation. In the presence of alkalis a delayed set ultimately occurred, and the effect of the admixture on the C_3S hydration approached that observed for portland cement. It seems that alkali reacts with lignosulfonate to destroy its inhibiting effect on the C_3S hydration.[58]

Smaller amounts of lignosulfonate, e.g., 0.1%, slightly retard or accelerate[36][86] the C_3S paste hydration depending on the chemical composition and molecular weight of the lignosulfonate (Fig. 21). Lignosulfonate fractions low in low-molecular weight organic molecules (such as sugar and sugar acids) act as slight accelerators, whereas lignosulfonate fractions high in low-molecular weight organic molecules delay the initiation of C_3S hydration rather than retard the hydration rate.[86] The induction period is prolonged from a few hours to 7 days, and at 10 days the degree of hydration is slightly higher than that of the control paste (Fig. 21). According to

Ramachandran[36] sugar-free lignosulfonate is as effective a retarder as a commercial lignosulfonate, whereas Milestone[86] has reported that lignosulfonate fractions not containing sugars cause as much delay as the corresponding lignosulfonate fractions containing sugars. Sugar acids rather than sugars seem to cause delay in the hydration of C_3S.

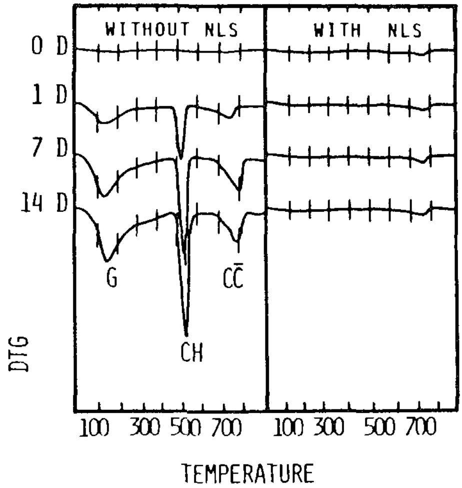


Figure 20. DTG curves for anhydrous and hydrated C_3S without and with 0.3% sugar-free sodium lignosulfonate.[84] G = C-S-H gel, C = CH, and CC = $CaCO_3$. *(© Pergamon Press, reprinted with permission.)*

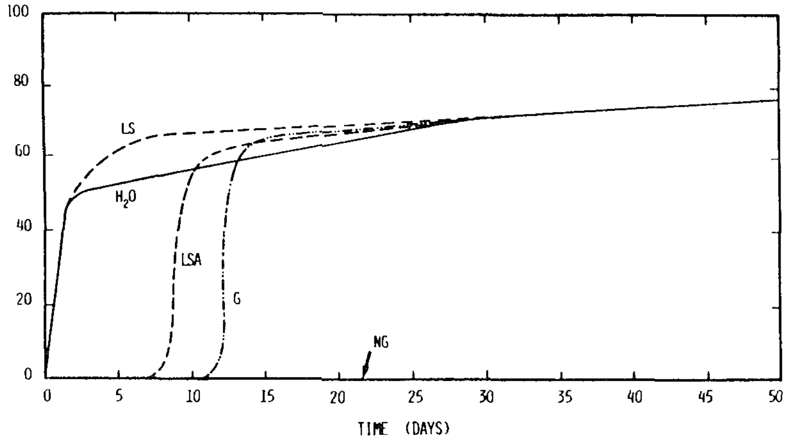


Figure 21. Influence of 0.1% glucose (G), sodium gluconate (NG) and lignosulfonate high or poor in sugar acids (LSA and LS respectively) on C_3S hydration.[86]

Addition of 0.1% glucose causes an initial delay in the C_3S hydration followed by slight acceleration, as found for lignosulfonate high in sugar acids.[86] However, the induction period is longer with glucose than with lignosulfonate (Fig. 21)

Salicylic acid, at a dosage of 0.125% is not found to retard the C_3S hydration significantly whereas the same dosage of calcium lignosulfonate retards the reaction rate during the initial 7 days.[43]

Addition of 0.1% sodium gluconate completely inhibits hydration up to 50 days (Fig. 21), whereas in smaller amounts, (0.01%) it accelerates the C_3S hydration rate after an induction period of 1–2 days.[86]

In the hydration of C_3S, as well as that of C_3A (see *Influence of Water Reducers/Retarders Other than Lignosulfonate on the Hydration of C_3A* earlier in this section), the retarding effect appears to be in the following decreasing order: sugar acids (such as gluconic acid) > carbohydrate (such as glucose) > lignosulfonate.

Hydration of C_3S in the presence of 0.1% glucose or lignosulfonate high in sugar acids or 0.01% gluconate, shows that before 7 days XRD does not reveal the presence of any hydration product (Fig. 21), and SEM shows that the surface of the C_3S particles is covered by a flaky C-S-H and not by the aciculae usually observed.[86] Only amorphous CH can be detected by DTA in this period. However, at later ages, SEM shows the presence of C-S-H aciculae similar to those formed in the absence of admixtures, and crystalline CH can be detected by both XRD and DTA.[86]

In C_3S suspensions (w/s = 20) containing no admixtures recrystallization of CH in the form of hexagonal plates and the crystal growth have been observed.[43] In the presence of large amounts of lignosulfonate (0.5%) transmission electron microscopy has shown the presence of crumpled foils of CSH around C_3S grains, up to 3 months of hydration, whereas the fibers or needle-forms of C-S-H appeared only as single particles.[89]

The heat evolution peak, occurring after the induction period, may be severely depressed by the addition of a mixture of Na_2CO_3 (2%) and lignosulfonate (1%). The conduction calorimetric techniques indicate a severe reduction in the hydration rate, but not complete inhibition in the initial stages according to Monosi et al.[84] Following hydration rate by means of DTA and DTG, for C_3S containing only 0.3% Na_2CO_3 + lignosulfonate, it can be concluded that hydration is inhibited for about 7 days (Fig. 22). In the presence of lignosulfonate only (0.3%), hydration is completely inhibited for at least 14 days. Thus it seems that the C_3S hydration is less retarded in the presence of sodium carbonate + lignosulfonate than in the presence of lignosulfonate alone. Analysis of the aqueous phase indicated lower Ca^{2+} and higher OH^- concentrations in the presence of both admixtures, than when only lignosulfonate was present. In the control sample the Ca^{2+} and OH^- concentrations were lower than those containing lignosulfonate.[47] On the other hand, the concentration of lignosulfonate in the aqueous phase of $C_3S + H_2O$ is much higher than that in the $C_3A + H_2O$ system.[47] Moreover, the lignosulfonate concentration in the liquid phase is much higher in the presence of Na_2CO_3 than in its absence. The effectiveness of the lignosulfonate-Na_2CO_3 combination may be due to the formation of an ionic complex between them.[47] It has been reported that in the mixture of Na_2CO_3 and lignosulfonate the zeta potential is higher than when lignosulfonate is used alone, especially for concentrations lower than 15 g/l.[84]

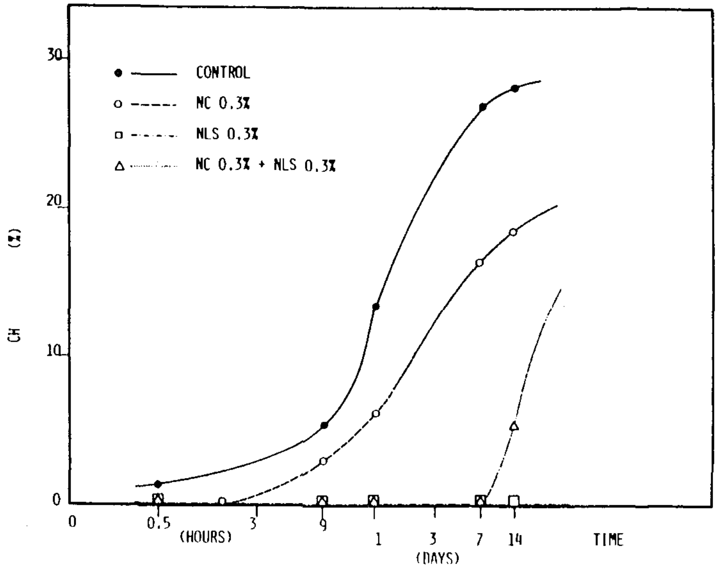


Figure 22. Amount of calcium hydroxide formed at different times in C_3S pastes with and without sodium carbonate (NC) and/or lignosulfonate (NLS).[84] *(© Pergamon Press, reprinted with permission.)*

The mechanism of the influence of lignosulfonate and other organic water-reducers on C_3S hydration is explained by four main theories.[63][64] Adsorption, precipitation and complex formation theories have already been described for the hydration of C_3A (see *Influence of Water Reducers/ Retarders Other than Lignosulfonate on the Hydration of C_3A* earlier in this section). The nucleation theory seems to be important to explain the effect of organic water reducers on the hydration of C_3S.[63][64][86]

Adsorption. Lignosulfonate does not adsorb on the anhydrous C_3S in a non-aqueous medium.[88] In the lignosulfonate-C_3S-H_2O system, Ramachandran found a steep increase in lignosulfonate uptake up to an initial concentration of about 1 g/l lignosulfonate (Fig. 23). This is due to the formation of larger amounts of C-S-H with a high specific surface area, as the hydration of C_3S is facilitated in the presence of low lignosulfonate concentration.[88] At lignosulfonate concentrations between about 1 and 3 g/l there is a decrease in the uptake value as the degree of hydration of C_3S is reduced. At concentrations above 3 g/l there is again a gradual increase in the amount of lignosulfonate uptake, although the hydration of C_3S seems to be substantially nil. Therefore, the gradual increase in the uptake value for concentrations above 3 g/l may be due either to a better dispersion of C_3S particles, which increases the surface available for lignosulfonate adsorption, or to the penetration of lignosulfonate molecules between the interlayers of the C-S-H phase.[88] This is confirmed by Milestone.[86]

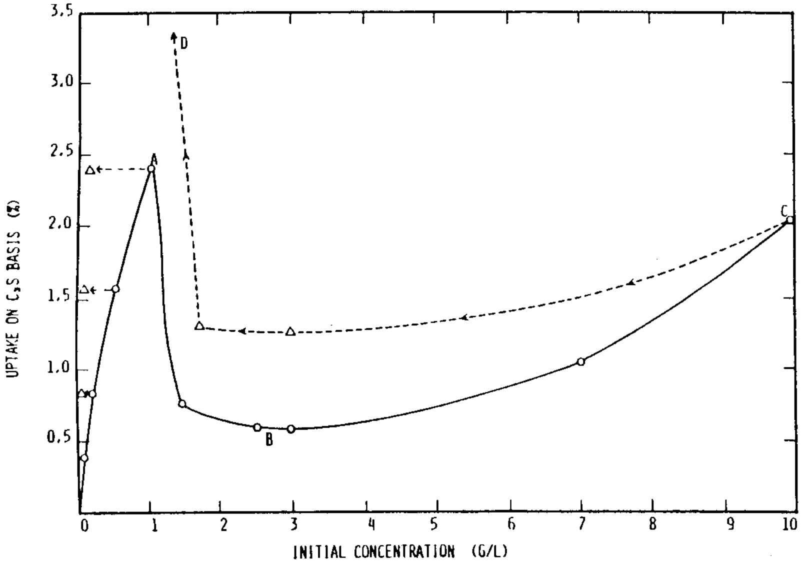


Figure 23. Adsorption of calcium lignosulfonate on C_3S in an aqueous medium.[88] *(© Pergamon Press, reprinted with permission.)*

On the desorption branches from points at low concentration levels there is a practically complete irreversibility of adsorption (Fig. 23), indicating that lignosulfonate is strongly adsorbed on the hydrated C_3S as a complex. Desorptions from points corresponding to an initial concentration of 5 g/l and beyond, show that there is some irreversibility in the amount of adsorption up to concentration levels of 1.5–2 g/l, thus confirming the existence of a surface complex involving lignosulfonate, H_2O and the ions on the surface of hydrating C_3S.[88] However, below concentration values of 1.5–2 g/l there is a steep and considerable increase in the lignosulfonate uptake on the desorption branch.[88] Figure 23 shows this desorption trend only from the point corresponding to the initial concentration of 10 g/l. The steep increase in the lignosulfonate uptake at a lower concentration than about 1.5–2 g/l may be ascribed to the formation of C-S-H and CH, since the C_3S hydration can start at a low lignosulfonate concentration.[88] This is confirmed by the fact that at concentration levels corresponding to the points A and D of Fig. 23, C_3S hydrates form C-S-H and CH, whereas no hydration product can be detected by means of DTA at concentration values corresponding to the points B and C of Fig. 23.[88]

Figure 24 shows the adsorption-desorption isotherms of lignosulfonate on a sample of completely bottle-hydrated C_3S.[88] There is a rapid initial adsorption of lignosulfonate followed by a much slower rate at concentrations higher than 0.5 g/l. The scanning desorption isotherms do not follow the adsorption isotherm, indicating the formation of increasing amounts of irreversibly adsorbed lignosulfonate as its concentration increases. A similar trend is evident in the isotherms using dimethyl sulfoxide (DMSO) as a solvent, but at any equilibrium concentration more lignosulfonate is adsorbed in the aqueous medium.[88] According to Ramachandran this is due to the fact that water disperses the C-S-H and CH particles better than DMSO and promotes penetration of lignosulfonate into the layer positions of the C-S-H phase. The indication that lignosulfonate not only chemisorbs on the C-S-H surface but also enters the interlayer positions, is confirmed by an exothermal effect at about 800°C in DTA.[88] XRD cannot be used to check the increase in the c-axis spacing in C-S-H unlike that in the hexagonal aluminates.[34][67] because C-S-H does not exhibit clear lines for the c-spacing.

In aqueous phase the amount of lignosulfonate adsorbed by CH increases with concentration. This may be due to dispersion of CH particles and to an increase in the physical and chemical interactions of lignosulfonate with CH.[88] The irreversible nature of the scanning desorption isotherm may indicate a chemical interaction between lignosulfonate and CH, whereas incomplete irreversibility at higher concentrations suggests a physical adsorption effect. An endothermal DTA peak at about 800°C of CH treated with lignosulfonate would confirm a partial chemical interaction.[88]

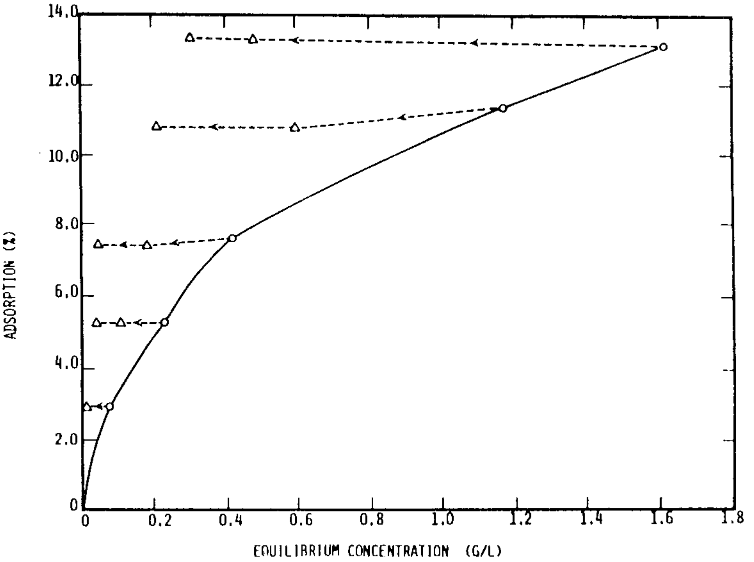


Figure 24. Adsorption-desorption isotherms of calcium lignosulfonate on completely hydrated C_3S in aqueous medium.[88] *(© Pergamon Press, reprinted with permission.)*

The above results confirm that lignosulfonate does not adsorb on C_3S, but only on its hydration products such as C-S-H and CH. It appears, therefore, that for C_3S and C_3A,[34] a retardation mechanism based on the adsorption of lignosulfonate on the C_3S particles should be altered in favor of the adsorption on the particles of hydrated products.

According to Ramachandran,[88] the influence of lignosulfonate on the C_3S hydration is mainly dependent on its concentration in solution and not on its proportion with respect to C_3S. It would seem that the C_3S hydration at early periods is inhibited in contact with a lignosulfonate solution of concentration above about 2.5 g/l. The retarding or inhibiting action of lignosulfonate would be related to the stability of the surface complex involving lignosulfonate, H_2O and the surface of the hydrating C_3S.[88] The higher the lignosulfonate concentration in the liquid phase, the higher the stability of the surface complex. According to this theory, C_3S hydration would proceed once the level of lignosulfonate has been reduced by adsorption on C-S-H or CH. This hypothesis necessarily implies that initial hydration does occur, at least to form a small amount of C-S-H and

CH. This theory cannot be directly applied to the effects occurring with the lignosulfonate-Na_2CO_3 combination.

Precipitation. This mechanism proposed by Suzuki and Nishi[71] has already been discussed for the C_3A hydration (see *Influence of Water Reducers/Retarders Other than Lignosulfonate on the Hydration of C_3A* earlier in this section). During the initial hours of hydration, C_3S releases Ca^{2+} ions into solution as rapidly as C_3A does. Therefore, if the reaction between Ca^{2+} and organic water-reducers producing insoluble salts were the main cause of the retardation of the hydration of C_3S and C_3A, this process, in the C_3S-C_3A-H_2O system, would be relatively independent of the C_3A/C_3S ratio. It is known however, that the retarding effect of organic water reducers increases by decreasing the C_3A/C_3S ratio.[63][64][87][88]

Complex Formation. At first contact with water C_3S releases calcium and silicate ions into solution. The retarding admixtures, such as sucrose and tartaric acid, increase the silica concentration in the liquid phase of the C_3S-H_2O system, whereas succinic acid, with no retarding action, causes negligible changes.[63] The complex formation in solution between Ca^{2+} and organic retarding admixtures may reduce the levels of Ca^{2+} although allowing the buildup of silicate ions as C_3S continues to dissolve.[86] Increase in the optical rotation of gluconate solution has been ascribed to the formation of a complex in the liquid phase.[76] Precipitation of this complex on the C_3S particles was explained as the cause for the decrease of the optical rotation. A complex involving the inorganic anion (silicate) rather than the calcium ion of C_3S, and hydroxyl and carboxylate groups of the admixture has been proposed. However, a complex between gluconate and Ca^{2+} with a stability constant of about 16 has been identified.[90] Complexes between Ca^{2+} and organic water reducers, such as gluconic acid and sugars can form.[90][91] Complex formation in solution would lower the concentration of Ca^{2+} in the liquid phase and reduce the growth of CH crystals, and thus contribute to the retarding effect.[86] However, complexing of Ca^{2+} in solution may not be an important factor, as the low stability constants of these complexes[90][91] and the low concentration cannot affect the relatively high levels of Ca^{2+} in the liquid phase.[63][90][91]

Nucleation. In the induction period, following the brief initial period of reactivity in the C_3S hydration, the rate-controlling factor is the diffusion of Ca^{2+} ions from the surface of hydrating C_3S into a liquid phase of increasing Ca^{2+} ion concentration.[64] The buildup of the C-S-H layer may be a diffusion barrier for the process.[92]

According to the hypothesis proposed by Greening and developed by Young,[63][64] silicate ions adsorb onto CH nuclei and poison their growth. Therefore, supersaturation with respect to CH is needed to overcome the poisoning effect. At the end of the induction period, when a certain level of supersaturation is reached, crystallization of CH and C-S-H occurs. Crystals of CH behave as calcium sinks and hence cause an increase in the C_3S hydration during the subsequent acceleratory period.[64] According to this theory, any compound that delays the nucleation and growth of CH would act as a retarder. The poisoning effect of organic admixtures could be ascribed to their ability to chelate with calcium on CH nuclei.[64] Most organic retarders have strong chelating property.[64] It has also been found[93] that organic admixtures affect the number of CH crystals in the C_3S paste hydration.[93]

Crystal growth of CH is delayed by lignosulfonate at concentration above about 2.5 ppm.[47] At a lignosulfonate concentration of about 200 ppm the crystal growth is completely inhibited. The retarding effect of lignosulfonate on C_3S hydration can therefore be ascribed to the delayed crystal growth of CH, the driving force for the early C_3S hydration. In the presence of effective retarders, the formation of relatively large amounts of amorphous CH has been attributed to the poisoning of the growth sizes on CH nuclei.

Sugar anions, such as gluconate are adsorbed on the positively charged C-S-H.[94] Consequently, not only the nucleation of CH, but also that of C-S-H aciculae may be prevented. Therefore in the presence of gluconate the sinks for both calcium and silicate ions in solution may be poisoned, and C_3S hydration is inhibited (Fig. 21).

Collepardi and Massidda[95]-[99] found that additions of relatively large amounts of alcohols, such as CH_3OH, C_2H_5OH, C_2H_7OH prolong the induction period and lower the C_3S hydration rate in the acceleratory period. They ascribe this retarding effect to the lower diffusion rate of Ca^{2+} ions from C_3S into the liquid phase and to the adsorption of alcohol molecules on C-S-H and CH. They also observed that alcohols cause a significant change in the morphology of C-S-H and appear to prevent the nucleation of C-S-H aciculae.[95] Thus it would seem that uncharged organic molecules, such as alcohols, poison the C-S-H nucleation sites.

Influence of Water Reducers/Retarders on the Hydration of C_3S in the Presence of C_3A. Adsorption of lignosulfonate on hydrated C_3A (Fig. 12) is of the same order of magnitude as that on hydrated C_3S (Fig. 24). However, C_3A during hydration adsorbs larger amounts of lignosulfonate from aqueous solution compared to hydrating C_3S.[47] This may be due to C_3A hydrating faster than C_3S. Therefore, in the C_3S-C_3A-H_2O system, hydrating C_3A may act as a sink for lignosulfonate. This is confirmed by Young,[87] Ramachandran,[35][39][88] and Monosi et al.[84]

Figure 25 shows the influence of 0.3% sugar-free sodium lignosulfonate on the paste hydration of C_3S (80%)-C_3A (20%) mixes.[84] A comparison of the thermograms in Figs. 20 and 25 shows that 0.3% lignosulfonate completely inhibits the hydration of C_3S in the absence of C_3A, at least within the first 14 days. The addition of 0.3% lignosulfonate to the C_3S-C_3A system blocks the C_3S hydration for more than 1 day (Fig 25).

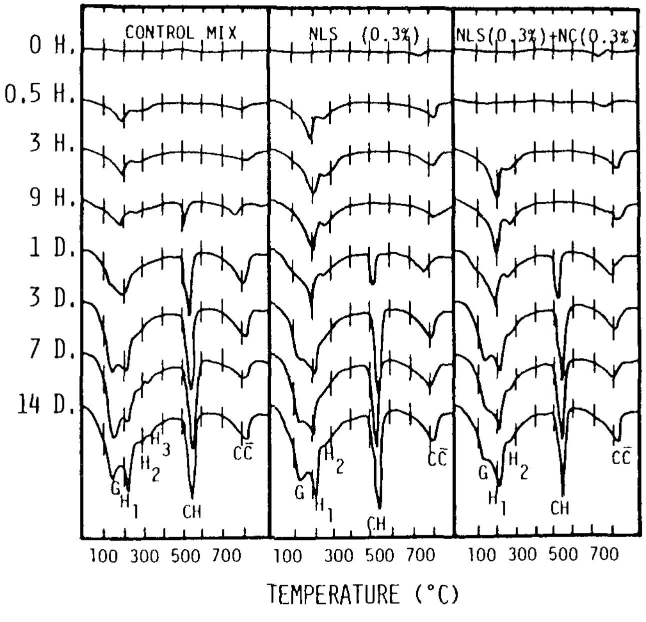


Figure 25. Influence of sodium lignosulfonate (NLS) and sodium lignosulfonate + sodium carbonate (NC) on the paste hydration of $C_3S(80\%)$-$C_3A(20\%)$ mixes.[84] G = C-S-H, H_1 and H_2 = first and second peaks for C_4AH_{13} and C_2AH_8, H_3 = C_3AH_6, CH = $Ca(OH)_2$, and $C\bar{C}$ = $CaCO_3$. *(© Pergamon Press, reprinted with permission.)*

At longer ages, such as 14 days, the amounts of C-S-H and CH in the mix with lignosulfonate appear to be almost the same as in the samples without admixture. No substantial change appears in the products of the

C_3A hydration whose rate seems to be slightly accelerated during the first hours of reaction, whereas the transformation of hexagonal hydrates into C_3AH_6 appears to be slightly retarded (Fig. 25).

Additions of C_3A destroy the strong retarding effect of lignosulfonate on C_3S hydration.[35][39][88] With larger amounts of lignosulfonate (0.5–1.0%) and lower amounts of C_3A,[87] the hydration of C_3A and in particular that of C_3S[35][39][88] may be delayed for longer periods than those shown in Fig. 25.

By increasing the percentage of lignosulfonate from 0.3 to 0.9% added to the C_3S (80%)-C_3A (20%) system, the hydration of C_3S can be inhibited for almost 1 day, whereas that of C_3A does not substantially change except for a slight retardation during the initial 30 min. Thus it appears that the higher the lignosulfonate/C_3A ratio, the less effective is the counteracting influence of C_3A.

The counteracting effect of C_3A is confirmed by the fact that the hydration of J alite ($C_{54}S_{16}AM$), containing about 3 to 4% C_3A, is less retarded by lignosulfonate than that of pure C_3S or M alite ($C_{302}M_{10}S_{101}A_2$) not containing C_3A.[87]

When C_3A is partially hydrated for 5 min before being mixed with C_3S,[87] or is replaced by the hexagonal aluminate hydrates,[39][88] a 5% addition is less efficient than 5% C_3A in destroying the retarding effect of lignosulfonate on the C_3S hydration. Similar results are obtained if the mixture of C_3S and C_3A (5%) is partly hydrated for a few minutes before lignosulfonate addition.[87] The addition of the cubic phase is practically ineffective in counteracting the inhibitive action of lignosulfonate on the C_3S hydration.[39][88] All these results clearly indicate that the relative amount of adsorption of lignosulfonate on the aluminate phase, which are in the decreasing order $C_3A > C_4AH_{13}$-$C_2AH_8 > C_3AH_6$ (see *Influence of Lignosulfonate on the Hydration of C_3A* earlier in this section), is the controlling factor for the action of lignosulfonate on the C_3S hydration.[39][88]

The combined effect of sodium lignosulfonate (0.3 %) and sodium carbonate (0.3%) in the C_3S (80%)-C_3A (20%) hydration (with respect to C_3S) is approximately similar to that of lignosulfonate, except for complete blocking of both C_3S and C_2A hydration for at least 30 minutes (Fig. 25). When higher dosages of both lignosulfonate and carbonate are used (0.9%) a longer induction period (1 day) occurs in the hydration of both C_3S and C_3A.[84]

The influence of other organic water reducers such as glucose and sodium gluconate, at additions of 0.1–0.3% on the C_3S hydration in the C_3S (80%)-C_3A (20%) system appears to be similar to that of lignosulfonate, except for a more effective retarding action of sodium gluconate.[99]

The effect of pure water reducers, such as desugarized sodium lignosulfonate, glucose or sodium gluconate on the C_3S hydration in the C_3S (77%)-C_3A (19%)-$CaSO_4$•$2H_2O$ (4%) system is shown in Fig. 26.

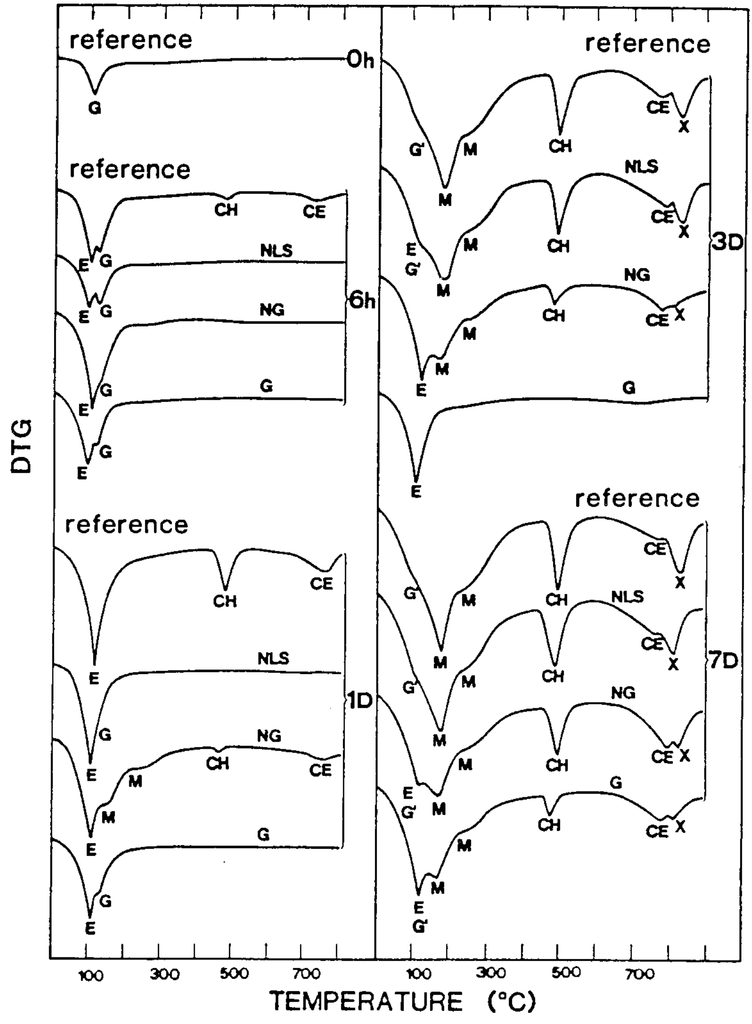


Figure 26. Influence of 0.3% sugar-free sodium lignosulfonate (NLS), glucose (G) or sodium gluconate (NG) on the paste hydration of the C_3S(76%)-C_3A(19%)-$CaSO_4$•$2H_2O$(5%) system by DTG. E = ettringite, M = monosulfonate, CH = calcium hydroxide, and G′ = C-S-H gel.[99]

Gluconate and in particular glucose stabilize ettringite and retard its conversion into monosulfate, although initial ettringite production (6 hours) seems to be accelerated.

The CH formation appears to be inhibited for about 1 day by 0.3% lignosulfonate or gluconate and for 3 days by 0.3% glucose.

Thus, the effect of these admixtures on the hydration of C_3S alone (Figs. 20, 21) seems to be much more in terms of hydration than that in the presence of C_3A and $CaSO_4 \cdot 2H_3O$ (Fig. 26). The hydration products of C_3A (ettringite and monosulfate) could adsorb admixtures and reduce their influence on the C_3S hydration. The retarding effect on the C_3S hydration appears to be in the following decreasing order: glucose > gluconate > lignosulfonate. This could result from the effect of the admixture on the C_3S hydration rate (see *Influence of Water Reducers/Retarders on the Hydration of* C_3S earlier in this section) and the amount of admixture adsorbed on ettringite or monosulfate.

Influence of Water Reducers/Retarders on the Hydration of C_2S. Salicylic acid (0.125%) retards the C_2S hydration at a high water-solid ratio.[43] Commercial calcium lignosulfonate (0.125%) has a better retarding effect so that no substantial hydration occurs up to 7 days. Recrystallization of $Ca(OH)_2$ in the form of hexagonal plates was not observed even at 30 days.[43]

Collepardi et al.[99] found that although sugar-free sodium lignosulfonate (0.3%) also retards the C_2S hydration, it does so to a lower extent than the commercial lignosulfonate (Fig. 27). Lignosulfonate is more effective in retarding C_3S hydration than that of C_2S (Fig. 22).

The combined action of sodium carbonate (0.3%) and lignosulfonate (0.3%) on C_2S hydration is much less effective than that of lignosulfonate (Fig. 27) and this effect is similar to that observed for the C_3S hydration (Fig. 22). Odler et al.,[100] found that a combination of sodium lignosulfonate (1%) and sodium carbonate (1%) was better than lignosulfonate in fluidifying a C_2S paste.

Influence of Water Reducers/Retarders on the Hydration of C_2S in the Presence of C_3A. Collepardi et al.[99] found that 0.3% lignosulfonate is much less effective in retarding the hydration of C_2S in the presence of 20% C_3A (Fig. 27). Hydrating C_3A may act as a sink for lignosulfonate so that the concentration of the admixture in the aqueous phase decreases and the C_2S hydration is not significantly retarded. Similar results have been obtained for the C_3S-C_3A system.

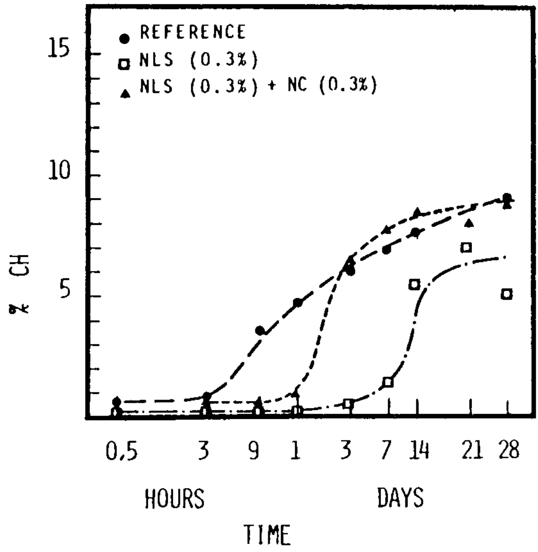


Figure 27. Influence of sodium lignosulfonate (NLS) and sodium lignosulfonate + sodium carbonate (NC) on C_2S hydration.[89] *(© Pergamon Press, reprinted with permission.)*

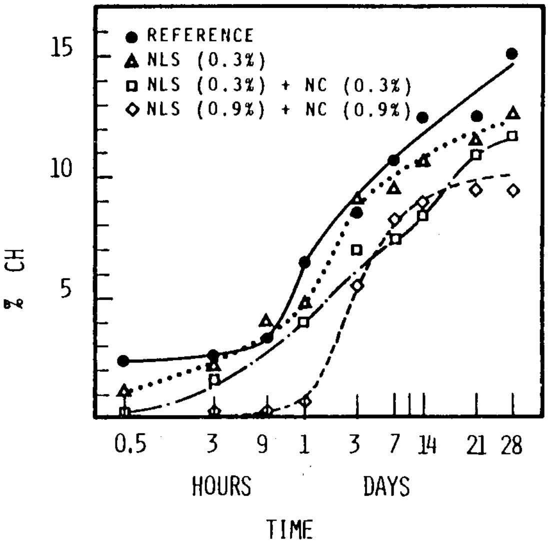


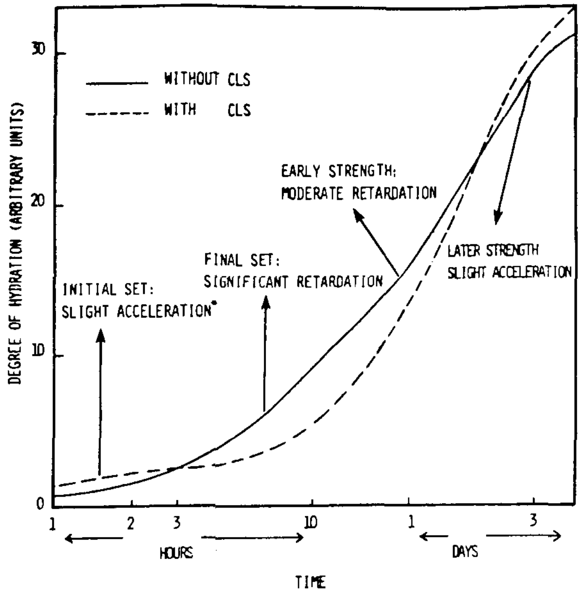
Figure 28. Influence of sodium lignosulfonate (NLS), or sodium lignosulfonate + sodium carbonate on the paste hydration of C_2S in the presence of 20% C_3A.[99]

The mixture of Na_2CO_3 (0.3%) and lignosulfonate (0.3%) retards the C_2S hydration in the presence of C_3A (Fig. 28) to a lesser extent than does lignosulfonate and this effect is different from that observed for the hydration of C_2S alone (Fig. 27). Higher dosages (0.9%) of both Na_2CO_3 and lignosulfonate, are required to inhibit the C_2S hydration for a longer time (Fig. 28). In the C_2S-C_3A system, the hydration of C_3A is blocked for only 30 minutes in the presence of 0.3% lignosulfonate and carbonate, and for 1 day in the presence of 0.9% of both admixtures.[99]

Influence of Lignosulfonate on Portland Cement Hydration. The effect of lignosulfonate on the portland cement hydration is very complex as the cement components can affect each other during their hydration. Thus, the influence of the admixture on cement hydration depends on the composition, and in particular on C_3A, alkali and sulfate contents. Other parameters are surface areas, lignosulfonate composition, molecular weight, sugar content, dosage of admixture and mixing procedure. All the above parameters are not always reported in the literature, so that it is difficult to explain the variable results that have been sometimes obtained under apparently similar conditions. In general, lignosulfonate at normal dosages (0.2–0.3% by weight of cement) and at the same w/c ratio causes: *(a)* slight retardation or acceleration of the initial set depending on the composition of cement and admixture; *(b)* retardation of final set as well as early strength development; *(c)* slight increase in strength at later ages. Figure 29 schematically shows the effect of commercial lignosulfonate on hydration, setting times and strength of portland cement.

(a) Very Early Hydration (Initial Setting). In cements, sodium lignosulfonate addition results in a very early acceleration of C_3A hydration, according to Eq. 3, because of the absence of CH in solution.[58] Lignosulfonate inhibits the release of CH from the C_3S hydration and, at the same time, the highly alkaline solution reduces the solubility of any CH present (see *Influence of Water Reducers/Retarders on the Hydration of C_3S in the Presence of C_3A* earlier in this section).

Collepardi et al.,[11] using high alkali (K_2O—1.2% and Na_2O—0.3%) cements, found that, at 0.2% addition, commercial calcium lignosulfonate containing sugars accelerates the C_3A hydration and inhibits the C_3S hydration during the first 2–3 hours (Table 9). Assuming that C_4AF behaves similar to C_3A and that the C_2S hydration is negligible during the first few hours, it could be concluded that the addition of lignosulfonate may accelerate the initial set of portland cement with high aluminate/C_3S ratios, and may retard the initial set of cements with low aluminate phase/C_3S ratios (Table 10). Khalil and Ward,[101] found that in the presence of sugar-free calcium lignosulfonate (0.28%), the usual immediate retarding effect of gypsum on the C_3A hydration does not occur. As a consequence, more heat evolves in the first few hours compared to that for the lignosulfonate-free cement paste.[101][102]



*Sugar-free lignosulfonate generally retards initial set particularly of low-alkali cements.

Figure 29. Effect of commercial calcium lignosulfonate (CLS) (0.2–0.3%) on the degree of portland cement hydration, setting, and strength.

Table 9. Hydration of Portland Cement ($C_3S \cong 60\%$; $C_3A \cong 6\%$) without and with Calcium Lignosulfonate[11] (© Il Cemento, *reprinted with permission.)*

	Relative X-ray line intensity		Relative X-ray line intensity	
Time	C_3S		C_3A	
(hours)	without CLS	with CLS	without CLS	with CLS
0	100	100	100	100
2	95	100	90	80
12	75	90	30	75
24	60	70	20	60
72	50	40	10	50

Table 10: Effect of 0.2% Commercial Calcium Lignosulfonate (CLS) on the Setting Times of Portland Cement Pastes with Different Aluminate Phase/C_3S Ratios[11] *(© Il Cemento, reprinted with permission.)*

$(C_3A + C_4AF)/C_3S$	Initial setting time (min)		Final setting time (min)	
Weight Ratio	without CLS	with CLS	without CLS	with CLS
$\frac{2 + 11.5}{70} = 0.19$	200	270	351	660
$\frac{3 + 11}{61} = 0.23$	231	189	411	735
$\frac{6 + 8.5}{60} = 0.24$	171	150	315	555

Ramachandran's data seem to contradict the results obtained by Khalil and Ward,[101][102] as he found that sugar-free calcium or sodium lignosulfonates retard the initial set.[36] Ordinary portland cement of low alkali type used by Ramachandran could partly explain this discrepancy. In addition, Ramachandran[36] used pure sugar-free lignosulfonates, whereas Khalil and Ward[101][102] utilized a formulated admixture containing sugar-free lignosulfonate and an accelerating agent.

Commercial calcium lignosulfonate at higher doses (0.3–0.5%) can cause quick set. This can be ascribed to the presence of sugar, as quick set is not observed with high doses, such as 0.3 to 0.5% of sugar free lignosulfonate.[36] For example, quick set is observed by using carbohydrate admixtures, such as sucrose and corn syrup.[58][103] The very early acceleration in the cement hydration which sometimes occurs with high alkali cements in the presence of normal doses of commercial lignosulfonate (Table 10) or sugar-free lignosulfonate[101][102] can be explained by a mechanism (see *Influence of Lignosulfonate on the Hydration of C_3A Containing Gypsum* and *Influence of Water Reducers/Retarders on the Hydration of C_3S in the Presence of C_3A* earlier in this section) different from that for the quick set observed with normal doses of carbohydrates[58][103] or high doses of commercial lignosulfonate containing sugar (see *Influence of Water Reducers/Retarders Other than Lignosulfonate on the Hydration of C_3A Containing Gypsum* earlier in this section, and *Influence of Water Reducers/Retarders Other than Lignosulfonate on Portland Cement Hydration* later in this section). A delayed addition of the admixture causes a decreased sorption with the elimination of early acceleration.[81] As a result, the higher concentration of the admixture in the liquid phase causes a greater retarding effect of all hydration stages than that which can be produced by addition with the mixing water.[58]

Some examples of abnormal early stiffening of cement-mixes containing water-reducing admixtures have been reported.[30][104][405] This effect can be ascribed to two distinct causes:[58] *(a)* acceleration of the early C_3A hydration, according to Eq. 3, causing flash set, and *(b)* retardation of the gypsum precipitation caused by lignosulfonate inducing false set in an otherwise normally setting cement. In flash set, stiffening is not reduced by further agitation, and an increase in sulfate content becomes necessary. On the other hand, in instances of false set caused by lignosulfonate, further agitation restores workability.

Kalousek[105] studied many cements showing abnormal setting with or without lignosulfonate and hydroxylated carboxylic acid. Cements were divided into four groups depending on the effect of admixtures. Group I had normal setting without admixture and false setting with 0.3% of admixtures. The addition of admixtures increased the amount of ettringite between 3 and 20 min, accounting for the false set. Group 2 showed false setting without admixtures and normal setting with 0.3% admixtures. No substantial change was caused by admixtures in gypsum recrystallization or ettringite precipitation between 3 and 20 minutes. This false setting, assumed to be of thixotropic nature, was ascribed to the interaction of opposite surface charges on cement grains induced by aeration. The adsorption of admixtures probably induced the same charge on all phases of the cements. Group 3 exhibited false setting with or without admixtures. False set in the absence of admixtures was largely due to gypsum crystallization from hemihydrate, although ettringite also had precipitated between 3 and 20 min. In the presence of admixtures a larger amount of ettringite precipitated, with gypsum crystallization. The behavior of Group 4 was similar to that of Group 3 except for gypsum crystallization which did not occur in the presence of admixtures possibly because of the rapid reaction of SO_4^{2-} ions from solution to form ettringite.

(b) Early Hydration (Final Setting up to 1 Day). The very early hydration period (2–3 hours), during which cement hydration in the presence of lignosulfonate can be accelerated or retarded depending on the many parameters, is always followed by a significant retardation up to about 1 day. Table 9 shows that lignosulfonate retards significantly both C_3S and C_3A hydration up to 24 hours. The final set is therefore retarded by the admixture (Table 10). Khalil and Ward,[101][102] and Ramachandran[36]

found that the early cement hydration is retarded by both sugar-free and commercial lignosulfonates (0.1–0.5%) and that the retarding effect is proportional to the amount added.

The influence of lignosulfonate on the hydration of C_3A in the presence of gypsum (see *Influence of Lignosulfonate on the Hydration of C_3A Containing Gypsum* earlier in this section) can explain these effects. As soon as ettringite is produced, it strongly adsorbs the organic molecules.[38] As a result, the C_3A hydration process is significantly retarded because of the retardation in the conversion of ettringite to monosulfate.[36][38] In addition, the lignosulfonate concentration in the liquid phase remains at such a level that the C_3S hydration is also retarded (see *Influence of Water Reducers/Retarders on the Hydration of C_3S*, and *Influence of Lignosulfonate on the Hydration of C_3A Containing Gypsum* earlier in this section). As a result, not only the final set, but also the early strength at 1 day is retarded (Fig. 29).

In the presence of sugar-free sodium lignosulfonate (0.14–0.28%), the degree of hydration between 3–4 hours and 1–2 days is lower for ordinary portland cement (Type I) than for low-C_3A content cement (Type V).[102] This can be ascribed to a higher adsorption of lignosulfonate by Type I cement, containing a larger amount of C_3A (see *Influence of Lignosulfonate on the Hydration of C_3A* and *Influence of Lignosulfonate on the Hydration of C_3A Containing Gypsum*), leaving smaller amounts of lignosulfonate to influence C_3S hydration (see *Influence of Water Reducers/Retarders on the Hydration of C_3S in the Presence of C_3A*). These results explain why water-reducing admixtures promote better performance and longer setting times in cements with lower C_3A and alkali contents.[106]

Extreme retardation of set in cements containing low amounts of both SO_3 and C_3A in the presence of lignosulfonate[107]-[109] is ascribed to insufficient sulfate in the cement to retard the deleterious effect of the ferrite phase on setting and early strength.[105] Without an admixture C_4AF reacts with gypsum, producing an F-rich ettringite so that these cements set normally. If insufficient sulfate is present, C_4AF releases ferric oxide gel which deposits on the hydrating C_3S and C_2S, strongly retarding both setting and strength.[110] Apparently, lignosulfonate retards the F-rich ettringite production by favoring the ferric gel formation.[105] Crepaz and Raccanelli[111] concluded that extended retardation of clinker hydration in the presence or in the absence of lignosulfonate is related more to reaction of the ferrite phase than to the retardation of the C_3S hydration. An alternative explanation can be based on the lower adsorption of lignosulfonate[53][58] on hydrating C_4AF in comparison with that on C_3A (see

Influence of Water Reducers/Retarders on the Hydration of C_4AF) so that at a higher concentration, the admixture[88] would retard the C_3S hydration (see *Influence of Water Reducers/Retarders on the Hydration of C_3S*) more effectively. The extreme retardation caused by the addition of lignosulfonate to portland cements with a low content of SO_3 and C_3A can be offset by increasing the amount of gypsum at the cement plant and/or decreasing the admixture dose at the concrete batching plant.[101] Low alkali cements can also cause extreme retardation[58] and hence a lower amount of lignosulfonate should be used.

Collepardi et al.[11] found that the 1-day strength of portland cement mortars at a given w/c ratio is reduced by adding 0.2% of a commercial lignosulfonate (Fig. 30). These results are similar to those obtained by Khalil and Ward.[101] Lignosulfonate is not very effective in reducing the degree of hydration (1-day) for cements with a high SO_3 content.[101] This could be related to the less retarding effect of lignosulfonate on the C_3A-gypsum-H_2O system (see *Influence of Lignosulfonate on the Hydration of C_3A Containing Gypsum*) than on the C_3A-H_2O system (see *Influence of Lignosulfonate on the Hydration of C_3A*).

(c) LaterHydration (1 Day and Later). Table 9 shows that at 72 hours the XRD peak intensity of C_3S is lower in cement containing lignosulfonate than in the admixture-free sample. These results show that the C_3S hydration, in the presence of C_3A or C_3A and gypsum (see *Influence of Water Reducers/Retarders on the Hydration of C_3S in the Presence of C_3A*) is initially retarded by lignosulfonate. However, at later ages hydrating C_3A adsorbs large amounts of lignosulfonate, so that the admixture concentration in the aqueous phase becomes so low, that C-S-H and CH nuclei are no longer poisoned. Therefore C_3S hydration is facilitated, possibly because of a better dispersion of cement particles (see *Influence of Water Reducers/Retarders on the Hydration of C_3S*). The time at which retarding effect changes to acceleration of C_3S hydration, depends on the fineness and composition of cement and on the type and amount of lignosulfonate. Cements with low specific surface area have the inversion point at later ages, particularly in the presence of relatively high dosages of commercial lignosulfonate. For ordinary portland cement the non-evaporable water is reduced in the presence of lignosulfonate (0.28%) at early ages, whereas at later ages (2–3 days) it is greater than for the control mix.[102] Using a cement with a low C_3A content, the inversion from a retarded to an accelerated stage of cement hydration, occurs after 10 days.[17][102][112]

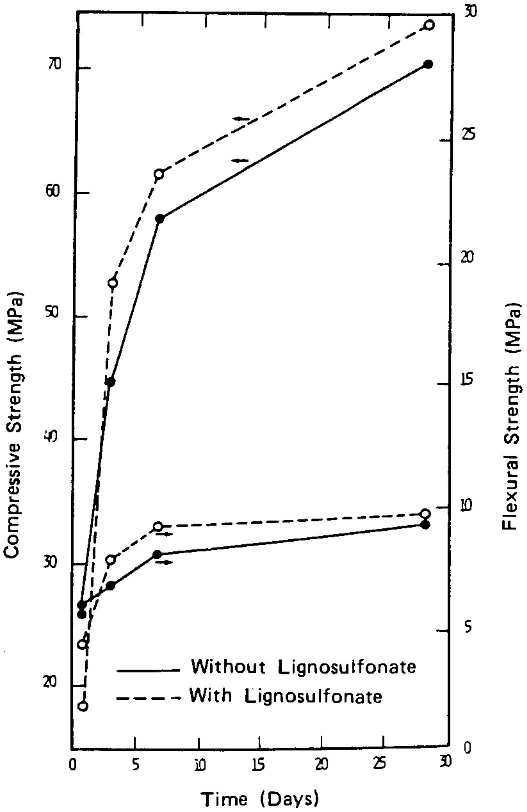


Figure 30. Compressive and flexural strengths of portland cement mortars at a given w/c ratio (0.50) with and without 0.2% commercial calcium lignosulfonate.[11] *(© Il Cemento, reprinted with permission.)*

Strength results at later ages (Fig. 30) agree with those of cement hydration schematically shown in Fig. 29.[11] After three days, compressive and flexural strengths are higher in mortars with commercial lignosulfonate (0.2%) than in control mixes. Similar results have been obtained[11] in ordinary and low C_3A portland cement both with a relatively high surface area (~ 4500 cm^2/g). With a low-C_3A portland cement, a reduction in 1- and 3-day compressive strengths has been observed.[101] Use of cement with lower fineness (3160 cm^2/g) may have been responsible for this observation. Sometimes lignosulfonate may not cause an increase in strength at later ages due to entrainment of air.[113]

Morphology and microstructure of portland cement pastes are not substantially altered by the presence of lignosulfonate, except that at longer ages the structure is slightly more dense in the presence of admixture.[114][115] This seems to be related to a better dispersion of cement particles in the presence of lignosulfonate. Ramachandran[113] found that, at the time of set, the mortar containing calcium lignosulfonate (0.1%) had a smaller amount of hydrated product than that in the plain mix. This confirms that the cement paste in the presence of admixture is better dispersed and forms a more dense structure.

Influence of Lignosulfonate-Carbonate Mixture on Portland Clinker or Cement Hydration. The combined effect of lignosulfonate (0.5–1%) and alkali carbonate or bicarbonate (0.5–1%) on portland clinker pastes (in the absence of gypsum) has been studied extensively.[100][116]-[120] A significant reduction in the w/c ratio can be achieved in clinker pastes. However, at a given w/c ratio, the strength of the clinker-lignosulfonate-carbonate system at 28 days is somewhat lower than that of the corresponding portland cement paste.[110] At 1 day the combined addition of lignosulfonate and carbonate strongly reduces strength, particularly in the presence of a larger amount of lignosulfonate.[110]

Strength development of concrete is even more strongly retarded by the combined addition of admixtures, so that steam-curing has to be used to obtain high early strength even with a w/c ratio as low as 0.26.[121] This could be ascribed to a weaker bond existing between the clinker paste containing the admixture and the aggregate.[121]

Although the reduction in the w/c ratio caused by the lignosulfonate-alkali carbonate system is very high, this admixture has not yet been used practically because of the lower strength development with respect to that performed by sulfonated naphthalene or melamine superplasticizers (Ch. 7). On the other hand, because of the relatively high dosage, the lignosulfonate-alkali carbonate admixture appears to be much more expensive than the traditional water reducers. Moreover, because of the high alkali content, this admixture could promote the alkali-aggregate reaction to a greater extent than other low-alkali and/or low dosage admixtures.

The combined addition of lignosulfonate and carbonate prevents flash setting of the portland clinker paste and strongly increases its fluidity at a given w/c ratio.[108] Odler et al.[116] found that additives control setting without any substantial change in the initial hydration rate of the clinker and in particular in that of C_3A. Collepardi et al.[40][42] found that the lignosulfonate and carbonate combination completely inhibits the hydration of pure C_3A, but does not affect the induction period in the hydration of the C_3A-Na_2O solid solution (Fig. 11). Differences described above are due to C_3A in portland clinker occurring in the form a C_3A-Na_2O solid solution.[120] Similar results have been obtained on the effect of gypsum on the hydration of the pure C_3A,[122] and C_3A-Na_2O solid solution,[43] both in the presence of CH and C_3A.[123] It seems that gypsum retards the hydration of pure C_3A but does not affect significantly the hydration rate of the C_3A-Na_2O solid solution and that of C_3A in portland clinker. According to Odler et al.,[120] the lignosulfonate-carbonate system controls setting by reacting with the clinker surface and, hence, prevents the clinker particles from an excessive aggregation which should result in the loss of plasticity of the paste. A similar mechanism has been proposed by Locher et al.[123] to explain the effect of gypsum on the setting of portland cement. Figure 31 shows the dispersing effect of the lignosulfonate-carbonate system of clinker particles.

The combined addition of lignosulfonate and carbonate causes a significant change also in the hydration of ordinary portland cement (in the presence of gypsum). Three heat evolution peaks, separated by two induction periods have been observed and these are explained by the formation of a highly anionic complex between lignosulfonate and CO_3^{2-} that should be a better dispersant than lignosulfonate. The lignosulfonate concentration in the aqueous phase of the cement paste is found to be much higher in the presence of Na_2CO_3 than in its absence.[47]

The exact mechanism of the lignosulfonate-carbonate mixture on the hydration of portland clinker and cement, as well as on the liquefying effect on the pastes, is still not completely understood.

Influence of Water Reducers/Retarders Other than Lignosulfonate on Portland Cement Hydration. *Organic Compounds.* The effect of carboxylic acids, such as gluconic acid, and carbohydrates such as glucose or sucrose, on portland cement hydration is very similar to that of lignosulfonate (see *Influence of Lignosulfonate-Carbonate Mixture on the Portland Clinker or Cement Hydration*) although different percentages of admixtures are required to obtain comparable effects.

In general these water reducers retard both the very early hydration (initial setting) and early hydration (final setting and 1-day strength) of portland cement, whereas they increase the degree of hydration at later ages. However, in some cases an acceleration of the very early hydration promoted by carboxylic acids or carbohydrates, cause quick set or early stiffening.

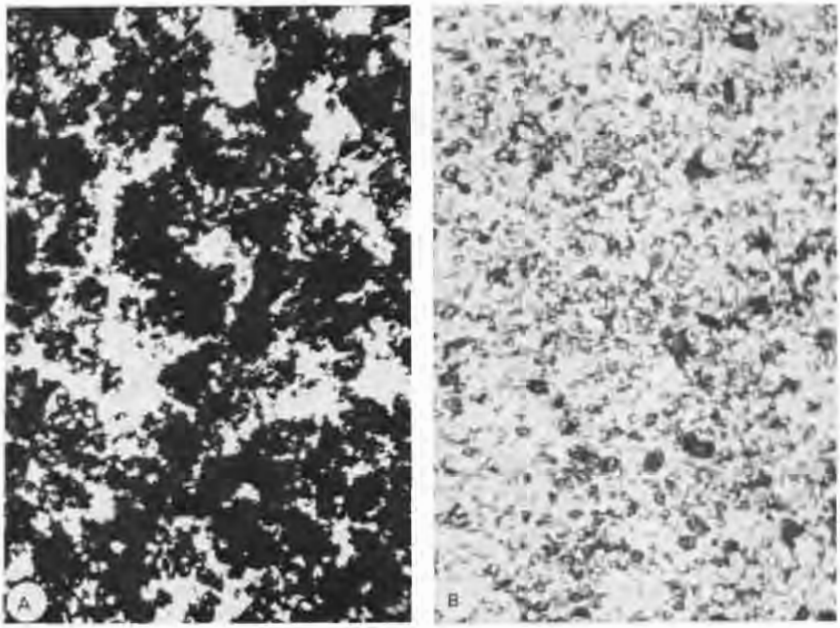


Figure 31. Dispersion of clinker particles by the combined addition of sodium lignosulfonate (1%) and Na_2CO_3 (1%). *(A)* without addition, and *(B)* with addition.

(a) Very Early Hydration. Ramachandran[113] found that, for a given percentage sodium gluconate, citric acid and in particular sucrose are better retarders of initial set of a normal low-alkali portland cement than calcium lignosulfonate, salicylic acid, sodium heptonate or boroheptonate. It is known that aluminate and sulfate contents of portland cements determine the retarding ability of organic water reducers. It has been found that hydroxycarboxylic acids retard setting times of cement pastes, containing low-alkali, low-C_3A cements more effectively than those of cement pastes with higher alkali and C_3A contents (Table 11). Similar retarding effects have also been found in heats of hydration. High-alkali content causes a lower concentration of $Ca(OH)_2$ in the liquid phase, and high-C_3A content reduces the concentration of the admixture in solution because of higher amounts of adsorption on hydrated aluminates. Both effects result in a less effective retarding action of hydroxycarboxylic acids on the hydration of C_3A and C_3S.

Table 11. Setting Times of Cement Pastes and Stiffening of Concrete Mortars without and with Admixtures on Hydroxycarboxylic Acids[106] *(© ASTM, reprinted with permission.)*

Cement	Alkali as Na_2O (%)	Admixture ml/kg of cement	Initial Set of paste* (hr)	Initial set of concrete mortar** (hr:min)
A	0.87	-	7	6:30
A	0.87	2.78	12	9:24
A	0.87	3.48	17	11.00
B	0.56	-	7	6:06
B	0.56	2.78	25	9-54
B	0.56	3.48	49	12:12

*Vicat test.

**Proctor penetration test: mortar was wet-screened from concrete mix (19 mm maximum size aggregate) on No. 4 sieve.

Quick setting has been experienced with white cements (with a low SO_3 content) containing a carbohydrate type admixture.[103] Similar results have been obtained using a high-alkali Type III portland cement in the presence of sugar.[124] According to Green.[103] in the presence of these admixtures the consumption of SO_3 is accelerated, so that insufficient SO_3 remains in the liquid phase for properly controlling the C_3A hydration. Figure 26 seems to confirm that at a high C_3A/gypsum ratio, water reducers accelerate the ettringite formation. A similar explanation can be offered for the acceleration by sucrose on Stage I hydration of portland cement.[58] (see *Influence of Water Reducers/Retarders Other than Lignosulfonate on the Hydration of C_3A Containing Gypsum*). The quick setting problem for white, as well as for grey Type I cements, may be solved by increasing the SO_3 content.[103][124] Factors other than SO_3 content, such as the hydration state of calcium sulfate, may be involved in quick setting in the presence of organic water reducers.[103]

It has also been found that 0.1% sugar accelerates initial set and retards final set of a high-C_3A, high-alkali Type I portland cement.[125] At 0.2–0.3% addition of sugar flash setting occurs. This stiffening is accompanied by a more rapid formation of a fine network of ettringite crystals.

As for lignosulfonate, early acceleration effect can be avoided[50][74] by delayed addition of organic water reducers; thus the retarding effect on both initial and final set increases markedly (see *Influence of Water Reducers/Retarders Other than Lignosulfonate on the Hydration of C_3A Containing Gypsum*).

The influence of hydroxycarboxylic acids on the false set of portland cement is very similar to that of lignosulfonate[105] (see *Influence of Lignosulfonate-Carbonate Mixture on Portland Clinker or Cement Hydration*). Seligmann and Greening[58] found that as small an amount as 0.05% sucrose prevents the premature stiffening of the paste when false-setting cement is used. This effect was ascribed to the acceleration of Stage I hydration (see *Influence of Water Reducers/Retarders Other than Lignosulfonate on the Hydration of C_3A Containing Gypsum*), so that the rate of removal of SO_4^{2-} ion from the liquid phase is increased and gypsum precipitation is prevented. On the other hand, sucrose is ineffective in preventing false set caused by the aeration of cement. Aeration is assumed to produce an inactivation of the C_3A surface, so that sucrose is unable to reactivate the aerated C_3A surface.

(b) Early Hydration. Final set and early strength, are retarded in the presence of 0.01% organic water reducers, and this effect is independent of their influence on initial set. These effects are related to the retardation of portland cement hydration at early ages.[126] The early hydration of C_3S is retarded (see *Influence of Water Reducers/Retarders on the Hydration of C_3S* and *Influence of Water Reducers/Retarders the Hydration of C_3S in the Presence of C_3S*) by the addition of glucose or sodium gluconate (Fig. 21), and this results in the retardation of final set and decrease of early strength of portland cement mixes.[46] Figure 32 indicates that 0.05% sucrose or 0.1% sodium gluconate slightly reduces compressive strength at 1 day; 0.2% should be more effective.

(c) Later Hydration. Glucose, gluconate, and lignosulfonate increase the degree of C_3S hydration at longer ages (Fig. 21), even though they are retarders for the early hydration (*Influence of Water Reducers/Retarders on the Hydration of C_3S*). The larger the C_3A amount, the earlier the inversion point from retardation to acceleration of C_3A hydration (*Influence of Water Reducers/Retarders on the Hydration of C_3S in the Presence of C_3A*). In the presence of a hydroxylated polymer (0.2%) the degree of hydration of portland cement at 3 and 7 days appears to be slightly higher than that in the absence of the admixture.[127] These results, which are very similar to those found with lignosulfonate (*Influence of Lignosulfonate-Carbonate Mixture on Portland Clinker or Cement Hydration*), can explain the increase in strength at later ages caused by sucrose and gluconate (Fig. 32).

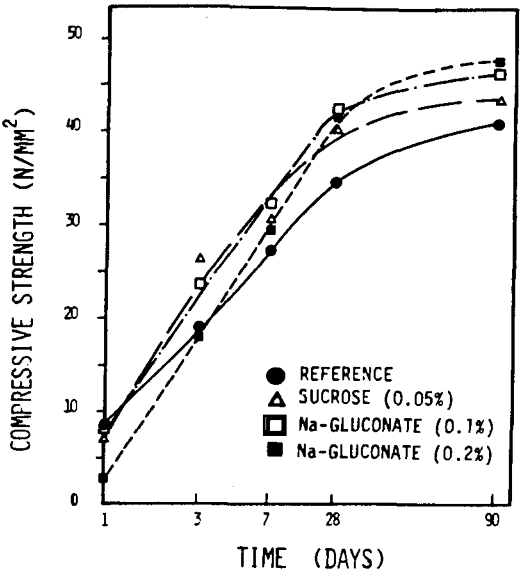


Figure 32. Compressive strengths of portland cement mortars containing sucrose or sodium gluconate at the same w/c ratio (0.47) as that of the reference mix.[113] *(© American Concrete Institute, reprinted with permission.)*

The super-retarding effect of phosphonates on the hydration of portland cement has been studied by Ramachandran et al.[24] They have used the isothermal conduction calorimetry to measure the heat evolved during cement hydration as a function of time with and without three phosphonic acids (Fig. 7) or their corresponding sodium salts in the range of 0.03–0.09% dosage. Figures 33 to 38 show the rate *(a)* as well as the integral amount of heat developed up to 72 hrs. An expanded view for both the rate *(c)* and integral heat *(d)* curves for the first 8 hrs of hydration is shown in Figs. 33 to 38. Phosphonic acid-based chemicals are able to form complexes with the inorganic species and, even if present in small amounts, can retard very strongly the portland cement hydration. The induction period, the time to attain the maximum heat effect, has been increased from about 3 hrs (for the reference mix) to greater than 72 hrs in the presence of these retarding admixtures. The phosphonic acids are more effective retarders than their corresponding salts and the sodium salt of DTPMP (Fig. 7) is the most efficient of all the salt retarders.

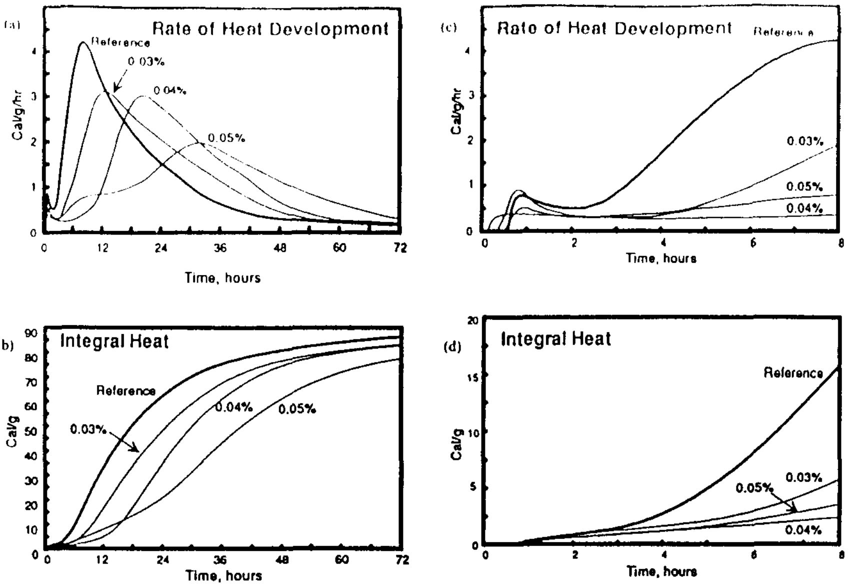


Figure 33. Conduction calorimetric curves of portland cement in the presence of phosphonate systems: ATMP.[24] *(© RILEM, reprinted with permission.)*

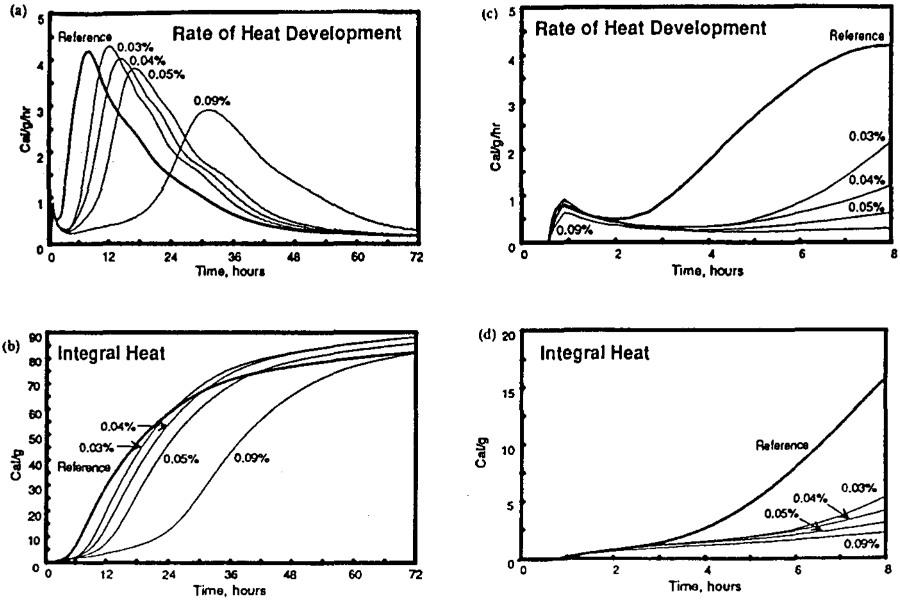


Figure 34. Conduction calorimetric curves of portland cement in the presence of phosphonate systems: Na_5ATMP.[24] *(© RILEM, reprinted with permission.)*

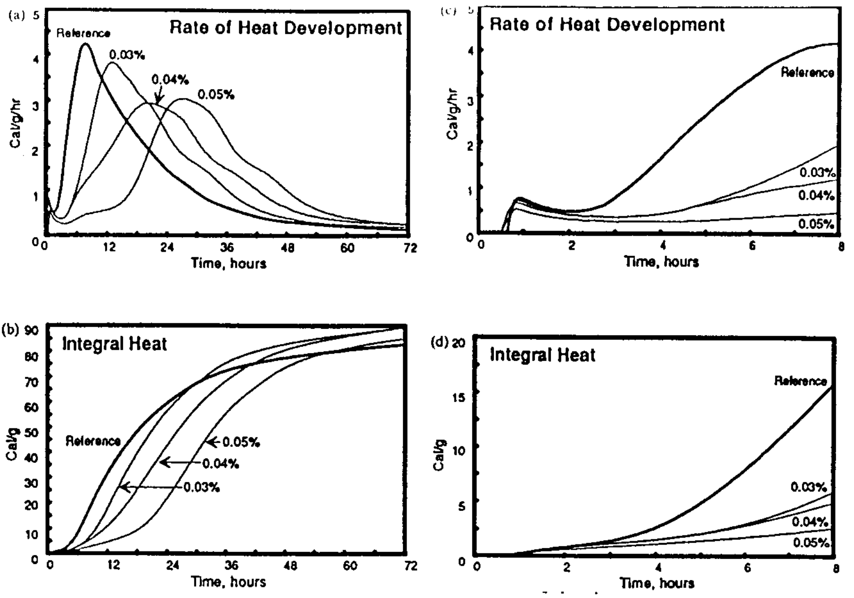


Figure 35. Conduction calorimetric curves of portland cement in the presence of phosphonate systems: HEDP.[24] *(© RILEM, reprinted with permission.)*

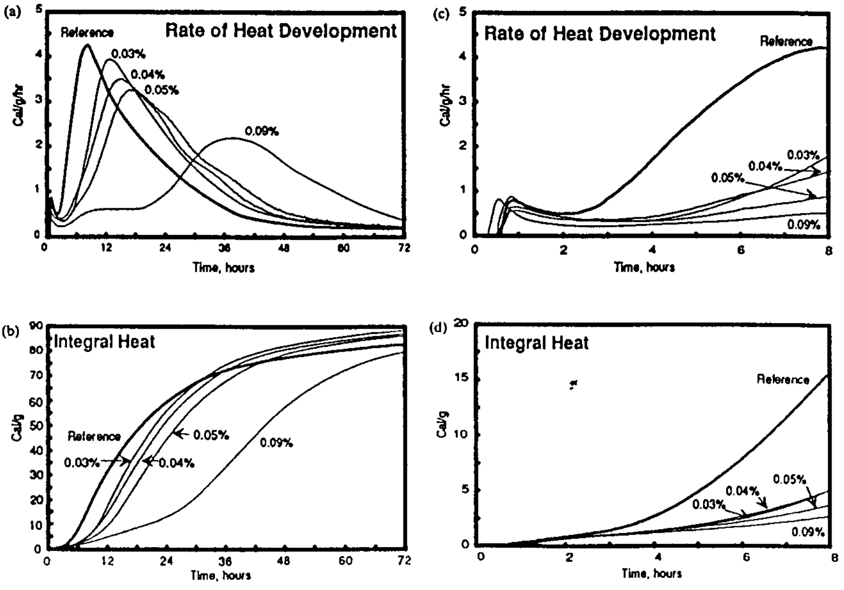


Figure 36. Conduction calorimetric curves of portland cement in the presence of phosphonate systems: Na_4HDEP.[24] *(© RILEM, reprinted with permission.)*

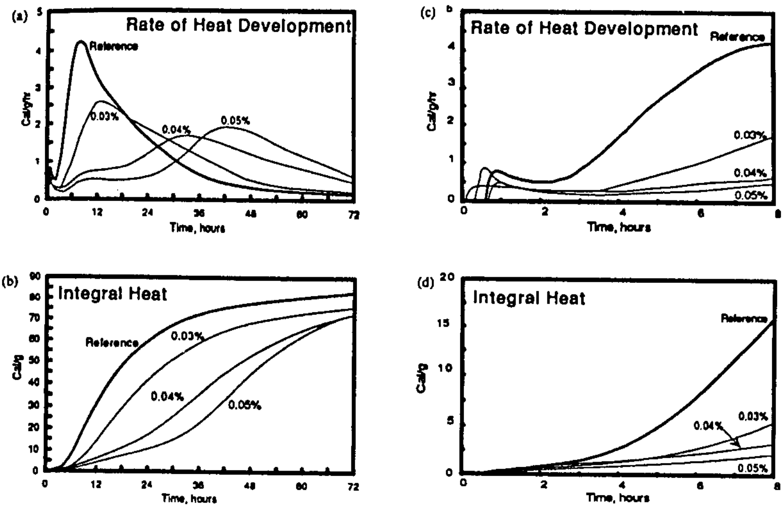


Figure 37. Conduction calorimetric curves of portland cement in the presence of phosphonate systems: DTMP.[24] *(© RILEM, reprinted with permission.)*

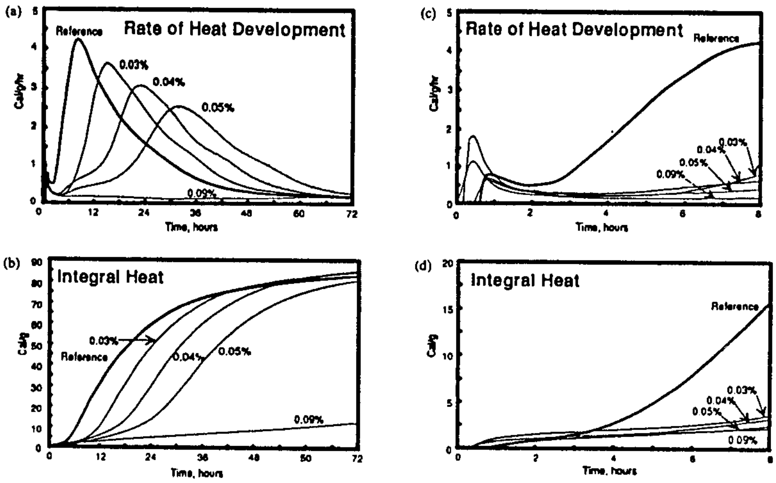


Figure 38. Conduction calorimetric curves of portland cement in the presence of phosphonate systems: Na_6DTPMP.[24] *(© RILEM, reprinted with permission.)*

Because of these performances, phosphonates may be classified as super-retarders and may find a special application in the recycling of concrete in ready-mix concrete operations.

Inorganic Compounds. Some inorganic compounds also act as retarding agents.[29] However, they are not practically utilized because they are more expensive and only slightly soluble in water and have some toxicological effects on waste waters.

Plumbous, stannous, cupric, ferric and aluminum salts strongly retard the C_2S hydration.[128] Zinc, copper and lead oxides retard the hydration of C_3S.[129]-[131] Zinc components retard C_3S hydration more effectively than they do that of C_3A.[132]

Borates, phosphates and salts of Pb, Zn, Cu, As and Sb are retarders for the portland cement hydration.[29] The initial retarding effect of salts with a given anion may decrease in the following order:[133] $Zn^{2+} > Pb^{2+} > Cu^{2+} > Sn^{2+} > Cd^{2+}$. All these retarders are assumed to form protective coatings of gelatinous hydroxides on the cement particles.[128][129][134][135] However, the cement hydration is not blocked as diffusion of water can occur although at a reduced rate.[135] Any changes in the microstructure of the coating, such as crystallization or chemical transformation, could modify the retarding effect at later ages. For example, zinc hydroxide does not show this effect. This could explain why CuO is a more effective long-term retarder than ZnO.[135]

The retarding effect of these admixtures on cement hydration, is reflected as retardation of initial rate of hardening of cement paste and concrete. However, for a given type of retarder, the effect depends on the type of cement and the dosage of admixture. For example, it has been found that after an initial retardation, the compressive strength of cement pastes with 0.1–0.4% PbO is higher than that of the control mix.[129] These results are contrary to those of Alford et al.[136]

Influence of Water-Reducers/Retarders on the Hydration of Cements Other than Portland Cement. The influence of water reducers on the hydration of pozzolanic or blast furnace cement appears to be similar to that on portland cement, the most important difference being a longer retarding effect on cement hydration. Table 12 shows initial and final setting times of portland cement and those of pozzolanic and blast furnace cements, produced by replacing 30% of the same portland cement with natural pozzolan or slag.[11] The slight accelerating effect in the initial set of this portland cement, caused by a commercial lignosulfonate (0.2%), is transformed into a significant retardation using pozzolanic and slag cement. The admixture increases more effectively the final setting times of pozzolanic or slag cement than those of portland cement.

Table 12. Effect of 0.2% Commercial Calcium Lignosulfonate (CLS) on the Setting Times of Portland, Pozzolanic and Slag Cement Pastes[11] *(© Il Cemento, reprinted with permission.)*

	Mixing water (%)		Initial setting time (min)		Final setting time (min)	
Cement Type	without CLS	with CLS	without CLS	with CLS	without CLS	with CLS
Portland	28.0	26.5	231	189	411	735
Pozzolanic	30.0	29.0	300	496	471	945
Slag	29.0	27.0	270	531	424	1040

The increase in strength at later ages (3–28 days) caused by lignosulfonate addition to portland cement mortar (Fig. 30) at a given w/c ratio becomes negligible when pozzolanic or slag cements are used.[11] Possibly, an increase in strength may be observed at 90 days and later. For the same workability, these cements give higher strengths at 3–28 days in the presence of lignosulfonate or hydroxycarboxylic acid (Fig. 39).[137]

Results indicate that compared to portland cement the retarding effect of organic water reducers continues for longer times in pozzolanic or slag cements. Table 13, shows the percentage of $Ca(OH)_2$ and loss on ignition in hydrated portland, pozzolanic and slag cements at 7 days. The lower amount of clinker in pozzolanic and slag cements means a higher percentage of admixture with respect to the weight of clinker compounds, and this could explain the longer retarding effect of the admixture. Lower amounts of $Ca(OH)_2$ in pozzolanic or slag cement are mainly due to the presence of lower amounts of portland cement present in them.

The above organic water reducers are not generally used in mixes with high alumina cement. No change in the consistency of high alumina cement paste may occur in the presence of 1% sodium lignosulfonate.[138] However, hydroxycarboxylic acids can reduce to a limited extent the mixing water requirements of aluminous cement.[138]

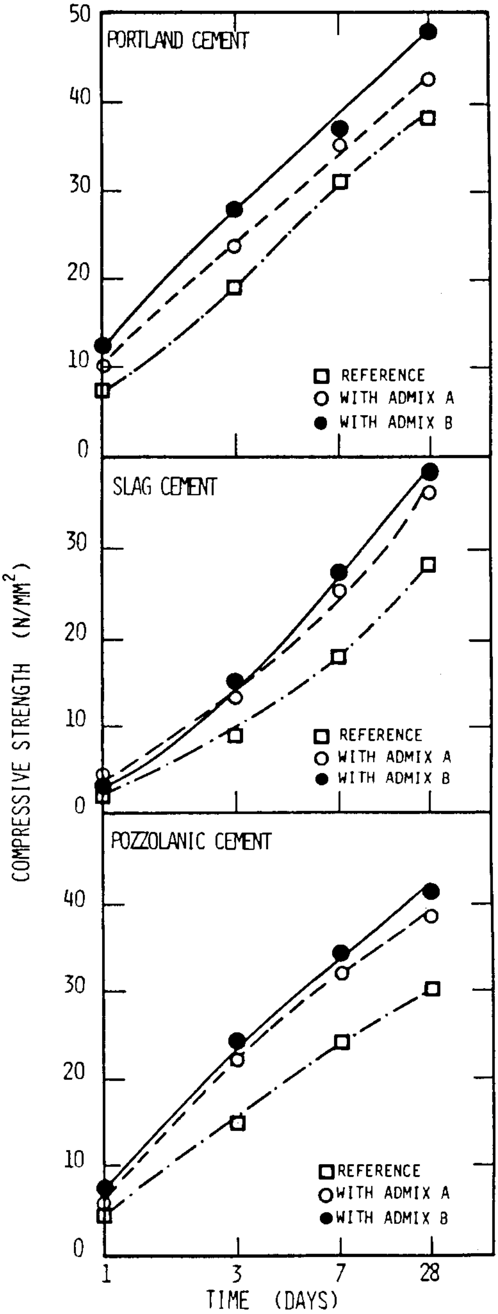


Figure 39. Compressive strength of portland, slag or pozzolanic cement (150 kg/cm^3) concretes containing commercial admixtures (0.25%) based on hydroxycarboxylic acid (Admix A) or lignosulfonate and hydroxycarboxylic acid (Admix B) at a given workability (slump = 100 mm).[137]

Table 13. Effect of 0.2% Commercial Calcium Lignosulfonate (CLS) on the Percentage of $Ca(OH)_2$ and Loss on Ignition (L.O.I.) of Portland, Pozzolanic and Slag Cements at 7 Days.[11] (© Il Cemento, *reprinted with permission.)*

	$Ca(OH)_2$ (% by weight of anydrous cement)		L.O.I. (% by weight of anydrous cement)	
Cement Type	without CLS	with CLS	without CLS	with CLS
Portland	13.7	15.3	12.0	13.4
Pozzolanic	3.5	3.6	10.8	10.8
Slag	7.0	7.1	11.6	11.6

4.0 EFFECT OF WATER REDUCERS/RETARDERS ON FRESH AND PLASTIC CONCRETE

The rheological properties of fresh concrete, such as workability and pumpability, and other properties of plastic concrete, such as finishing, setting and plastic shrinkage can be modified significantly by adding water-reducing admixtures. The change is mainly due to chemical and physical effects of the organic molecules of water reducers on the surface of the hydrating cement.

4.1 Mechanism of Action

When portland cement is mixed with water, solid particles tend to stick to each other in clusters, because of a lack of mutual electrostatic repulsion of particles. The water-cement system flocculates and appears as that shown in Fig. 31A. In the presence of a water reducer the clusters of particles break up almost as individual particles, i.e., cement disperses and appears as that shown in Fig. 31B. A reduction in the forces of attraction between particles allows them greater mobility,

Many mechanisms have been suggested to explain the fluidifying effect of water reducers added to concrete at a given water-cement ratio: *(a)* reduction of interfacial tension; *(b)* multilayer adsorption of organic molecules; *(c)* increase in electrokinetic potential; *(d)* protective adherent sheath of water molecules; *(e)* release of water trapped among cement particle clumps; *(f)* retarding effect on cement hydration; *(g)* change in morphology of hydrated cement. All mechanisms, except *(f)* and *(g)*, are based substantially on the dispersion of cement particles.

(a) According to Prior and Adams,[61] a dispersed system is thermodynamically unstable compared to that in a flocculated state, where the liquid-solid interface and therefore the interfacial tension is reduced. Dispersion is facilitated by adsorbed molecules making the transition from the solid phase to the aqueous phase less abrupt.

(b) The presence of an adsorbed layer of thickness corresponding to several tens of molecular layers[63] would change the interparticle interaction energy. Banfill[138] believes that such a multilayer adsorption would give steric stabilization a role in the dispersing action, as for instance, the change in zeta potential.

(c) Electrophoretic measurements of water-cement suspensions indicate that cement particles do not migrate in an electrical field, whereas cement particles in a lignosulfonate solution move towards the anode, demonstrating that a negative charge is present on solid particles.[7] Ernsberg and France ascribed this negative charge to adsorbed lignosulfonate anions, and dispersion of cement to a mutual electrostatic repulsion among particles.[7] Similar results have been obtained by Mielenz[18] with salts of hydroxy acids.

(d) The negative charge on the cement surface orients the water dipoles forming a hydrated sheath which prevents cement particles from coalescing.[61]

(e) According to Scripture[139] part of the mixing water, that otherwise would be trapped within the particle clusters, is made free to contribute to the fluidity of fresh concrete as a result of the dispersion of cement.

(f) According to Massazza and Costa[38] the slower rate of ettringite formation caused by the presence of lignosulfonate is responsible *per se* for the reduction in water demand. A similar hypothesis, based on the slower rate of formation of hexagonal aluminate hydrates, has been proposed to explain the fluidifying action of the Na_2CO_3-lignosulfonate combination.[37][40][42]

(g) A decrease in the interlocking effect of the ettringite bridges connecting solid particles has been observed in the presence of lignosulfonate (Figs. 15–16). This may be caused by a reduction in the crystal size of ettringite with the resulting improvement in the rheological behavior.[38] A similar hypothesis has been suggested to explain also the fluidifying effect of the Na_2CO_3-lignosulfonate addition to a clinker paste.[120]

4.2 Water Reduction

Less mixing water is required in a concrete mix for a given slump when a water-reducing agent is added. Water reduction is desirable in a concrete mix, as an increase in strength or a reduction in shrinkage and cement content may result (Fig. 1). Recommended dosages allow a decrease in mixing water of 5–15% for a specified workability. The actual water reduction depends on many factors, such as *(i)* type, brand and dosage of admixture; *(ii)* addition procedure; *(iii)* workability level and water-cement ratio; *(iv)* type and brand of cement; *(v)* cement content; *(vi)* type of aggregate; *(vii)* type and amount of the additive such as slag and fly-ash; *(viii)* air volume.

(i) Table 14 shows that sodium gluconate appears to be more effective than glucose and lignosulfonate[137] in terms of water reduction. The effect of different brands or types of commercial water reducers on water reduction depends on the chemical composition of the admixture and its concentration.[140] The higher the dosage of the admixture, the higher the water reduction. However, at amounts greater than 0.1% (solid water reducer by weight of cement) there is no substantial reduction in mixing water.

Table 14. Effect of Water-Reducing Admixtures (0.1% by Weight of Cement) on the Water Reduction at a Given Workability[137]

Cement content = 300 kg/m^3				
Water reducer	Nil	Na gluconate	Glucose	Sugar-free Na lignosulfonate
Slump (mm)	95	100	95	100
Water-cement ratio	0.68	0.61	0.63	0.65
Water reduction (%)	-	10.3	7.3	4.4

(ii) The influence of the addition procedure on water reduction has been discussed in *Addition Procedure* in Sec. 2.2 (Table 5), and the relevant mechanism in *Influence of Lignosulfonate on Portland Cement Hydration,* and *Influence of Water Reducers/Retarders Other than Lignosulfonate on Portland Cement Hydration,* both in Sec. 3.0.

(iii) Cordon[141] found that water reduction is more at 75 mm slump than at 200 mm slump. Figure 40 shows that water reduction is about 6% at a 50 mm slump and about 11% at a 150 mm slump.[137] On the other hand, a concrete mix (300 kg of Type I cement per m^3) in the presence of a water reducer requires an increase in water from 179 to 190 kg per m^3 in order to increase the slump from 75 mm to 200 mm, whereas the same concrete without water reducer requires an increase in water from 189 to 210 kg per m^3 for the same variation in slump.[141] This means that water reducers permit increases in slump with less than usual variations in mixing water and water-cement ratio.

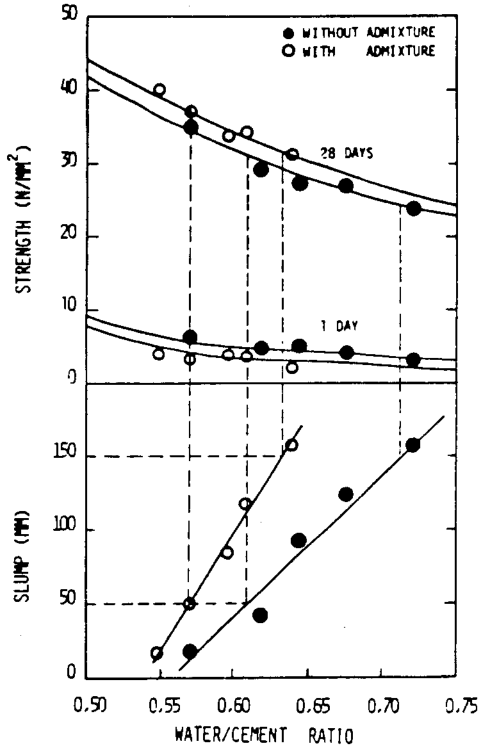


Figure 40. Effect of lignosulfonate (0.3%) on the reduction of the water-cement ratio and the compressive strength at 1 and 28 days of concretes at a 300 kg/m^3 cement content.[137]

(iv) Water reducers are more efficient in reducing the amount of mixing water for concretes with low-alkali and low-C_3A cements than those containing high-alkali and high-C3A cements.[140] Different brands of the same cement type may not show the same water reduction with a given admixture.[140]

(v) According to Vollick,[140] different types of admixture may not have the same influence on water reduction, all other conditions being the same. Water reducers that entrain air are generally found to be more effective in reducing mixing water in lean mixes than in rich mixes. They also entrain more air in concretes with lower cement contents.[140]

(vi) A substantial water reduction can be obtained by adding water reducers to concretes containing different types of rounded or angular aggregates; in some cases aggregates from a particular source may have a different effect on water reduction compared to those from other sources.[140]

(vii) Water reducers are also effective in reducing mixing water requirements for concretes containing fly ash as an addition or a replacement for part of the cement.[140] A higher dosage of admixture should be added to concretes containing fly ash in order to obtain the same water reduction as that of plain mixes without fly ash. This could be due to a higher sorption of water reducers by fly ash particles.

(viii) An air-entraining agent reduces mixing water but additional water reduction is required when a water reducer and air-entraining agent are added simultaneously to concrete.[140] Increased water reduction is obtained, with a combined addition of air-entraining agent and water reducer, when air volume is increased.[140]

4.3 Workability

Workability of concrete is improved when water reducers are incorporated in the mixture at a given water content. The increase in workability, generally measured by slump test, depends on the same factors as described under Sec. 4.2. For example, the effect of a water reducer on workability (at a given water content) is higher at a higher slump or a higher water content; the addition of the same amount of water reducer causes an increase in slump of about 30 mm in a plain concrete mix at 20 mm slump and of 80 mm in a plain mix at 70 mm (Fig. 40). Table 15 shows the effect of water reducers on the slump of concrete at a given water content. The effectiveness of water reducers on workability decreases in the same order (gluconate > glucose > lignosulfonate) as that found for water reduction (Table 14).

Table 15. Effect of Water-Reducing Admixtures (0.1% by Weight of Cement) on the Slump for a Given Water-Cement Ratio[137]

	Cement content = 300 kg/m^3			
Water reducer	Nil	Na gluconate	Glucose	Sugar-free Na lignosulfonate
Water-cement ratio	0.68	0.68	0.68	0.68
Slump (mm)	95	195	160	135
Slump increase (mm)	-	100	65	40

For a given slump, the admixture-treated concrete with reduced water is generally more workable. According to Howard et al.,[142] a concrete without water reducer at a slump of 3.5 in showed a Kelly ball penetration of 1.75 inches; a concrete with admixture at the same slump showed a 2 inch Kelly ball penetration.

In concretes with and without lignosulfonate of equal slump or water-cement ratio, the mortar screened from the concrete shows a greater flow in the presence of the admixture.[143] The admixture-treated concrete shows lower loss of workability.[144]

The above results show that admixture-treated concretes, even with a reduced amount of water and cement, have lower bleeding and segregation characteristics.[142]

4.4 Slump Loss

Most water reducers are also retarders as they increase the time required to reach the vibration limit. Therefore, it has been assumed that these admixtures also reduce slump loss. This effect is almost always confirmed in many tests of slump loss. Laboratory and field experience demonstrates that water reducers or retarders in general do not substantially affect slump loss.[30][54][145] Wallace and Ore,[30] Tuthill et al.,[104] and Tuthill[145] have given examples of large projects in which different cement types, admixtures and temperatures (water reducing/retarders) were used but no slump loss difficulties occurred.

However, in many instances the rate of slump loss can be increased significantly when these admixtures are used. Distinction must be made between admixture addition at a given water-cement ratio and at a given slump. Ramachandran[113] examined the effect of some water reducers/

retarders on the slump loss of concrete at a given water-cement ratio. The initial slump of concrete increased with the addition of admixtures, particularly when lignosulfonate (0.15%) and sodium gluconate (0.05–0.10%) were used. Although a higher rate of slump loss occurred in the presence of these admixtures, the slump value of admixture-treated concretes was significantly higher than that of the reference mix, even after 2 hours.

By laboratory tests Meyer and Perenchio[124] found that, at a given initial slump, water reducers increased the rate of workability loss, but the rate was generally much lower than that caused by a melamine based superplasticizer. However, with a high-alkali Type II cement, a by-product industrial sugar caused a significantly higher rate of slump loss than did the superplasticizer, whereas lignosulfonate or polyhydroxycarboxylic acid admixtures did not change the slump of the control mix to any significant extent. With the same cement by adding calcium sulfate (1% SO_3) the rate of slump loss in the presence of sugar admixture could be reduced significantly, particularly when a 50/50 mixture of gypsum and hemihydrate was added. Hersey,[146] and Erlin and Hime[147] have described field examples of slump loss caused by water-reducing and set-retarding admixtures when high alkali and/or low-SO_3 cements were used. Call[148] found that slump loss with a Type K shrinkage-compensating cement is aggravated using some "normal" water-reducing admixtures, whereas retarding water reducers based on lignosulfonate decrease slump loss.

The effects of water reducers and retarding water reducers on the slump loss during mixing for 2 hours have been studied.[149][150] The results show that while concretes containing admixtures have a slightly higher slump loss than reference concrete, the use of these admixtures allows a significant reduction in the total water required after retempering. This seems to be related to the fact that the presence of admixtures makes the concrete mix more sensitive to water content in relation to slump (Fig. 40).

Although complicated factors are involved in slump loss phenomena, the slump loss due to admixtures may be related to insufficient sulfate and high alkali contents in cement, accelerated formation of ettringite, or to an excess of sulfate in a form that gypsum is precipitated or when an inadequate amount of C_3A is present to control sulfate released into solution. The details of these mechanisms that also determine false setting or acceleration of initial set, have been discussed in Sec. 3.3, *Influence of Lignosulfonate on Portland Cement Hydration*, and *Influence of Water Reducers/Retarders Other than Lignosulfonate on Portland Cement Hydration.*

Independent of the chemical mechanisms causing a higher rate of slump loss in the presence of water reducers or retarders, a delayed addition of the admixture by (*Influence of Lignosulfonate on Portland Cement Hydration*, and *Influence of Water Reducers/Retarders Other than Lignosulfonate on Portland Cement Hydration.*) a few minutes after mixing, or the addition of a further dosage of admixture after the loss of workability,[151] may alleviate or solve the slump loss problem on the job site at least until other definitive measures can be taken.[146] Other methods may include variation in sulfate content at the cement plant.[103][124] replacement of one cement brand by another with a different chemical composition,[106][124] change in the type[126][148] and/or dosage[147] of admixture and decrease in concrete temperature.[147]

Examples of retarders and water reducers decreasing or eliminating slump loss have been reported in literature.[58][105][142][152] They are generally related to false setting phenomena in reference mixes. Such phenomena disappear in the presence of admixtures (*Influence of Lignosulfonate on Portland Cement Hydration*, and *Influence of Water Reducers/Retarders Other than Lignosulfonate on Portland Cement Hydration.*).

4.5 Bleeding and Settlement

Water reducers and retarders affect the rate and capacity of fresh concretes to bleed and settle under the influence of gravity.

In Fig. 41, the influence of three water-reducing agents on the bleeding of fresh concretes at a given slump (100 mm) is shown. Lignosulfonate and particularly glucose reduce the rate and capacity of bleeding. Conversely, sodium gluconate increases the capacity for bleeding even though the mixing water is reduced (Table 14).

In Fig. 42 the effect of water-reducing agents on bleeding of fresh concretes at given water-cement ratio (0.68) is shown. Gluconate increases bleeding, whereas glucose decreases it, and lignosulfonate has no effect on it.

These results confirm the observations concerning the effect of commercial water reducers on the bleeding of concrete. Commercial water reducers based on lignosulfonate[140][153] and particularly glucose[127] reduce bleeding for a given slump value. A higher reduction is observed in the presence of an air-entraining agent even when the air content of the concrete with the admixture is equal to that of the reference mix.[140] Conversely, commercial admixtures based on hydroxy acids and their salts increase the rate and capacity of fresh concretes to bleed.[140][152]

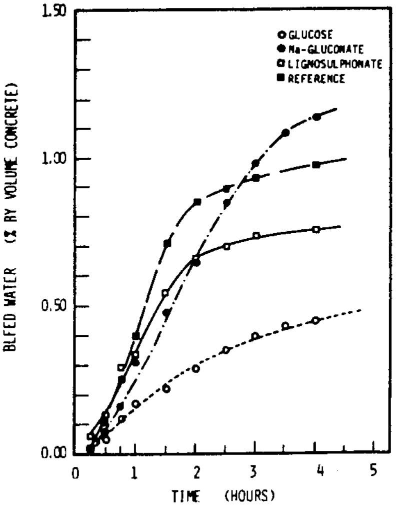


Figure 41. Effect of water reducers (0.1%) on bleeding of fresh concretes for a given slump. Composition and characteristics of the mixes are reported in Table 14.[137]

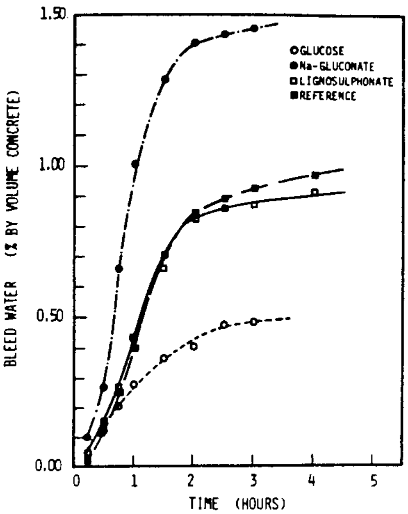


Figure 42. Effect of water reducers (0.1%) on bleeding of fresh concretes at a given water-cement ratio. Composition and characteristics of the mixes are reported in Table 15.[137]

Anionic water-reducing agents reduce the bleeding rate of fresh cement pastes and mortars, at a given water-cement ratio, more than can be accounted for by the presence of entrained air.[154] However, according to Mielenz[18] it is questionable whether these results can be applied also to hydroxylated anionic water-reducing agents. Wheeler and Chatterji[155] found that calcium lignosulfonate (0.1%) increases the rate of settling of a cement paste, at a given water-cement ratio, as a result of the greater mobility of cement particles. By increasing the amount of lignosulfonate to 0.25%, the increase in particle mobility caused channelled bleeding and hence a greater rate of settlement.

4.6 Entrainment of Air

Some commercial water reducers or retarders at normal dosages cause entrainment of 2 or 3 percent of air. Even higher values, up to 7 to 8 percent entrained air, can be entrapped using admixtures at higher dosage rates than those recommended by manufacturers, particularly at lower temperatures.[104] This can be due either to the basic chemicals used, such as unrefined lignosulfonate, or to a certain amount of air-entraining agent intentionally incorporated in the admixtures.

The entrainment of 2 or 3 percent of air is partly responsible for the water reduction or plasticity increase of fresh concrete. The benefit due to water reduction from such a volume of air usually outweighs whatever reduction there may be in strength. Moreover, some of this air is removed from placed concrete through vibration.

When the volume of entrained air is more than the desired amount, refined basic chemicals or defoaming agents should be used.

When a certain amount of entrained air is required to improve durability in freezing climates, and the water reducer does not entrain sufficient air for frost resistance, an air-entraining agent must be added. In general, when water reducers or retarders are added, for a given workability, to an air-entrained concrete mixture of low slump (20–50 mm), the air content does not increase significantly; if they are added to an air-entrained concrete mix having a slump of 70–150 mm, the air content increases.[140]

For concretes requiring a certain air content and containing water-reducing or retarding agents (that entrain a certain content of air) less air entraining agent is needed. Tests should be made on field mixes on the job, under job conditions, and with job materials.[104]

4.7 Appearance

Concrete containing a water reducer at a given slump, even with the reduced cement, has a different appearance than the reference mix without admixture. According to Howard et al.,[142] it looks sticky, has less bleed water and no mortar-aggregate separation. Moreover, the "fat" does not work up to the surface as readily and this is probably due to the smaller volume of cement paste.[141]

4.8 Pumpability

Special admixtures (pumping aids) are available to improve pumpability of lean mixes, but they are not included in this chapter as they are neither water reducers nor retarders. However, for normal and rich concrete mixes, water reducers are beneficial in transforming stiff concrete mixtures into plastic and more pumpable mixes at a given water-cement ratio. This may involve an increase in the sand content of concrete for reducing bleeding that may occur.

On the other hand, water reducers are beneficial in giving more pumpability to mixtures even with reduced water and cement at a given slump. Wallace and Ore[30] were able to reduce the power required to pump a concrete by about 30%, when a lignosulfonate admixture was used to reduce water and cement at a given slump (about 100 mm).

A certain content of entrained air, such as 3 to 5 percent, is also beneficial in making the mix cohesive, plastic and hence more pumpable. However, for long pipelines this may result in compression of air rather than in a benefit for the movement of the mix.[1]

4.9 Uniformity

A constant water-cement ratio should be maintained in order to obtain concrete of uniform quality in mixing operations. Temperature change is one of the main factors contributing to the variation in the water content of the mixture. As temperature rises, more water is required to obtain the same slump. Increased mixing water requirement, as a result of increased temperature, can be counteracted by an increase in the amount of water reducer, that results in a uniform slump and water-cement ratio. If the amount of admixture is not properly adjusted, an increase in temperature will cause a larger variation in water content and quality of concrete. It has been found that plain concrete requires about 21 kg extra water per cubic meter to maintain a constant slump with a variation in temperature from 4.4 to 37.7°C;[156] under some conditions concrete containing a water reducing and retarding admixture requires only about 8 kg extra water per cubic meter.

Moisture changes in the aggregate can cause a larger variation in the slump of a concrete containing a water reducer than in that in a plain mix. The introduction of the water reducer makes the concrete mix more sensitive to the water content in relation to workability (Fig. 40). Moisture content in aggregate should be determined in order to maintain a constant workability and water-cement ratio, particularly when water reducers are used.[141]

4.10 Finishing Characteristics

In the presence of retarders or water-reducing and retarding admixtures, concrete may remain plastic enough to be vibrated several hours after placing, thus reducing the number of air pockets and cold joints. Wallace and Ore[30] found a significant improvement in the finishing characteristics of a continuously placed tunnel lining, due to the retarding effect of lignosulfonate admixture.

The available period between screeding and trowelling operations of the surface of concrete slabs becomes longer when retarders or water-reducing and retarding admixtures are used. This is very useful in the finishing operation of large slabs because a reduced number of finishers would be needed.[30] This characteristic is particularly important in hot weather, where a proper amount of admixture can adequately delay setting times (Sec. 4.11). However, in hot weather the concrete surface may dry out and these admixtures do not prevent the formation of a crust on the concrete surface. Under these conditions, careful and prolonged curing is required in order to obtain a uniform set in the whole concrete slab; otherwise, due to the retarding effect, the concrete below the surface crust will be rolled under the weight of the heavy mechanical trowel causing the surface crust to crack.[30]

Another drawback caused by water reducers on finishing may occur using lean concrete mixes when admixtures are used only to reduce cement and paste; as a result of the reduced cement paste the "fat" does not work up to the surface as readily.[141] This undesirable effect can be eliminated by applying on the surface a powder comprising cement, water reducer and fine sand during the setting time.

4.11 Setting

(a) Retarders and Water-Reducing and Retarding Admixtures. Retarders, and water-reducing and retarding admixtures generally cause a delay in initial and final setting times. However, in some cases an acceleration of the initial setting time has been experienced; this can be prevented by a delayed addition of the admixture. (See *Influence of Lignosulfonate on Portland Cement Hydration,* and *Influence of Water Reducers/Retarders Other than Lignosulfonate on Portland Cement Hydration.)*

Table 2 and Tables 10 to 12 show the effect of commercial retarders and retarding water reducers on the initial and final setting times of different cements. These results demonstrate that specific retardation with a particular cement can be determined only by trial runs.

Initial and final setting times of pozzolanic and slag cements are in general more retarded than those of portland cement (Table 12).

Table 11 indicates that the evaluation of setting times with water-reducing and retarding admixtures for concrete should not be based on tests of cement paste since significantly different results are obtained. Generally cement pastes show longer setting times than those of concrete mixes. Daugherty and Kowalewski[157] found that the optimum percentage of admixtures to retard setting of concrete was approximately half of that required to retard cement pastes. Many factors may affect the setting time of retarded concrete in the field, the most important of which is the amount of the mixing water.[158]

A comparison of the Proctor penetration test with that of pin pullout tests for evaluating the influence of retarding admixtures on setting time has shown that the Proctor test is more suitable and reproducible than the pin pullout test.[159]

By changing the dosage of the admixture, the vibration limit can be delayed for the desired length of time for convenient pouring of each layer of concrete to avoid cold joints (Fig. 43). For any initial temperature of the concrete the dosage can be adjusted to maintain the time for the vibration approximately constant (Fig. 44).

The retardation in initial and final setting times, caused by a given amount of admixture, may be different at different temperatures if the retarding effect is expressed in hours. However, if the number of hours of the initial and final set of the admixture-treated concrete is expressed as a percentage of the number of hours required for the reference mix to reach the same degree of setting, the retardation caused by the admixture is not significantly different at different temperatures[140] (Table 2).

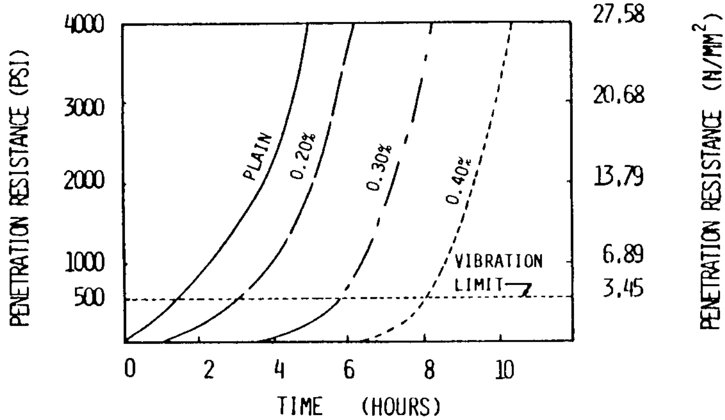


Figure 43. Effect of a water-reducing and retarding admixture on the vibration time limit of concrete mortars.

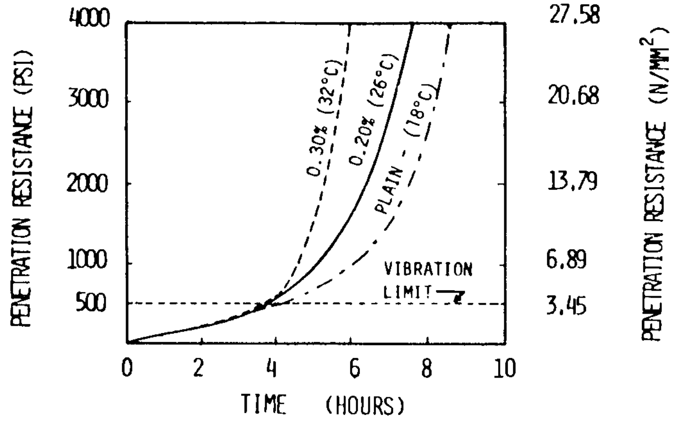


Figure 44. Concrete mortars with and without water-reducing and retarding admixture of approximately the same vibration limit at different temperatures.

Daugherty and Kowalewski[157] found that ASTM C 494 (Sec. 6.2) for chemical admixtures for concrete is inadequate at other than normal temperature conditions. They increased the dosage rates of commercial and laboratory water reducers and retarders in order to conveniently retard setting time at a high temperature of 90°F (32.2°C). They concluded that temperatures above the prescribed for normal 75°F (23.9°C) should be used in evaluating the retarding effect for hot weather concreting. For a more realistic mixing time, longer than 6 min (ASTM C 494) should be recommended.

The dosage of admixture recommended by the manufacturer should be used unless specific retardation, such as that for high-temperatures concreting, is required. Overdosage may cause excessive retarding effect requiring longer curing times. However, an accidental overdosage of proven admixtures does not damage strength at longer ages, provided that the surface is properly cured and forms are not removed until sufficient strength level has been obtained.[140]

(b) Water Reducers. Commercial water reducers may contain some chemical products that accelerate cement hydration and counteract the retarding effect of the main water-reducing components, so that the setting time of the concrete is approximately within ± 1 h of the control mix. The actual values of this limit for a water reducer depend on the standards and codes of practice (Sec. 6). Table 1 (control and N′ mixes) and Table 5 show the effect of commercial water reducers on setting times. A delayed addition of the admixture causes a retarding effect which can be reduced by decreasing the dosage of the water reducer (Table 5)

(c) Water-Reducing and Accelerating Admixtures. A certain amount of accelerator to counter the retarding effect of water-reducing components is generally present in these types of admixtures. Accelerating agents other than chloride salts may be used to produce chloride-free, water reducing and accelerating admixtures. Table 1 (control and A′ mixes) shows the accelerating effect on the setting times of a commercial chloride-free water-reducing and accelerating admixture.

On many jobs, such as conduits and tunnel lining, the level of strength attained within 12 or 24 hr is important for stripping the forms earlier than 1 day after placement. This entails acceleration in setting times, as concrete must be strong enough in about 12 hr to allow removal of forms.[104] Also for advancing the finishing operations of concrete slabs, a water-reducing and accelerating admixture can be useful particularly in cold weather.

4.12 Heat of Hydration

Water-reducing agents delay the time of rapid heat evolution in cement hydration. Forbrich[160] found that combinations of calcium lignosulfonate, orthohydroxy benzonic acid and calcium chloride in various proportions can control in almost any direction the heat developed by the cement hydration at early ages. Moreover, Forbrich found that formulated admixtures increase the ratio of strength of concrete to heat released from cement pastes.

Initial amount of heat is reduced, whereas at 38 days the amount of heat is generally increased or unaltered by the use of retarders and water reducers,[17][30] except when water-reducing and accelerating admixtures are used.

A decrease in initial heat release, using retarders or water reducers, can be useful to eliminate some cracking problems (Sec. 4.14), particularly in hot weather. On the other hand, water-reducing and accelerating admixtures can be advantageously used to increase the initial heat development in cold weather.

4.13 Temperature Rise

At a given cement content, the adiabatic temperature rise of a concrete containing a water reducer or retarder substantially depends upon the effect of the admixture on the cement hydration rate, and hence on the heat liberation (Sec. 4.12).

In general, the temperature rise of concretes containing water reducers and retarders is less at early ages, about the same at about 3 days, and slightly higher at later ages compared to the reference mix.[30] The opposite is true of concretes containing water-reducing and accelerating admixtures.

Composition and cement content affect the temperature rise more significantly than the admixture does *per se*. At a given strength and slump, water reducers decrease the temperature rise only because of the reduction in the cement content. Wallace and Ore[30] found a difference of about 4.5°C at 28 days between the temperature of a control mix and that of the concrete containing the admixture with a 5% reduction in cement content.

4.14 Plastic Shrinkage

Retarders, and water-reducing and retarding admixtures can accentuate plastic shrinkage by retarding setting, unless concrete is protected from loss of moisture. If cracks are caused by plastic shrinkage, these admixtures can aggravate the cracking problem. Only if cracks are caused by early accelerated hydration of cement, (hence rapid heat development) retarders and water-reducing and retarding admixtures may solve the cracking problem.[142]

5.0 EFFECT OF WATER REDUCERS/RETARDERS ON HARDENED CONCRETE

Physical, mechanical and chemical properties of hardened concrete can be affected by retarders and water reducers, particularly when admixtures are used to reduce water.

5.1 Physical Properties

These properties include specific gravity, porosity, surface properties, permeability, drying shrinkage and creep.

Specific Gravity. Specific gravity of concrete at a given strength can be increased by adding admixtures that reduce mixing water, provided the air volume is not increased. Vollick[140] found an increase of 0.6 to 1.2% in the specific gravity of concrete at a given air content using water-reducing admixtures.

Porosity. The influence of water reducers on the porosity of cement paste or mortar depends upon the degree of hydration and water-cement ratio. At longer ages, when the degree of hydration is not significantly affected by admixtures, the porosity of cement paste is reduced as the water-cement ratio is decreased. As a result, reference concretes without admixtures, and admixture-treated concretes with reduced cement content and mixing water, show similar porosity and pore-size distribution for the mortar phase.[161]

At a given water-cement ratio, admixtures affect porosity and pore-size distribution to a less remarkable extent. Figure 45 shows the pore-size distribution of a portland cement paste (water-cement ratio = 0.5) with and without 0.2% commercial lignosulfonate.[11] The pore-size distribution, in the range of 10–75 Å pore radius, is not substantially modified by the addition of lignosulfonate. The volume proportion of pores, whose radius larger than 75 Å, is larger in the paste containing lignosulfonate than in the reference mix (Fig. 45). The total porosity, including pores with a smaller radius than 200 Å, is slightly higher in the presence of lignosulfonate in portland cement pastes, whereas no significant difference has been found in pozzolanic or slag cement mixes (Table 16). Similar results have been obtained by Stupackenko[162] who reported that lignosulfonate admixture (0.25%) does not significantly change total porosity. However, the volume proportion of pores whose radius is higher than 100 Å, is larger by 8% in mortar and 30% in cement paste containing lignosulfonate.

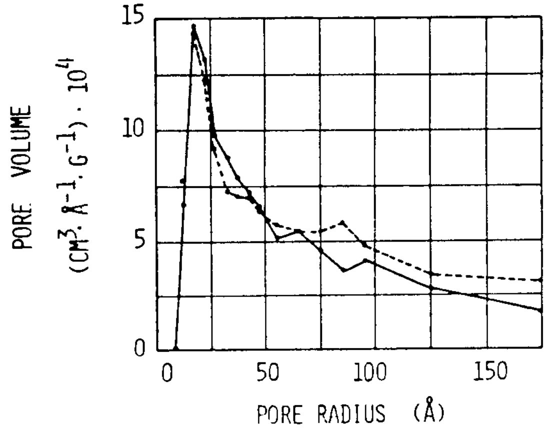


Figure 45. Pore-size distribution of portland cement paste with (—) and without (---) 0.2% lignosulfonate at 7 days.[11] (© Il Cemento, *reprinted with permission.)*

Table 16. Porosity and Surface Properties of Cement Pastes (Water-Cement Ratio = 0.50) without and with 0.2% Commercial Calcium Lignosulfonate (CLS) at 7 Days[11] (© Il Cemento, *reprinted with permission.)*

Cement type	V_p(ml/g)*		S_{BET}(m²/g)**	
	without CLS	with CLS	without CLS	with CLS
Portland	0.12	0.11	43.2	47.6
Pozzolanic	0.11	0.11	45.4	47.1
Slag	0.10	0.10	43.7	46.0

*V_p= pore volume with radius less than 200 Å referred to cement paste.

**S_{BET} = specific surface area determined by BET method referred to cement paste.

Surface Properties. Table 16 shows that, at a given water-cement ratio, the specific surface area, determined by BET method at 7 days, is somewhat higher in cement pastes containing lignosulfonate than in reference pastes. Similar results have been obtained for the cumulative specific surface area determined by the pore-size distribution.[11] The increase in the specific surface area is partly related to a higher degree of cement hydration at 7 days, and hence to a higher volume of hydrated cement (Table 13).

Permeability. Due to the reduction in the water-cement ratio, the porosity of cement paste (see *Porosity*) and hence the permeability of the corresponding concrete are reduced. Figure 46 indicates that at a given cement content (300 kg/m^3) and slump (100 mm), the addition of a commercial hydroxylated polymer water reducer (0.2%) decreases the permeability of concrete both at early and longer ages.[126] Similar results have been obtained using ammonium lignosulfonate,[30] commercial lignosulfonate and hydroxylated carboxylic acid mixtures.[163] The reduction in permeability caused by water reducers also occurs with reduced cement content,[163] probably because of a higher degree of hydration of cement in the admixture-treated concrete.

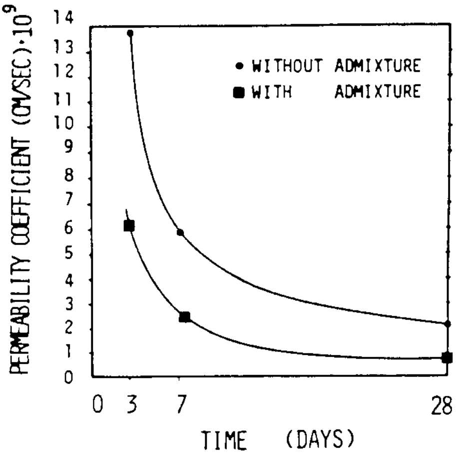


Figure 46. Permeability of concretes with and without water reducer at a given slump.[127]

Drying Shrinkage. Results of drying shrinkage tests performed on mortar (Table 17) or concrete (Table 18) with and without water reducers indicate that these admixtures have no detrimental effect or that they affect the ultimate drying shrinkage only to a small extent.[11][126]

Table 17. Drying Shrinkage of Mortars without and with 0.2% Calcium Lignosulfonate (CLS)[11] (© Il Cemento, *reprinted with permission.)*

Cured 1 day and dried at 50% relative humidity and 20°C				
	Drying shrinkage (millionths)			
	7 days		90 days	
Cement type	without CLS	with CLS	without CLS	with CLS
Portland	530	740	910	900
Pozzolanic	630	780	930	940
Slag	500	620	890	890

Table 18. Drying Shrinkage of Concretes without and with 0.2% Commercial Hydroxylated Polymer Admixture[127]

Cured for 7 days and dried at 65% relative humidity and 20°C					
Slump (mm)	Cement content (kg/m³)	Water/cement ratio	Admixture (%)	Drying shrinkage (millionths) 90 days	180 days
100	300	0.44	-	310	450
100	300	0.42	0.2	270	420

Table 17 shows that, at a given water-cement ratio (0.5), in the presence of a commercial lignosulfonate (0.20%), drying shrinkage occurs more rapidly, so that reference mortars without admixture have lower drying shrinkage values at 7 days and substantially equal values at 90 days in comparison with admixture-treated mortars.[11] Similar results have been obtained using calcium lignosulfonate, sodium gluconate and sucrose, or mixtures of calcium lignosulfonate and calcium chloride and mixtures of calcium lignosulfonate and triethanolamine.[164] Mielenz[18] found that hydroxylated admixtures also cause an increase in drying shrinkage at early ages, however, this effect decreases with passing time and possibly is reversed after several months. The higher volume proportion of larger pores (Fig. 45) caused by the presence of admixture and higher surface area could partly explain a higher drying shrinkage of admixture-treated mortars or concretes.[11] Higher degree of hydration (hence the higher volume of cement paste at early ages) may also be an important factor.[18]

According to Daugherty and Kowalewski[157] drying shrinkage is affected by admixture type and admixture dosage level. In many cases they found a reduction in drying shrinkage or no substantial change.

Wallace and Ore[30] studied the effect of water reducers, based on lignosulfonate or hydroxycarboxylic acids, on drying shrinkage of lean mass concretes with reduced mixing water or reduced cement content and mixing water. Their results indicate that at 28 days to 1 year, admixture-treated concretes had lower drying shrinkages than the reference mixes. At early ages, such as 3 to 7 days, in some cases concretes with admixtures showed somewhat higher drying shrinkage. They also found that autogenous shrinkage occurring in sealed specimens is reduced by lignosulfonate admixture at early and later ages up to 5 years.

Creep. Concrete creep is affected by a multitude of factors, such as type of cement, mix composition, type of aggregate, age at loading, degree of hydration at loading, incremental hydration under load, movement of moisture in the cement gel under conditions of hygral equilibrium between the ambient medium and concrete, and moisture loss from the concrete under sustained load (drying creep).

Only limited data exist on the influence of water reducers and retarders upon creep of cement mixes, and most of them do not take into account all the above mentioned factors.

Khalil and Ward[165] studied the influence of a commercial lignosulfonate admixture on basic creep of mortars containing ASTM Type I and V cements, at a given water-cement ratio. The specimens under load were submerged in lime-saturated water. An age at loading was chosen so that the degree of hydration was equal for all the mixes. The admixture increased the rate and total creep at all ages when Type I cement was used, thus confirming other data previously reported in the literature.[166][167] On the other hand, no significant effect was found when Type V cement was used. When creep results were examined with respect to the period of hydration under load, they indicated that, independent of the type of cement or the presence of lignosulfonate, creep was the same at equal times of hydration under load.

Jessop et al.[168] studied the influence of lignosulfonate and hydroxycarboxylic acid admixtures on creep in Type III cement pastes at a given water-cement ratio, after a very short time after loading (12 hr). The relative humidity of the test environment was 50%, so that both basic and drying creep took place. It seems that the increased creep of the paste with lignosulfonate, compared to that of the reference mix without admixture, is related substantially to a greater ease of moisture movement inside and outside of the cement paste.[168] This hypothesis is supported by data in Fig. 45. Cement paste with lignosulfonate has a higher volume proportion of larger pores, compared with plain cement paste at equal water-cement ratio.[11][162] The reduced surface tension of water in the presence of lignosulfonate could contribute most to the increase in creep.[168]

Both creep and moisture loss for the mix with hydroxycarboxylic acid were lower than those for the reference mix. However, the trend of the moisture loss curve is such that at later ages the ultimate loss of water might be higher in the cement paste with the admixture. Accordingly, this could explain why in earlier tests[166][169] in concrete with hydroxycarboxylic acid, the long-term creep was in most cases higher than that for the plain concrete. However, in the tests for lightweight concrete[169] the hydroxycarboxylic acid admixture seemed to decrease creep under most conditions examined, even at longer ages of loading.

Although no significant change in the morphology of hydration products of portland cement has been observed in the presence of lignosulfonate (see *Influence of Lignosulfonate on Portland Cement Hydration*), sequence and rates of formation of the hydration products might change significantly in the presence of these admixtures. This could explain partly the effect of water-reducers and retarders on creep, particularly when the degree of hydration at loading and the incremental hydration under load are changed in the presence of admixtures.

5.2 Mechanical Properties

The mechanical properties, such as compressive strength, flexural strength, tensile strength, shearing strength, modulus of elasticity, bond strength and abrasion resistance, are all more or less related to each other. A change in one of these properties is generally reflected in the same direction in the others, although not to the same extent.

Strength. ***Compressive Strength at 28 Days.*** The reduction in water caused by water reducing agents (Fig. 1, I) results in a net increase in strength at 28 days (Fig. 3). In general this increase in strength is greater than would be expected simply from the reduction in water. In Fig. 40 the curve of 28 days strength for admixture-containing concrete is higher in comparison with that of the plain mix. This seems to be related to the greater degree of hydration at later ages caused by these admixtures (Fig. 29), and hence leads to a higher strength even at the same water-cement ratio (Fig. 1, III). Figure 2 shows the commercial accelerators, retarding and normal water reducers increase the 28 days compressive strength of concretes with respect to the control mix made at the same water-cement ratio. Results of Figs. 30 and 31 substantiate that, even at a given water-cement ratio, water-reducing agents and set retarders such as lignosulfonate, sucrose and gluconic acid, increase compressive strength at 28 days.

Mielenz,[170] using a commercial calcium lignosulfonate (0.266%), found the following relationships between 28-day compressive strength and the void-cement ratio:

Eq. (8) $S_a = 8518 - 183\ V_a$

Eq. (9) $S_p = 8190 - 1992\ V_p$

where S_a and S_p are the 28-day compressive strength of the admixture concrete and reference mix respectively; V_a and V_p are the void (water + air)/cement ratio by volume of the corresponding concretes. These relationships show that on the average, at a constant cement and air content, for air-entrained concrete a 19% increase in 28-day strength results even with a water reduction of only 5%, whereas for concrete without an air-entraining agent an increase in strength of about 15% might be expected with a water reduction of 10%.

Wallace and Ore[30] carried out extensive laboratory and field tests of structural and mass concretes containing water reducers and set-retarding agents. In general, they found that for a given cement content and slump, the compressive strength of the laboratory specimens containing admixtures exceeded, by an average of about 20% of that of the reference specimens. Field control tests substantiated the results obtained in the laboratory: for a given strength and slump, and average water content, cement reduction was about 8%.

Increase in 28-day compressive strength, at a given slump and cement content (Fig. 1, I), or reduction in water and cement content, at a given slump and 28 day strength (Fig. 1, II), are confirmed by extensive investigations on cements with and without pozzolans.[104][141][142][163] However, according to Howard et al.,[142] it is impossible to specify the percentage reduction in cement content caused by admixtures, since each cement has a particular performance characteristic in the presence of a given admixture.

Compressive Strength at Other Ages. The rate of strength gain depends on whether retarding, accelerating or normal water-reducing agents are used (Figs. 2 and 3). In general, beyond 28 days the increase in strength (compared to the reference) caused by these admixtures is approximately the same as that obtained at 28 days. Wallace and Ore[30] substantiated this statement with tests up to 5 years.

At very early ages, such as 1 day, compressive strength of concretes containing water-reducing agents, such as lignosulfonate, gluconic acid and sucrose, is lower than that of the reference mix at the same water-cement ratio (Figs. 30 and 32) because of the retarding effect of these admixtures on the early hydration of cement (Fig. 29). The higher the dosage of the water-reducing and retarding agent, the more effective the retardation (Fig. 31). When admixture-treated concrete is compared with the plain mix, at a given slump and cement content, the reduction in 1-day strength may be somewhat lower; however, it depends mainly on the type of admixture. Figure 40 indicates that, for a commercial water-reducing and retarding admixture, the curve of 1-day strength is lower in comparison with that of the reference mix without admixture. Figures 2 and 3, and Table 5 indicate that the 1-day strength of concrete containing normal water reducers, and in particular water-reducing and accelerating admixtures, is higher than that of the plain mix at the same slump. However, the effect depends on other factors, such as dosage and addition procedure of the admixture (Table 5) and type of cement (Fig. 39).

At 3 and 7 days the strength increase is generally greater than at 1 day and 28 days. Even when retarders and water reducing agents are used at a given water-cement ratio, the compressive strength of admixture-treated concrete is usually higher than that of the plain mix (Figs. 30 and 32), except when an overdosage of retarding agent is used (Fig. 32).

Flexural Strength. Increase in flexural strength of about 10% for concretes at 7 days to 1 year has been reported for lignosulfonate or hydroxycarboxylic acid admixtures at a given slump and cement content.[163] For a given flexural strength, a reduction in cement content of about 15% is possible in admixture-treated concrete with respect to the plain mix.[163]

Increases in flexural strength at 3 days and beyond have been obtained for portland cement mortar containing calcium lignosulfonate, compared to a reference mix at the same water-cement ratio (Fig. 30). Similar results have been obtained for pozzolanic and slag cements.[11]

Tensile Strength. Due to the difficulty in the testing procedure, only erratic values have been obtained on tensile strength; however, the trend of the tests has shown that admixture-containing concretes have equal or higher tensile strength than that of the reference mix.[30]

Shear Strength. Wallace and Ore[30] found that the shearing stress at zero normal stress was in general higher for concretes containing lignosulfonate and hydroxycarboxylic acid admixtures than for the reference concrete.

Modulus of Elasticity. Although the modulus of elasticity is assumed to be approximately proportional to the square root of compressive strength, no definite relationship exists between these two properties. An increase in the modulus of elasticity of 7% with an increase in compressive strength at 24%, was obtained using a hydroxycarboxylic acid admixture at equal workability.[163]

Increases in the modulus of elasticity of 2 to 8% have been found, in 1 to 5 years, in a concrete containing lignosulfonate admixture, even with reduced cement content and mixing water, as a consequence of the higher volume ratio of aggregate to cement paste.[163] In this case the increase in the modulus of elasticity of the concrete would have been due to aggregates with a higher modulus of elasticity.

Bond Strength. MacPherson and Fischer[163] found that lignosulfonate admixtures increase bond strength by about 15 to 20% and reduce the slip between reinforcing bar and concrete at given bond stresses. The effect is ascribed to the decrease in water-cement ratio. According to them, the reduction in bleeding and shrinkage can contribute to better adhesion and hence improved bond strength.

Abrasion Resistance. Some results reported in the literature suggest that abrasion resistance is proportional to compressive strength.[171] Therefore, the use of water-reducing agents should result in an increased abrasion resistance. According to MacPherson and Fischer,[163] retarders permit proper surface finishing, particularly in hot weather, and hence greatly improve the wear resistance.

5.3 Durability

Resistance to freezing and thawing is usually considered as a measure of durability. However, concrete durability really means the ability of the material to resist destructive agents including other types of attack such as sulfate and chloride attack.

Frost Resistance. It is commonly recognized that resistance to freezing and thawing depends on the air content, distribution of air bubbles in the cement paste, and degree of saturation of the cement paste and aggregate.[18] However, reduction in water-cement ratio or increase in workability of the mix caused by the addition of water reducers can effect the quality of the cement paste matrix or the distribution of air voids. The use of water reducers alone without air entrainment is not sufficient to achieve frost resistant concretes.[172]

Wallace and Ore[30] examined the effect of the addition of water reducers to air-entrained mixes and found that on the average, the resistance to freezing and thawing was 39% greater than that of the corresponding reference mixes. Other results substantiate the advantage of water reduction plus air entrainment in comparison with air-entrainment alone, not only to further improve the frost resistance, but also to outweigh the reduction in strength caused by air-entrainment.[163]

According to Edmeades and Hewlett,[161] addition of admixtures to concrete, to reduce cement content and water (Fig. 1, II), does not change durability in comparison with the corresponding plain mix having same strength, slump and air content.

Examples of reduced resistance to freezing and thawing of air-entrained concrete containing a water-reducing admixture have been reported.[18] These instances of reduced frost resistance are perhaps related to a deficient air content or improper air-void system.

Addition of an admixture (containing a water reducer and air entraining agent) to concrete permits some control problems. Addition of water reducer and air-entrainment agent separately permits achieving an adequate air content and a proper air-void system.

Sulfate Attack. The attack of sulfate water, such as sea water, occurs at the cement paste surface. Therefore, the rapidity of the attack primarily depends on the permeability of cement paste in concrete, and also on the ability of the cement to resist the sulfate attack (determined by the percentage of the aluminate phase).

Due to the reduction in water-cement ratio caused by water reducers, permeability of cement paste in concrete (see *Permeability)* and hence sulfate penetration into concrete is assumed to be reduced. This statement is substantiated by the results reported in Fig. 47, which indicates that the admixture-treated concrete expands to a lower extent, in comparison with the control mix, as a result of the reduced reaction rate between sulfate ion and the aluminate phase.[166] Wallace and Ore[30] found that water reducers, used to reduce water-cement ratio, always improved the resistance to sulfate attack of concrete structures. In one case where the reference mix and the admixture-treated concrete did not resist sulfate attack, it was attributed to a particular Type I cement which by itself had little resistance to sulfate attack.

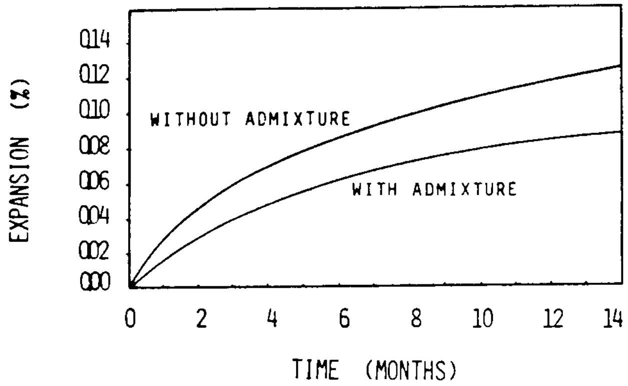


Figure 47. Expansion as a function of time for concrete containing water reducer and plain mix submerged in a 20 g/l Na_2SO_4 solution.[127] (Characteristics of concretes are reported in Table 18 and Fig. 46.)

When water reducers are used to increase workability, at a given water-cement ratio, an improvement in water tightness, and hence in resistance to sulfate attack, can be expected, because gross defects, such as honeycombing, are reduced as a result of the greater workability of the admixture-treated concrete.

Leaching of Cement Paste. Leaching of cement paste by percolation of water through concrete, and in particular soft water, mild acidic aqueous solution, or of water containing aggressive CO_2, can be decreased significantly by reducing the permeability (see *Permeability)* of the cement paste in concrete.[173] Therefore, water-reducing admixtures, used to reduce water-cement ratio or gross defects (such as honeycombing) by improving workability, are expected to decrease leaching effects.

Chloride Attack and Corrosion of Steel. Besides attack caused by chloride salts, particularly $CaCl_2$, on concrete,[174]-[176] chloride ions can cause corrosion of steel when present in reinforced concretes and particularly in prestressed concretes.[173]

Chloride ions can be present in the cement mix originating either from concrete components, including admixtures or from exposure. In the former case the total chloride content in the concrete mix must be under specified limits: 0.06% for prestressed concrete; 0.10% for conventionally reinforced concrete in a moist environment and exposed to chloride; 0.15% for conventionally reinforced concrete in a moist environment but not exposed to chloride.[173] In this case the chloride content of water-reducing and accelerating admixtures must be very low or substantially zero, depending on the chloride content of the other concrete components. However, reduced permeability of concrete caused by water reducers (see *Permeability)*, could allow somewhat higher limits for chloride content, especially when chloride-free components of concrete are not available.

Chloride ions coming from the prevailing conditions, such as sea water in marine environment or from some de-icing agents used for highways concrete structures, can penetrate the concrete cover and attack reinforcement. To decrease this potential hazard, a cover over steel of adequate thickness and relatively low permeability, and a specified limit in the chloride content in the concrete mix are recommended.[173] To reduce the permeability of the steel cover, a reduction in the water-cement ratio up to 0.40 is recommended.[173] Collepardi et al.[177][178] demonstrated that diffusion of chloride ions into concrete is significantly reduced by decreasing the water-cement ratio and increasing the compactness of the concrete mix. Both these effects can be realized using water-reducing admixtures to reduce the mixing water and improve the workability of stiff mixes respectively.

Alkali-Aggregate Reaction. It is well recognized that water or moisture of the ambient medium is partly involved in alkali-silica reaction. Therefore, any means of reducing the exposure of concrete containing potential reactive aggregate to water may extend the useful life of the structure.[173]

Scripture[139] found that the addition of calcium lignosulfonate slightly decreases the rapidity and severity of the alkali-aggregate expansion. However, he suggested that calcium lignosulfonate is not a cure for the alkali-aggregate reaction, but can only ameliorate it.

6.0 STANDARDS AND CODES OF PRACTICE

Different types of water reducers and retarders are recognized by American, Canadian, European, and Japanese standards.

6.1 ACI (American Concrete Institute) Codes of Practice

According to ACI Committee 212,[179][180] the materials generally used as water-reducing admixtures and set-retarders fall into five general classes:

1. Lignosulfonic acids and their salts.
2. Modifications and derivatives of lignosulfonic acids and their salts.
3. Hydroxylated carboxylic acids and their salts.
4. Modifications and derivatives of hydroxylated carboxylic acids and their salts.
5. Other materials, which include:
    - *i.* inorganic materials, such as zinc salts, borates, phosphates, chlorides;
    - *ii.* amines and their derivatives;
    - *iii.* carbohydrates, polysaccharides, and sugar acids;
    - *iv.* certain polymeric compounds, such as cellulose ethers, melamine derivatives, naphthalene derivatives, silicones, and sulfonated hydrocarbons.

The ACI Committee 212 describes the general purpose and precautions for the use of admixtures as well as the methods of their storage and use. According to this Committee water-reducing and set retarding admixtures should meet the requirements of ASTM C-494 standard on "Chemical Admixtures for Concrete" (Sec. 6.2). It also describes the use, preparation and batching of the admixtures. Information is also given on properties, and many effects of these admixtures.

6.2 ASTM (American Society for Testing and Materials) C-494 Standard

Three types of water reducers are recognized by the ASTM C-494-92 standard on *Chemical Admixtures for Concrete.* Type A is a water-reducing admixture; Type D is a water-reducing and retarding admixture; Type E is a water-reducing and accelerating admixture. The main standard requirements are shown in Tables 19, 20 and 21 respectively. All three admixtures should reduce the water content by at least 5%.

Table 19: Comparison of Standard Requirements for Water-Reducing Admixtures

Standard	Type of admixture	Initial setting time (with respect to control mix)	Water reduction, min (with respect to control mix)	Compressive strength min. (% of control mix)	Shrinkage max. (% of the control mix)
ASTM C-494-92	Type A: water-reducing	Min: 1 h earlier Max: 1½ h later	5%	110 (3, 7, 28 days)	135•
BS 5075: 1982[x]	Normal water-reducing	Min: 1 h earlier*• Max: 1 h later**	8%	110 (7, 28 days)	-
CAN 3 - A266, 2- M78	Type WN: normal setting	Min: 1 h 20 min earlier Max: 1 h 20 min later	5%	115 (3, 7, 28 days)	135*
AFNOR NF P 18 - 103	Water-reducing	Min: 1½ h earlier Max: 3 h later	6.9%***	110 (3, 7, 28, 90 days)	105
JIS A 6204	Type A: water-reducing	Min: 1 h earlier Max: 1½ h later	4%	115 (3 days) 110 (7 and 28 days)	120
UNI 7102 - 72	Water- reducer (plasticizer)	After 1 h on cement paste	5%	105 (1, 3 days) 110 (7 days) 115 (28, 90 days)	0.01[+]

• % of control limit applies when shrinkage of control is not less than 0.030%; when shrinkage of control is less than 0.030%, the increase over control limit should be less than 0.010%.

** Penetration resistance of 0.5 N/mm^2

*** A minimum value of 8.6% is required for low - C_3A cements (≤4%).

[+] Maximum increase over control (mortar).

[x] Compacting factor relative to control mix: not more than 0.02 below

Table 20. Comparison of Standard Requirements for Water-Reducing and Retarding Admixtures

Standard	Type of admixture	Initial setting time (with respect to control mix)	Water reduction, min (with respect to control mix)	Compressive strength, min (% of control mix)	Shrinkage max (% of the control mix)
ASTM C-494-92	Type D: water-reducing and retarding	Min: 1 h later Max: 3½ h later	5%	110 (3, 7, 28 days)	135*
CAN 3 A266.2 - M78	Type WR: water reducer, set retarder	Min: 1 h later Max: 3 h later	5%	115 (3, 7, 28 days)	135*
BS 5075 - 82[x]	Retarding, water-reducing	Min: 1 h later**	8%	110 (7, 28 days)	
JIS A 6204	Type D: water-reducing and retarding	Min: 1 h later Max: 3 h later	4%	105 (3 days) 110 (7, 28 days)	120
UNI 7107 - 72	Retarding water reducer	Min:¾ h later	5%	100 (3 days) 110 (7 days) 115 (28 days)	0.01[+]

* % of control limit applies when shrinkage of control is less than 0.030%; when shrinkage of control is less than 0.030%, the increase of over control limit should be less than 0.010%.

** Penetration resistance of 0.5 N/mm^2

[+] Maximum increase over control (mortar).

[x] Compacting factor relative to control mix: not more than 0.02 below

Table 21. Comparison of Standard Requirements for Water-Reducing and Accelerating Admixtures

Standard	Type of admixture	Initial setting time (with respect to costrol mix).	Water reduction, min. (with respect to control mix).	Compressive strength, min. (% of control mix).	Shrinkage, max (% of the control mix).
ASTM C-494-92	Type E: water-reducing and accelerating	Min: 1 h earlier Max: 3½ h earlier	5%	125 (3 days) 110 (7, 28 days)	135*
BS 5075 - 82^x	Accelerating water reducing	More than 1 h**	8%	125 (1 day) 110 (28 days)	
JIS A 6204	Type E; water reducing and accelerating	Max: ½ h later	4%	125 (3 days) 115 (7 days) 110 (28 days)	120
UNI 7108 - 72	Accelerating water reducer	Mln: ½ h earlier	5%	115 (1, 3 days) 110 (7, 28, 90 days)	0.01$^+$

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* % of control limit applies when shrinkage of control is not less than 0.030%; when shrinkage of control is less than 0.030, the increase over control limit should be less than 0.010%.

** Penetration resistance of 0.5 N/mm^2

$^+$ Maximum increase over control (mortar).

^{x} Compacting factor relative to control mix: not more than 0.02 below

Flexural strength should increase only for Type E by at least 10% at 3 days. In all the other cases, admixtures should produce concretes of at least the same flexural strength as that of the control mix.

A relative durability factor of at least 80 is required for concretes containing all three admixtures.

Type B is a retarding admixture and its requirements are shown in Table 22. No reduction in water content is required, although commercial retarding admixtures generally have water reducing characteristics.

Practical experience on job site, particularly in hot weather, indicates that ASTM requirements for setting time of Type B and D admixtures are limited in application. According to Daugherty and Kowalewski[157] temperatures above the normal 75 F (23.9°C) should be used to conveniently evaluate these admixtures for hot weather concreting (Sec. 3.4, *Setting).* Alternatively longer setting times should be permitted as in Canadian Standard (Table 22), French AFNOR Standard (Table 22), or British Standard 5075 (Tables 20 and 22). Also a realistic requirement for compressive strength at 3 or 7 days, (not existing for Type B in ASTM C-494 standard) could avoid undesirable retarding effect to the hardening process.

6.3 CAN 3-A266.2-M78 (Canadian Standard Association)

Two types of water reducers are recognized by CAN 3-A266.2O-M78: a normal setting water reducer which is called Type WN (Table 19) and a water reducing and retarding admixture which is called Type WR (Table 20). The standard requirements are very similar to those of ASTM C-494.

Two retarding agents are recognized (Table 22): a moderate set retarder (Type R) and an extended set retarder (Type R_x). There is a requirement of at least 3% in the reduction of water content. This seems to be reasonable, as many retarders are also water reducers.

A guideline for the use of water reducers and retarders,[181] describes types, composition, effects and applications of these admixtures.

6.4 European Standards

Some typical European standards, such as those existing in France, Italy, and United Kingdom are reported. No standards on water reducers and retarders, comparable to the above, were available from Germany and USSR.

Table 22. Comparison of Standard Requirements for Retarding Admixtures

Standard	Type of admixture	Initial setting time (with respect to control mix).	Water reduction, min. (with respect to control mix).	Compressive strength, min. (% of control mix).	Shrinkage, max (% of the control mix).
ASTM C-494-92	Type B: retarding admixture	Min: 1 h later Max: 3½ h later		90 (3, 7, 28 days)	135*
BS 5075 - 82[x]	Retarding	Min: 1h later**		90 (7 days) 95 (28 days)	
CAN 3-A266.2 - M78	Type R: moderate set retarder	Min: 1 h later Max: 3 h later	3%	110 (3, 7, 28 days)	135*
CAN 3-A266.2 - 78	Type Rx: extended set retarder	Min: 5 h later	3%	100 (3 days) 110 (7, 28 days)	135*
AFNOR NF P 18 - 103	Retarding admixture	Min: 1 h later Max: 3 days later		80 (7 days) 90 (28 days) 100 (90 days)	125 (7 days) 110 (28, 90 days)
UNI 7104 - 72	Retarding admixture	Min: ¾ h later		100 (28 days)	0.01[+]

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* % of control limit applies when shrinkage of control is not less than 0.030%; when shrinkage of control is less than 0.030%, the increase over control limit should be less than 0.010%.

** Penetration resistance of 0.5 N/mm^2.

[+] Maximum increase over control (mortar)

[x] At the same w/c ratio of the control mix; compacting factor: not more than 0.02 below that of the control mix.

British Standard 5075. Three types of water reducers described by the British standard—normal, retarding, and accelerating—are shown in Tables 19, 20 and 21, respectively. The requirements are similar to those of ASTM C-494.

A retarding admixture is recognized with requirements shown in Table 22.

French Standard AFNOR NF P 18-103. Only one water reducer with a specified reduction in water content of at least 6.9% for ordinary portland cement and 8.6% for low C_3A cement is recognized (Table 19).

A retarding admixture with a maximum deviation in the initial setting time of 3 days is described. However, compressive strength at 7 days should be at least 80% of the control mix (Table 22).

Italian Standard UNI. Three types of water reducers (normal, retarding and accelerating) with requirements similar to those at ASTM C-494 are recognized (Tables 19–21).

The requirements of the retarding admixture are described in Table 22.

6.5 JIS (Japanese Industrial Standard) A 6204

Three types of water reducers (normal, retarding and accelerating), with requirements similar to those described by ASTM C-494, are recognized (Tables 19–21). No separate standard exists for retarding mixture.

6.6 RILEM Guide for Water-Reducers and Retarders

The RILEM technical committee has published a guide for use of admixtures in concrete.[182] Table 23 shows the changes in concrete properties caused by water reducers and retarders according to this committee.

7.0 ADMIXTURE ESTIMATION

Admixture estimation of all the components that constitute a particular water reducer or retarder, is not easy. It also depends on whether admixture estimation has to be carried out on the admixture as supplied (Sec. 7.1), or on fresh or on hardened concretes (Sec.7.2). Analysis and interpretation of the data can only be done by an experienced researcher in chemical admixtures.

Table 23. Effect of Water Reducers and Retarders on Concrete Properties[182]

Properties	Water Reducers	Retarders
Fresh Stage		
Unit mass (kg•m^{-3})	Increase	No effect or increase
Workability	Can modify setting times	
Water demand	Decrease** or No Effect*	No Effect or Decrease
Consistency	NoEffect** or Increase*	No Effect or Increase
Consistency loss	No Effect** or Increase*	No Effect
Pumpability	Increase	Can modify water demand
Segregation	Decrease** or No Effect*	No Effect or Increase
Setting & Hardening Stage		
Setting time		
Initial	No Effect or Increase	Increase
Final	No Effect or Increase	Increase or No effect
Strength development	Increase** or No Effect*	Decrease
Bleeding	Decrease** or Increase*	No Effect or Increase
Plastic Shrinkage	No Effect or Decrease	Increase
Hardened Stage		
Strength		
Flexural		
<3 days	No Effect or Increase** or Decrease*	No Effect or Decrease
>28 days	Increase** or No Effect*	No Effect
>91 days	Increase** or No Effect*	No Effect or Increase
Compressive		
<3 days	No Effect or Increase** or Decrease*	No Effect or Decrease
>28 days	Increase** or No Effect*	NoEffect
>91 days	Increase** or No Effect*	No Effect or Increase
Modulus of elasticity	No Effect or Increase	
Durability		
Permeability	Decrease** or No Effect*	No Effect or Decrease
Freeze/thaw resistance	Increase** or No Effect*	No Effect or Increase
Thermal expansion	No Effect	No Effect
Creep	No Effect or Increase	Increase
Shrinkage	No Effect or Increase	No Effect or Increase
Corrosion of Steel	Decrease** or No Effect*	No Effect or Increase

* at given water-cement ratio

** at given slump

7.1 Estimation of Admixture as Supplied

The purpose for which an estimation of water reducers and retarders as supplied is required, is as follows.

(i) To determine the chief organic components of the admixtures, such as lignosulfonate, hydroxycarboxylic acids or carbohydrate, several investigators[183]-[188] have published methods to characterize proprietary admixtures. Chromatographic methods[187]-[189] and infrared (IR) spectroscopy[183]-[186] are the most useful techniques to identify and/or estimate the main components of the admixture. Paper chromatography is particularly useful to separate and identify the various types of sugar which may be present in a retarder.[188] IR spectrum is referred to as the 'fingerprint' of a substance, as each chemical has its own characteristic IR spectra. Although the main groups can be identified by IR spectroscopy, it is difficult to assess as to whether these groups belong to one or more chemical compounds. Therefore, a preliminary separation of the admixture into individual components should be carried out using methods such as solvent extraction, distillation, precipitation, etc. IR spectra of individual components allows for a more positive identification.[190] For quantitative analyses other methods, such as ultraviolet spectroscopy[183][185] can be used. These methods, in general, do not characterize the materials as accurately as the IR analysis and therefore are not suitable for quantitative measurements.

(ii) To check whether the composition of the various admixture shipments from the manufacturer is the same an IR spectrum carried out on the admixture as supplied is useful to check whether all chemical groups, which should be present in the components of the admixture, are actually present in a particular batch. In addition to IR analysis, other simple physical and chemical measurements, such as specific gravity, pH, and total solid determination are useful to check the quality of a particular admixture shipment.

(iii) To determine the amount of a particular component, such as chloride, with a potential damaging effect on concrete, the minimum concentration of a component that could damage concrete should be known. Preliminary separation of this component from other products in the admixture is generally required. Traditional chemical analysis or spectroscopy methods can be used to determine the amount of this component present in a mixture.

7.2 Estimation of Admixture in Concrete

Analysis of water reducers or retarders in concrete may be required to check whether some problems, such as excessive retardation in setting time and low strength development could be related to the use of an improper type and dosage of an admixture. In some cases the so called "admixture problems," were in fact related to concretes which were deficient in cement, or to an improper batching of cement.[191]

Qualitative and quantitative analysis of admixtures in hardened concrete are in general more difficult than the corresponding direct analysis of the admixtures. This is due to several factors, such as *(a)* the difficulty of extraction of admixtures from concrete matrix, *(b)* the presence of very low amounts of organic substances in concrete, and *(c)* possible reactions of organic products in the alkaline environment in the cement paste. In spite of these difficulties, some methods of analysis for admixtures in concrete are available.[1][191]-[194] References to papers concerning identification and estimation of individual chemicals in concrete can be found in a review of Connoly et al.[191]

All these methods are based substantially on the extraction of admixtures from concrete. Most of these extraction techniques have been developed by Connoly, Hime and coworkers.[190][191][195] They include extraction with a 10% sodium carbonate solution to determine lignosulfonate, and boiling water extraction to determine polysaccharides, hydroxycarboxylic acids and sugars.

After extraction, the specified chemical may be estimated by UV absorbance measurements (340 nm for lignosulfonate) or in the visible-range (such as 595 nm for hydroxylated products).

In some cases, particularly in old concretes, the extracted material may be altered from the original composition. Swenson and Thorvaldson[196] found some changes in the ultraviolet spectrum of extracted lignosulfonate due to the formation of vanillin by alkaline hydrolysis of lignosulfonate. Other changes could be caused by the extraction process.[190] Analysis of admixtures in concrete should be based on trials involving extraction from concrete containing known amounts of an admixture.

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7

Superplasticizers

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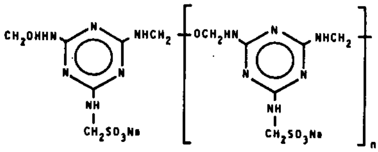
1.0 INTRODUCTION

Superplasticizers belong to a class of water reducers chemically different from the normal water reducers and capable of reducing water contents by about 30%. The admixtures belonging to this class are variously known as superplasticizers, superfluidizers, superfluidifiers, super water reducers, or high range water reducers. They were first introduced in Japan in the late 60's and in Germany in early 70's. In North America they were used from 1974.[1]

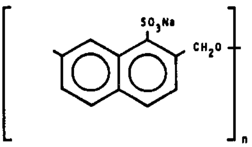
The advantages derived by the use of superplasticizers include production of concrete having high workability for easy placement, and production of high strength concrete with normal workability but with a lower water content. A mix having a combination of better than normal workability and lower than normal amount of water, or that with less cement but having the normal strength and workability are other possible applications. Reliable statistics on the extent of the use of superplasticizers are not available. The data provided by Malhotra[2] in 1989 provides some indication. In industrialized countries, the percentage of ready mix concrete utilizing superplasticizers varied between 1 and 20%. In precast concrete however, the use varied between 20 and 100%.

The superplasticizers are broadly classified into four groups: sulfonated melamine-formaldehyde condensate (SMF); sulfonated naphthalene-formaldehyde condensate (SNF); modified lignosulfonates (MLS);

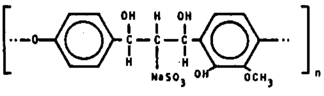
and others including sulfonic acid esters, polyacrylates, polystyrene sulfonates, etc. Blends of different superplasticizers have also been investigated. For example, blending of lignosulfonate with superplasticizers has economical and technological advantages. A blend of SNF and SMF-based superplasticizer may be used to realize certain benefits.[3] Variations exist in each of these classes and some formulations may contain a second or third ingredient. Most available data, however, are based on SMF-and SNF-based admixtures. A large amount of work that has been carried out on these admixtures is to be found in research papers, chapters, books, proceedings of conferences and patents. The basic units of lignosulfonate, sodium salt of sulfonated melamine formaldehyde, and the sodium salt of sulfonated naphthalene formaldehyde are as follows: The lignosulfonate molecule consists of substituted phenyl propane units with hydroxyl, methoxy, carbonyl, and sulfonic acid groups. The molecular weight may vary between a few hundred to 100,000. The SMF-based superplasticizer may have a molecular weight of about 30,000. In the SNF-type superplasticizer, n may be as low as 2. Such a structure will be able to reduce surface tension of water in the mix and entrap air. This can be prevented by using a higher molecular weight polymer, typically one having a value of n = 10. The structures of these superplasticizers are given below.



SODIUM SALT OF
SULFONATED MELAMINE FORMALDEHYDE
(a)



SODIUM SALT OF
SULFONATED NAPTHALENE FORMALDEHYDE
(b)



SODIUM LIGNOSULFONATE
(c)

Chemical structure of superplasticizers.

The superplasticizers are either synthesized or obtained as industrial by-products. The sulfonated melamine formaldehyde is obtained from melamine which is first converted to trimethyl melamine and then treated with formaldehyde. It is then reacted with sodium bisulfite and polymerized. The sulfonated naphthalene formaldehyde is obtained by sulfonation of naphthalene with sulfuric acid or SO_3 and then reacted with formaldehyde. The acid is then treated with sodium hydroxide. Another method of production of superplasticizer is to use naturally occurring plant materials. For example, cashew nut shell liquid is fractionated, sulfonated and condensed with formaldehyde in the presence of additives to produce a superplasticizer.[4]

The most important property of a superplasticizer is its ability of dispersing the cement particles. Electron microscopic examination reveals that in water suspensions of cement, large irregular agglomerates of cement particles form. By the addition of a superplasticizer, the material is dispersed into small particles. The particle size analysis of a cement suspension containing cement and SMF or SNF is illustrated in Fig. 1. Dry cement has a much higher percentage of fine particles than that treated with water.[5] Compared to cement suspension without the admixture that with plasticizers shows better dispersion with the formation of finer particles.

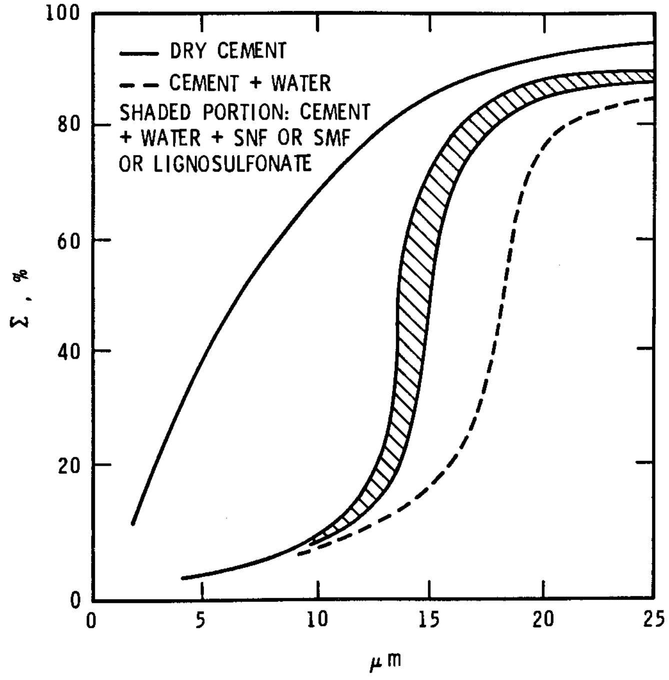


Figure 1. Effect of dispersants on the particle size distribution in cement.

The fluidizing effect of 0.3% SMF on cement is illustrated in Fig. 2. While the cement without this admixture appears wet, the paste containing the superplasticizer flows like a liquid.[6]

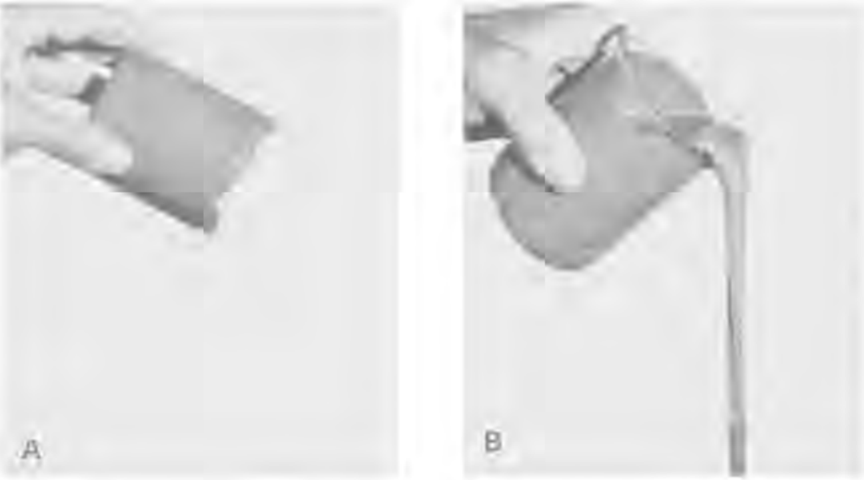


Figure 2. Effect of superplasticizer on cement. A: Cement + water. B: Cement + water + superplasticizer.

The fluidifying effect of the superplasticizer may be envisaged as follows. Portland cement in contact with water has a tendency to flocculate due to van der Waals' forces, electrostatic interactions between the opposite charges and surface chemical interactions between the hydrating particles. This will result in the formation of an agglomeration of particles with open structure with spaces that entrain water molecules. These water molecules are not immediately available for hydration and do not have a lubricating effect. In the presence of a superplasticizer, deflocculation or dispersion of cement particles occurs due to adsorption and electrostatic repulsion. This process does not allow the formation of entrapped water and discourages surface interaction of the particles. Some stearic hindrance is possible especially when high molecular weight superplasticizers are used. Such a phenomenon would also prevent particle-particle interactions.

2.0 APPLICATIONS

Superplasticized concrete enables placement in congested reinforcement and in not easily accessible areas. The problem of cutting and adapting the formwork for vibration is thus eliminated. Easy and quick placement characteristics of flowing concrete and the need for only very nominal vibration makes it suitable for placement in bay areas, floors, foundation slabs, bridges, pavements, roof decks, etc. Pumping of concrete is very much facilitated by incorporation of superplasticizers. Superplasticizers have also found successful application for placing concrete by tremie pipe, particularly in underwater locations. They have also been used for spray applications and for tunnel linings, and where special shapes are desired as in architectural work. Superplasticizers are used by the precast industry because strengths of the order of 40 MPa are achieved in 8 to 18 hrs, and the fuel costs and amount of cement used are reduced. They have also been used to produce concrete of strength of more than 100 MPa in combination with silica fume. Other important advantages include production of concrete with reduced permeability, improved surface finish, reduced shrinkage, and overall cost savings.

In addition to producing high strengths and flowable concretes, superplasticizers offer other possible benefits. There is a great need to use marginal quality cements and aggregates for the production of concrete. In such instances, the use of superplasticizers permits production of concrete at low w/c ratios and with good durability characteristics. Superplasticizers can be used advantageously in the production of fly ash concrete, blast furnace slag cement concrete, composites with various types of fibers and lightweight concrete. By using higher than normal dosages of superplasticizers, a new type of concrete known as *high volume fly ash* concrete, containing higher than normal amounts of fly ash, has been produced. The properties and durability of these concretes are discussed in Ch. 12. The dispersing effect of superplasticizers is not limited to portland cement only and hence they may find application in other cementitious systems.

Although superplasticizers show some remarkable advantages in producing concrete, there are some limitations associated with their use. Superplasticized concrete shows a high rate of slump loss. The relative effects of the materials, production method, economy, and external conditions that influence this phenomenon are a subject of much study. Also, more investigations should be carried out on the compatibility between superplasticizers and other admixtures such as water reducers, retarders, accelerators, and air-entraining agents. Though surface area, C_3A, SO_3, and alkali contents in cement seem to play a role in the action of superplasticizers on different cements, no definite trend has been established. Use of superplasticizers necessitates changes in the normal procedures for making concrete.

The proportions of cement, sand, aggregate, and the dosage of superplasticizer should be adjusted to avoid segregation. High flowing concrete generates more than normal pressures on the forms and hence they should be designed to withstand the greater pressures. Flowing concrete is not amenable to easy placement on slopes exceeding 3° to the horizontal. Use of superplasticized mortars may pose problems in concrete finishing applications and, in such cases, mix proportions and time of finishing should be controlled properly. In many instances, incorporation of more than normally suggested dosage of a superplasticizer yields further advantages but this does not mean that excessive amounts can be tolerated; beyond a particular amount, the superplasticizer may produce undesirable effects such as bleeding, segregation, low strengths, and change in air entrainment characteristics in concrete.

Most available data on superplasticized concrete pertain to the use of SMF-and SNF-based superplasticizers. Even within a single type, variations in the behavior may occur because of the differences in the type of cation associated with the superplasticizer and in its molecular weight. Consequently most data indicate only general trends. The future use of superplasticizers will be dictated by the cost of the admixture and the operating costs. When it is desired to use a superplasticizer it should be verified that the normal water reducer cannot perform as well for a particular job.

3.0 CEMENT PASTE

Cement paste (comprising mainly calcium silicate hydrate, calcium hydroxide, and aluminate hydrate phases), although constituting a small proportion in concrete, influences significantly many properties of concrete. The action of chemical admixtures such as superplasticizers on concrete is mainly dictated by their effects on cement. A study of the effect of superplasticizers on rheology, adsorption, hydration, microstructure, and zeta potential characteristics of hydrating cement and cement components is essential for an understanding of the role of superplasticizers in fresh concrete.

3.1 Rheology

The type and amount of cement present in concrete determines to a great extent the properties of the fresh concrete. Rheological studies of cement paste comprise a study of the deformation behavior under stress. Such studies are useful in explaining the role of superplasticizers in cement. The rheological properties depend on water-cement ratio, type of cement, specific surface area of cement, mixing procedure, time after mixing, and temperature of hydration.

A viscometer is used to measure yield stress and viscosity. In this method, the shear stress is plotted against the shear rate. If the relationship is a straight line passing through the origin, the body is known as a Newtonian liquid. Non-Newtonian fluids are not characterized by a constant value for the shear stress to shear rate. Cement paste is considered to exhibit approximately the Bingham plastic behavior according to the equation: $\tau = \tau_\gamma + \mu_\rho \nu$ where τ = shear stress, τ_γ = yield value, μ_ρ = plastic viscosity, and γ = shear rate.

The coefficient of viscosity is related to the reciprocal value of the line in the plot of shear stress and shear rate and this value is related to the consistency of the material. Systems which exhibit an intercept on the shear stress axis show plastic flow behavior. The value of the intercept is called *yield stress* and is related to cohesion.

Superplasticizers may significantly influence the rheological behavior of cement paste. These admixtures reduce the yield value, plastic viscosity, and thixotropy. In an investigation of the yield value of cement paste containing SNF, Banfill[7] found that the yield value decreased as the concentration of SNF increased and at 0.8% the value was nearly equivalent to zero.

Figure 3 shows the effect of concentration of SMF on the relative yield values in cement paste.[7] The value decreases to zero at 1.0%.

At a constant w/c ratio, viscosity and total stress at a particular shear rate are decreased by the addition of superplasticizer. These results can be explained by adsorption and zeta potential effects. In Fig. 4, the viscosity changes in cement paste containing SNF and exposed to different times are plotted.[8] At any particular time, the viscosity is lower for the paste containing the admixture. The values are even lower at a higher admixture concentration. It has also been reported that 1% superplasticizer at a w/c = 0.3 shows the same fluidity effect as a cement paste at w/c = 0.4 without the admixture.

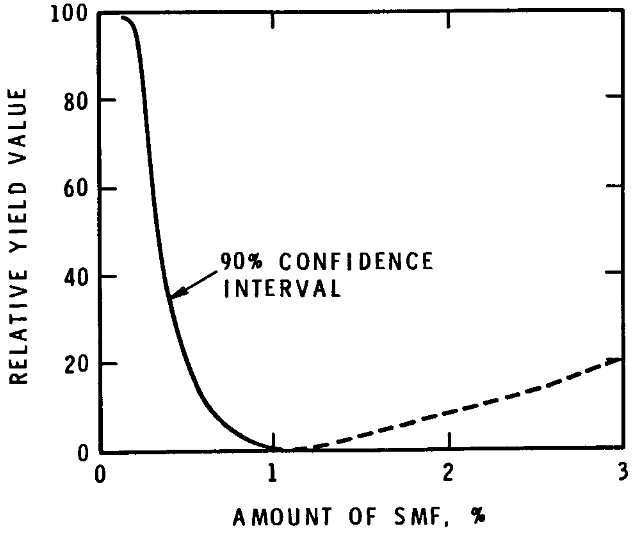


Figure 3. Effect of sulfonated melamine formaldehyde on the yield value of cement pastes.

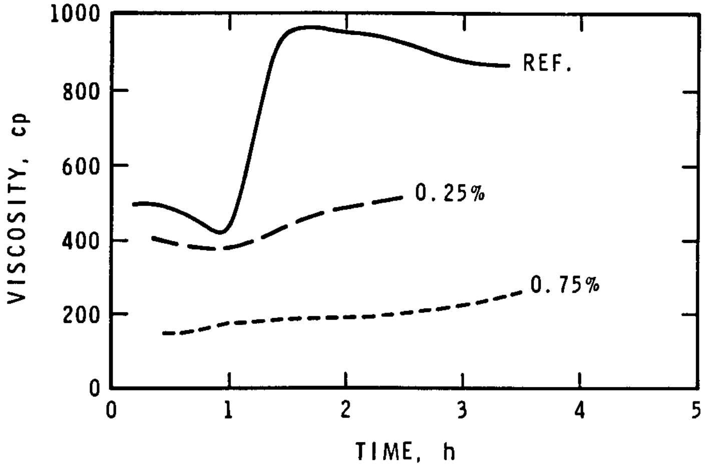


Figure 4. Effect of sulfonated naphthalene formaldehyde on viscosity of cement paste.

Boragafio and Macias[9] compared the rheological properties of three types of cements—low C_3A cement containing 2.5% C_3A, high alkali cement with 0.95% Na_2O, and a high fineness cement having a surface area of 5000 cm^2/g. They were treated with different amounts of lignosulfonate, SNF, and SMF. The addition of all these admixtures decreased the yield value of the cements. The effect was more pronounced in cements containing SNF than SMF. Addition of lignosulfonate to these admixtures slightly enhanced the yield value. However, an addition of gluconate to SNF or SMF resulted in very low yield values. The efficiency of the superplasticizers depended on $C_3A/CaSO_4$ ratio of cement; increased ratio decreased the fluidifying effect. The viscosity also depends on the type of sulfate added to cement. The sulfate may be in the form of dihydrate, hemihydrate, or anhydrite. Figure 5 shows the influence of SNF on the viscosity of three cements. At 0.6% SNF, the viscosity is lowest with dihydrate and maximum with the hemihydrate.[10] The main factor that is responsible for the varied effects of these sulfates is the different rates of their dissolution in water. In another study, Nawa et al.[11] examined the effect of the amount of sulfate on the viscosity of cement pastes. In the presence of sulfate, viscosity was reduced. This was attributed to the lower amount of adsorption of the superplasticizer by the C_3A and C_4AF phases when the sulfate is present. Therefore, in the presence of sulfates, the dispersion of the silicate phases is enhanced and the fluidity of the paste is increased. Excessive amounts, however, produced increased viscosity caused by the compressed double layer.

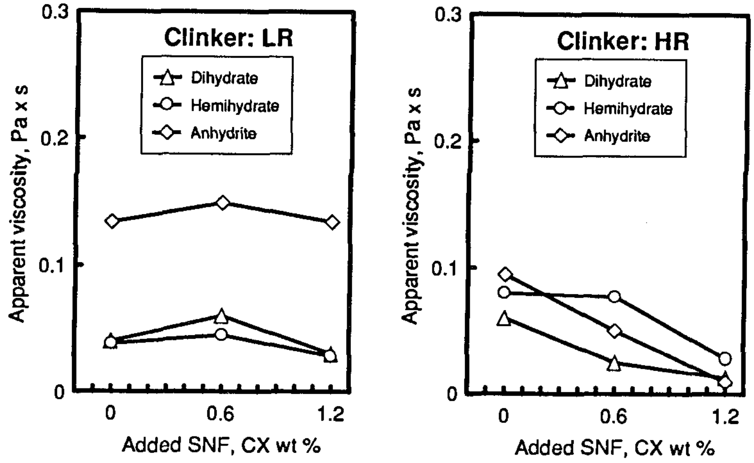


Figure 5. Effect of the type of sulfate on the viscosity of cement paste containing SNF.

The apparent viscosity of cement pastes containing superplasticizers depends also on the fineness of cement. There is an apparent increase in viscosity at higher Blaine fineness values. A linear correlation exists between the fine fraction lower than 11 micrometer and viscosity.[10]

When a large number of superplasticizers have to be evaluated for their effect on the slump of concrete, the use of the standard cone may be time consuming and it would also need a large amount of the materials. A minislump has been devised by Perenchio[12][13] that measures the pat area of the cement paste formed when a small cone is used (height = 57 mm, top diameter = 19 mm and bottom diameter = 38 mm). There is an approximate relationship between the minislump values and those obtained for concrete using the standard slump cone. A linear correlation was obtained by Ramachandran et al.[14] between the pat area for cement pastes and mortars when the pat areas were plotted against the areas formed by concrete in slump tests (Fig. 6).

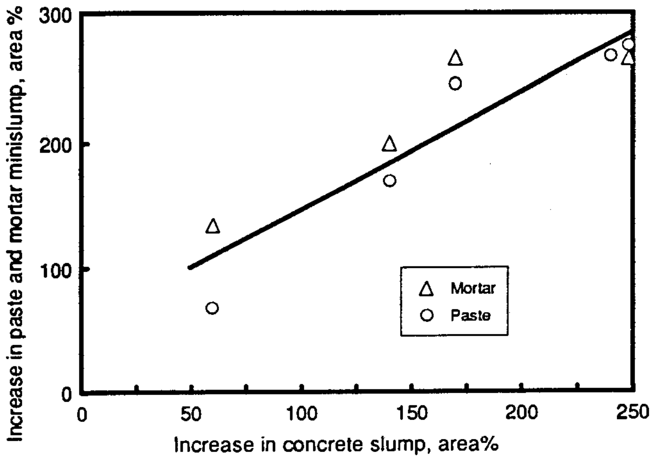


Figure 6. Comparison of workability of paste, mortar, and concrete based on areas.

The minislump method has been applied to study the role of cations associated with the superplasticizer in influencing the workability of cement pastes. Figure 7 shows the minislump values for two cements, a and b, containing sodium polynaphthalene sulfonate (NaPNS), calcium polynaphthalene sulfonate (CaPNS), and sodium polymelamine sulfonate (NaPMS). In both cements, the efficiency of the superplasticizers to increase the fluidity is in the order NaPNS > CaPNS > NaPMS. The results indicate that Na salt of naphthalene sulfonate is more efficient than the Na salt of melamine sulfonate.[15] The effect of H^+, Na, Ca, TEA, and Mg as counter ions in SNF superplasticizer was also investigated.[16] The dispersive effect of Mg was only marginal. Others showed good dispersive effect except that it was reduced after about 2 hrs in the presence of Ca-SNF.

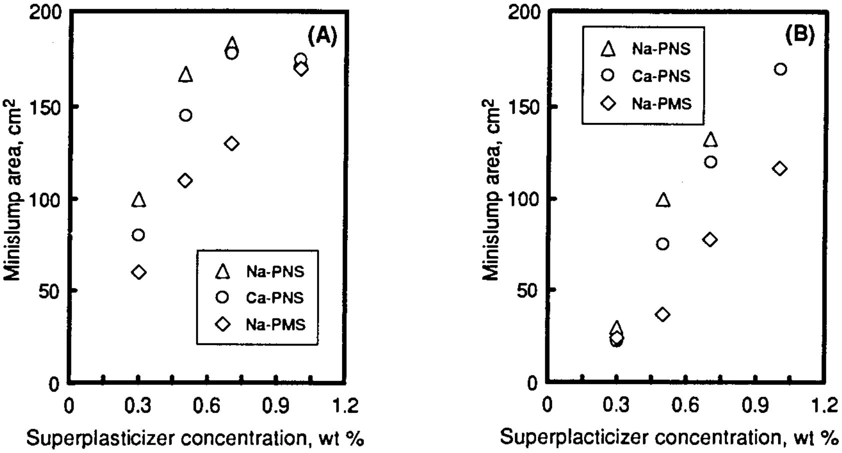


Figure 7. The minislump values with superplasticizers containing different cations.

The molecular weight of the superplasticizer is also an important factor determining the viscosity of the cement paste. Using SNF of various molecular weights, it has been reported that the fluidity increases as the molecular weight is increased up to a point, and then further increase in the molecular weight results in an increase in the viscosity values.[17] Figure 8 shows that the minislump value increases as the number average molecular weight of SNF increases. The curve appears to taper off at a molecular weight of about 500.

The rheological parameters of cement paste, although very useful in describing the behavior of concrete, should be used with caution. For example, superplasticizers reduce both the yield value and the paste viscosity of cement paste. They also reduce the yield value of fresh concrete, but either reduce or increase plastic viscosity, depending on the mix proportion.[7] Superplasticizers are also advocated for use in pumping of concrete. Factors affecting the pumpability of superplasticized concrete are described in Sec. 5.14.

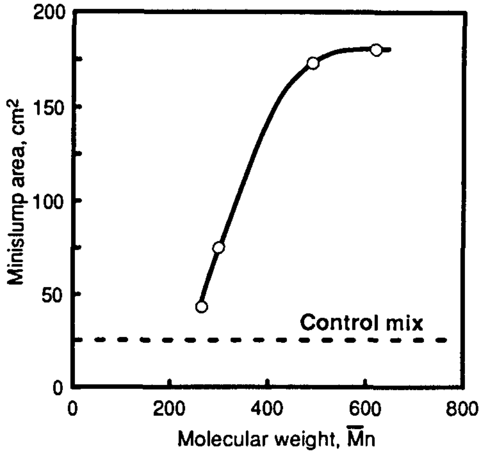


Figure 8. Minislump values of cement paste as a function of the molecular weight of SNF.

3.2 Adsorption

The dispersive action of the superplasticizer is related to its interaction with cement compounds. A study of the rate and amount of adsorption of various superplasticizers on the hydration products provides information on rheological and setting properties of cement.

Adsorption measurements are carried out by monitoring the amount of superplasticizer left unadsorbed in a system consisting of the sample, superplasticizer, and water. The difference in the amount of superplasticizer added originally and that left in the solution gives the percentage of adsorption. The concentration of superplasticizer in the solution may be determined by the spectrophotometric method. For example, sulfonated melamine formaldehyde can be estimated using a wavelength of 219 nm.[18]

Admixtures may be in a free state or adsorbed when they are mixed with cement and hydrated for different periods. Figure 9 shows the adsorption characteristics of sulfonated melamine formaldehyde on cement, C_3A, and C_3S in an aqueous medium.[19] Adsorption of superplasticizer on C_3A occurs in substantial amounts even within a few seconds. Hexagonal aluminate is known to adsorb irreversibly large amounts of SMF. The retardation of conversion of hexagonal to the cubic form in the system C_3A-H_2O-SMF can be explained by the formation of complexes between SMF and the hydrating C_3A. That the adsorption of superplasticizer occurs on the hydrating rather than on the unhydrated phases, has been corroborated by the work of Rossington and Struble.[20] The possibility of the superplasticizer entering the interlayer of C-S-H phase has to be considered.[21] A study on the hydrated C_3S phase indicates a large amount of adsorption. The mechanism is similar to that reported for the hydration of C_3A in the presence of calcium lignosulfonate.[22][23] Adsorption experiments on C_3S show that in the first hour a small amount of adsorption occurs on the surface.[19] Further adsorption after 5 hrs is both due to increased dispersion and hydration. The amount of SMF adsorbed on cement varies with the length of exposure to solution. After immediate adsorption, it is almost nil up to about 4–5 hrs, but after that it is continuous. Adsorption beyond 5 hrs is caused by the hydrating C_3S component in cement.[19]

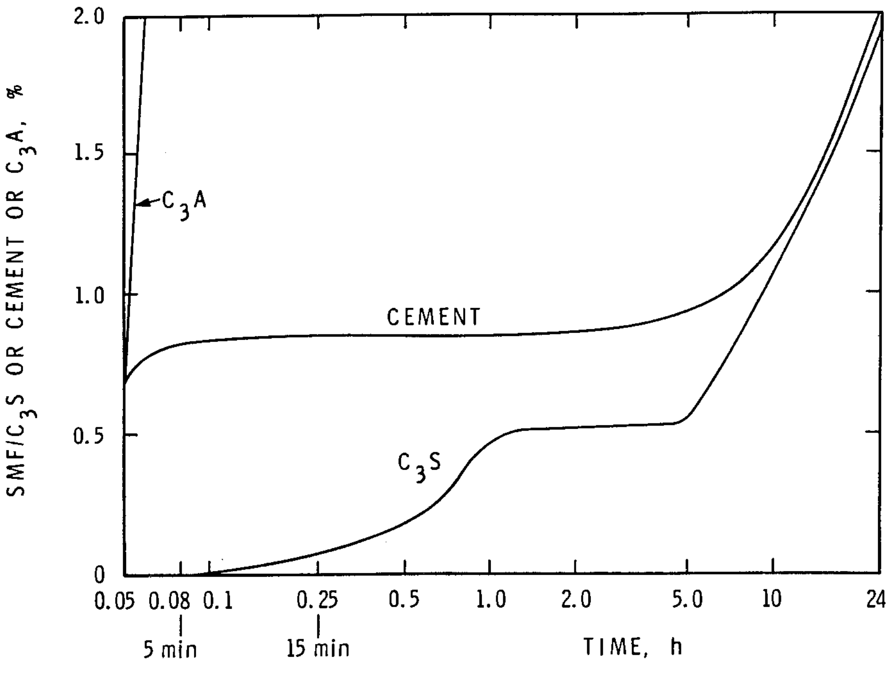


Figure 9. SMF adsorption on cement compounds during hydration.

The role of superplasticizer in the first hour of its contact with cement is very important for understanding the fluidifying or plasticizing effect. Adsorption of SMF has been studied on C_3A + gypsum prehydrated for various periods (Fig. 10).[18] The mixture that was not prehydrated adsorbs almost all SMF within a few minutes. The rate and amount of adsorption are lower for the mixture prehydrated for 5–30 mins. In these samples, products are formed on the surface of C_3A so that diffusion of SMF is lowered. It is possible that, given sufficient time, all SMF will be adsorbed. At 6 hrs to 2 days, the main phases present are the low sulfoaluminate and C_3A. There is evidence that low sulfoaluminate adsorbs a large amount of superplasticizer.[24] Desorption experiments indicated that SMF is irreversibly adsorbed. A surface chemical or chemical interaction seems to occur between C_3A and C_3A-gypsum mixture with SMF. The enhanced dispersing effect of superplasticizer, when it is added a few minutes after mixing water is added to concrete, can be explained as follows. Added along with the mixing water, the superplasticizer is rigidly attached in substantial amounts by C_3A-gypsum mixture, leaving only small amounts for dispersion of the silicate phases. By late addition, the admixture is adsorbed to a lesser extent and there will be enough of the admixture left in the solution to promote dispersion of the silicate phases and to lower the viscosity of the system. The adsorption of superplasticizer is decreased in portland cement–silica-fume systems when the admixture is added 6 mins after mixing with water.[25] The alkalis play an important role in the adsorption of admixtures on cement phases. This has been substantiated in the work on C_3A-gypsum system.[26] It was found that in the C_3A-gypsum mixtures containing 0.25 M KOH and 0.025 M NaOH, within 5 mins the adsorption of superplasticizer decreased by 50% in comparison with that in the presence of pure water. One explanation is that the alkali enters the hydration products, affecting the adsorption characteristics.

Amount of adsorption of superplasticizer on cement can be related to workability. Using SNF, Collepardi and co-workers found that the minislump values increased as the amount of adsorption increased (Fig. 11).[27] In another series of experiments, Collepardi and co-workers studied adsorption and minislump characteristics using SNF both as a monomer and polymer. Adsorption and slump were both low with the monomer. Late additions of the polymer increased further the slump from 15 cm^2 to 95 cm^2. Adsorption was also generally greater at higher water-cement ratios.[28]

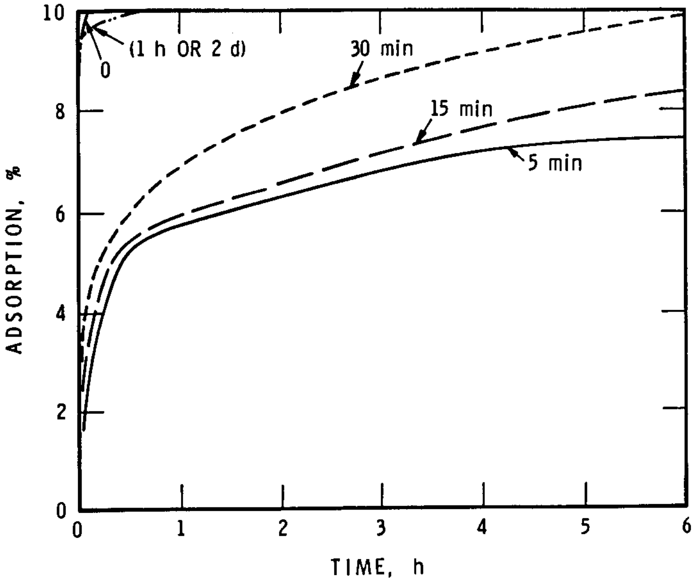


Figure 10. Adsorption of SMF on C_3A + gypsum prehydrated to different periods.

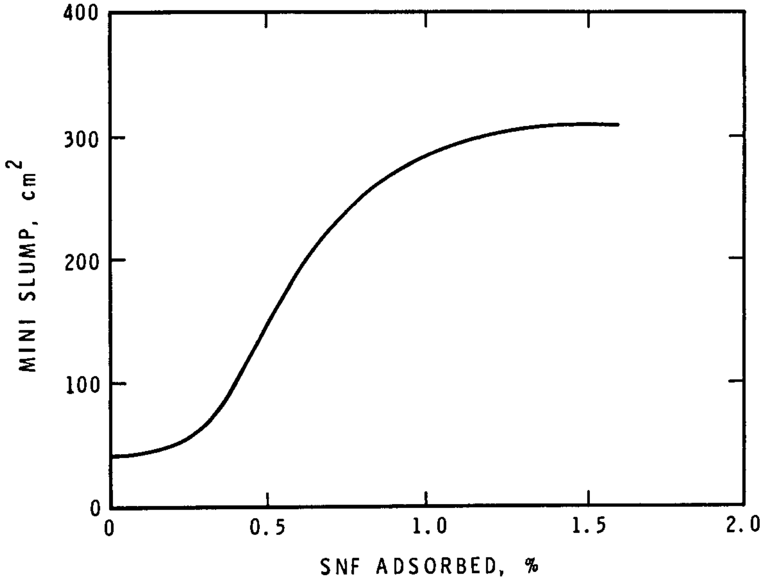


Figure 11. Dependence of slump on the adsorption of sulfonated naphthalene formaldehyde in cement pastes.

The correlation between adsorption and rheological behavior may not always be valid as, for example, when superplasticizers of certain molecular weight range are used. An example of the effect of molecular weight of sodium salt of polystyrene on the zeta potential of cement has been provided by Andersen and Roy.[29] In Fig. 12, the maximum amount of adsorption is plotted as a function of molecular weight of the superplasticizer. Maximum adsorption occurs at a molecular weight of 16,000 g/mole. Comparison of the adsorption results with those of zeta potentials indicates that most effective adsorption does not coincide with the largest zeta potential. It has been concluded that the polymer, even though not highly adsorbed, can generate more negative charges in the Stern layer than the polymer that is effectively adsorbed because of loop and train adsorption mechanisms.

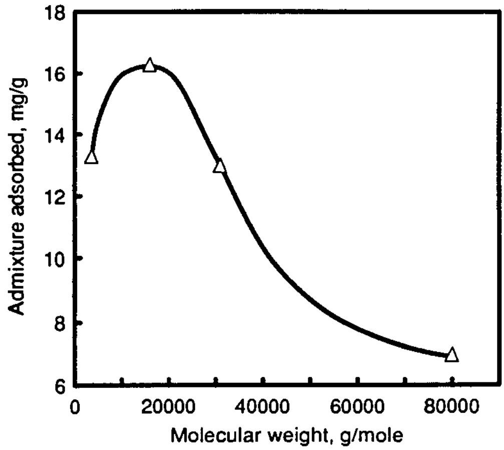


Figure 12. The effect of molecular weight of superplasticizer on its adsorption on cement. *(Reprinted from* Cement Concrete Res., *18:980-986, P. J. Andersen and D. M. Roy, © 1988, with kind permission from Elsevier Science Ltd, The Boulevard, Langford Lane, Kidlington 0X51GB.)*

Burk and others[30] studied the adsorption characteristics of SNF on three types of cement. Figure 13 gives the amount of adsorption of SNF as a function of equilibrium concentration on Type I, II and III cements. The amount of adsorption is in the order Type III > Type I > Type II. The C_3A/SO_3 ratios in the cements also followed the same trend. That the adsorption is mainly dependent on the C_3A content becomes more obvious because, for attaining the same workability, a higher dosage of superplasticizer is required for Type I than Type V cement.[31]

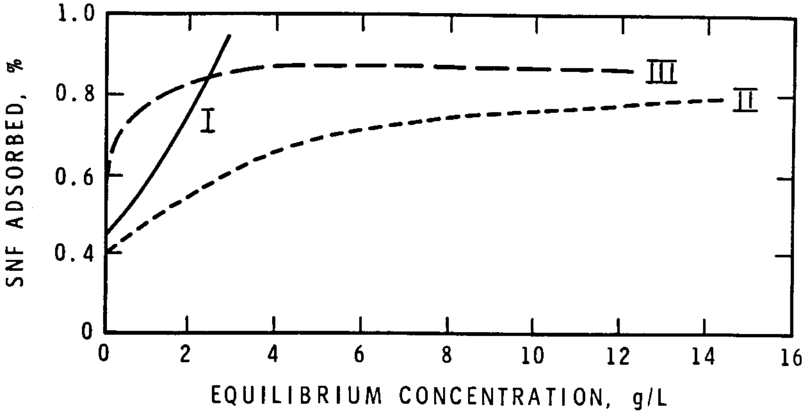


Figure 13. Adsorption characteristics of sulfonated naphthalene formaldehyde on three types of cement.

Recently some work has been carried out on the role of sulfates and relative amounts of cement components on the adsorption characteristics of various superplasticizers. The influence of surface area and alkali sulfates in cement has been reported by Nawa and Eguchi.[10] The amount of adsorption was found to increase with increase in fineness of cement. However, the extent of adsorption was influenced more by the sulfate content than by the fineness. Fig. 14 shows the adsorption of SNF on two cements containing high (HR) and low (LR) SO_3 contents. These cements were ground with dihydrate, hemihydrate, or anhydrite. The results demonstrate that adsorption not only depends on the sulfate content but also on the type of sulfate that was used. In the high sulfate content cement, adsorption is lower and is only about 3–5 mg/g. However, in the cement containing low sulfate, the total amount of adsorption depends on the type of sulfate used. Adsorption is very much higher in LR containing anhydrite. In a separate series of experiments, it was found that the hemihydrate suppressed adsorption of SNF by C_3A and C_4AF. The higher adsorption on LR clinker with smaller amounts of SO_3 was not enough to inhibit adsorption.

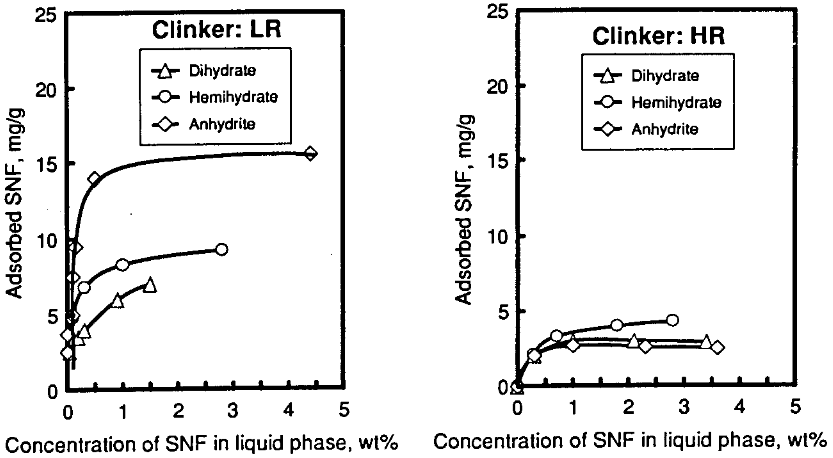


Figure 14. Adsorption of SNF on two cements.

In a systematic study of the influence of the cement phases (in cement) affecting adsorption of superplasticizer, Asakura et al. found a strong dependence of the silicate phases ratio (C_3S/C_2S) and aluminate phase ratio (C_3A/C_4AF) on the rate and amount of adsorption.[32] Adsorption characteristics of SNF on eight cements having different C_3S/C_2S and C_3A/C_4AF ratios were investigated (Table 1). The average particle size and Blaine surface area of the samples were the same. In series S-1, S-2, and S-3, the amounts of C_3A and C_4AF were constant, whereas in series I, the C_3S and C_2S contents were constant. The apparent adsorption isotherms are given in Fig. 15. Cements with higher C_3S/C_2S and C_3A/C_4AF ratios adsorb larger amounts of SNF. The fact that samples I-3 and I-2 adsorb larger amounts of SNF is an indication that the C_3A phase in cement adsorbs larger amounts of SNF than the C_4AF phase. It is also evident that the C_3S phase adsorbs larger amounts of SNF than the C_2S phase because S-3, containing 67% C_3S, adsorbs significantly larger amount of the superplasticizer than the S-1 sample containing only 43% C_3S. Conclusions can also be drawn on the significance of adsorption on rheology and dispersion effects.

Table 1. Composition of Cements used for Adsorption Experiments

Sample No.	Mineral Composition (%)			
	C_3S	C_2S	C_3A	C_4AF
S-1	43	34	9	10
S-2	54	23	10	10
S-3	67	10	9	10
I-1	54	24	3	16
I-2	54	23	8	11
I-3	55	23	14	5

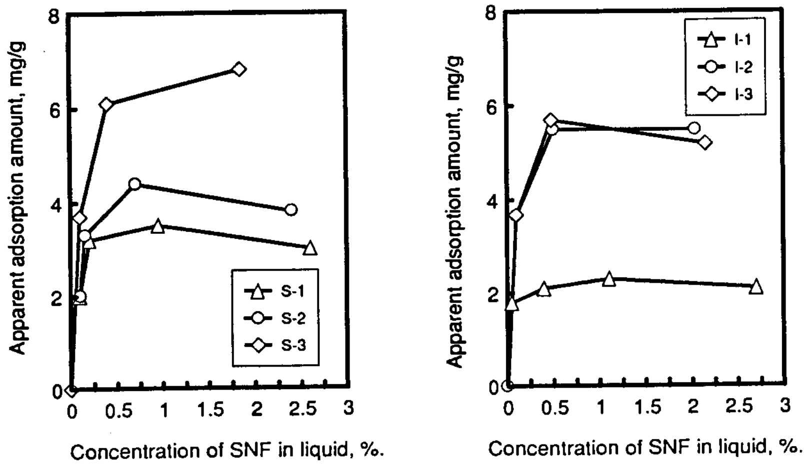


Figure 15. Adsorption isotherm of SNF on cement.

3.3 Zeta Potential

The stability of colloidal particles is usually due to the development of charge as a result of adsorption of ions. These particles develop the same charge, repel each other, and prevent agglomeration or precipitation. Hydrated cement, especially the calcium silicate hydrates, are in the form of extremely small interlocking particles and, in the presence of some admixtures, are dispersed. Hence, colloidal chemical principles have been applied to cement-water-admixture systems.

Generally, when two phases are in contact with each other, the region between them develops electric charges. For example, if there are ions or excess electrons in one or both phases or ionogenic groups present, there will be a tendency for the electric charges to distribute themselves non-uniformly at the interface. The potential gradient is high within a distance of one ion of the dispersed phase of a colloid and farther in the dispersing medium, the potential gradient becomes low and may even change sign. The first layer of adsorbed ions is tightly bound. The difference in potential between the outer fixed layer of adsorbate and the bulk of the dispersing medium constitutes the electrokinetic potential or zeta potential. This potential carries the sign of that of the tightly bound adsorbed ions. At glass-water interface, for example, the observed zeta potential value of -0.05 volts can be ascribed to the adsorption of (OH) ions by glass.

The stability of the colloidal system is a function of the zeta potential and hence the determination of zeta potential enables studies of the mechanism of the action of superplasticizers on the hydrating cement.

The zeta potentials are measured by the following techniques. The electroosmosis method is based on the application of a potential to two locations in a liquid separated by a porous membrane or set of capillaries. This results in the flow of liquid through the membrane caused by the zeta potential developed between the membrane and the liquid. The streaming potential method is a reverse of electroosmosis. In this technique, when liquid is forced through a capillary, charges in the mobile portion of the double layer close to the wall are carried towards the end, resulting in an electric field. The sedimentation potential method is based on the sedimentary particles in a liquid acquiring potential different from that of the surrounding liquid (Dorn effect). Application of an electric field producing migration of colloidal particles due to the potential and charge being different from the surrounding medium constitutes the basis for the electrophoresis method.

Attractive forces exist in cement particles suspended in water and, in time, the particles form a rigid body. Admixtures such as lignosulfonates are adsorbed on the cement particles and exert an electrostatic repulsion and thus decrease the viscosity of the system.[23][33]-[37] Petrie's work has shown that attractive forces existing between the surfaces of the cement particles can be neutralized by the adsorption of anionic surfactants such as naphthalene sulfonic acid condensates.[38]

The zeta potential development in suspensions of cement, alite, C_3A, and $Ca(OH)_2$ containing superplasticizers has been studied.[27][39][40] Figure 16 shows the zeta potential of cement containing sulfonated naphthalene formaldehyde.[40] Addition of the superplasticizer results in large -ve potentials. Although, with time, this potential decreases, the value is still high, even at 20 hrs.

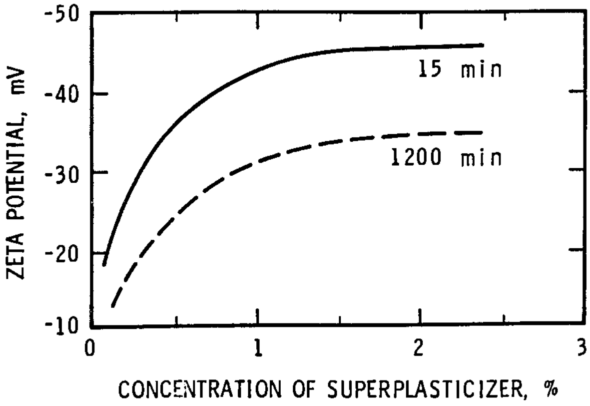


Figure 16. Zeta potential values as a function of concentration in cement suspensions containing sulfonated naphthalene formaldehyde.

A recent study has described how the C_3S/C_2S and C_3A/C_4AF ratios in cement affect its zeta potentials.[32] The samples used in this study are described in Table 1. The zeta potentials of cements containing different proportions of silicate and aluminate phases are tabulated (Table 2). The reference cement without any addition exhibits a zeta potential values between + 0.1 and + 6.5. The potentials increase as the amount of added SNF is increased. It is also evident that the higher the silicate or aluminate ratio, the lower the zeta potential; the viscosity increases with the increases in these ratios. The low absolute values of zeta potential causes the viscosity to increase.

High negative zeta potentials occur in alite and C_3A suspensions containing superplasticizers (Fig. 17).[39] Large negative potentials have also been determined in suspensions containing C_3A + gypsum.[41] The effect of different amounts of SNF on the zeta potential of C_3S and C_3A treated with saturated solution of calcium sulfate has been tested.[10] The zeta potential of C_3S was -9 mV and that of C_3A, 23 mV. In the presence of $CaSO_4$, the values were reduced to -12 mV and 0 mV respectively. However, when SNF was added, the absolute zeta potential value increased to about -25 and -40 mV respectively.

Table 2. Zeta Potential Values of Cement Containing Different Silicate and Aluminate Ratios

		SNF (%)		
Sample	Ref	0.2	0.4	0.8
S-1	+0.1	-32.1	-33.6	-34.8
S-2	+1.1	-33.1	-30.7	-33.0
S-3	+6.5	-19.4	-20.7	-27.7
I-1	+5.6	-30.1	-31.9	-33.5
I-2	+3.7	-28.0	-27.0	-31.1
I-3	+0.5	-10.9	-16.2	-25.1

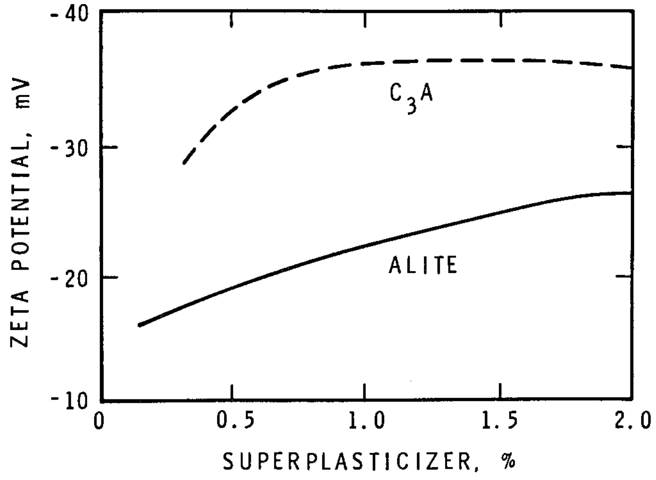


Figure 17. Zeta potential development in alite and C_3A suspensions in the presence of superplasticizer.

Although $Ca(OH)_2$ suspensions exhibit a positive zeta potential of about + 33.5 mV, in the presence of sulfonated naphthalene formaldehyde the value becomes negative, indicating adsorption of the superplasticizer. In the presence of a retarder and a superplasticizer, lower changes occur in the zeta potential.

The workability of cement paste depends on the time at which the superplasticizer is added and is generally higher when the superplasticizer is added a few minutes after mixing with water. Figure 18 compares the zeta potential values of cement pastes to which the superplasticizer is added along with mixing water, with those to which the superplasticizer was added after a few minutes.[28] Large negative values are observed for the system but somewhat higher values result by delayed addition.

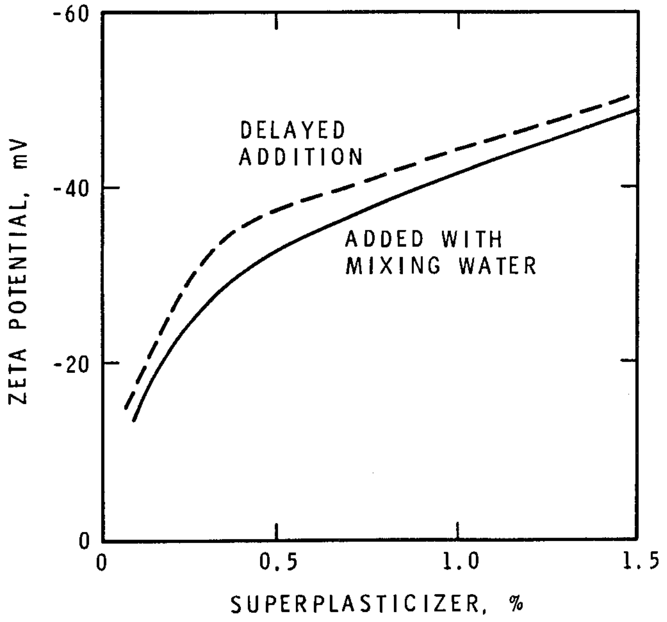


Figure 18. Dependence of zeta potential on the time of addition of superplasticizers.

These results suggest that the water reduction effect of the superplasticizer is related to its dispersion abilities, as indicated by zeta potential. It has been suggested that a certain number of sulfonic groups linked to the polymer are essential to give rise to flat adsorption and efficient dispersion. Zeta potential measurements offer a method of evaluating the relative effectiveness of various superplasticizers. Sekaguchi et al.[42] compared the properties of concrete containing Ca-sulfonated polystyrene (PSS-Ca) and Na-naphthalene sulfonate (SNF-Na). The slump of concrete in the presence of PSS-Ca was much higher than that containing SNF-NA. The zeta potential values also confirmed that, at the dosages between 0.1 and 0.3%, concrete with PSS-Ca showed much higher zeta potentials (Fig. 19).

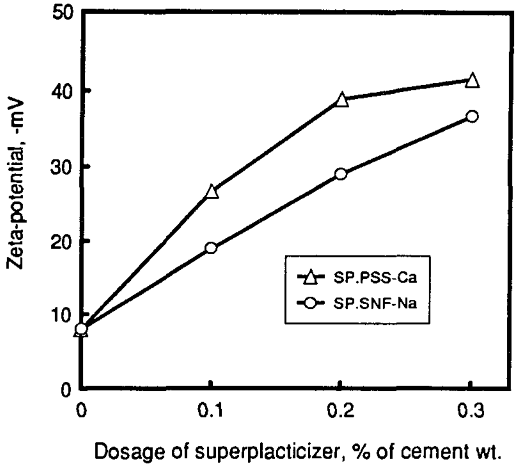


Figure 19. The zeta potentials of concrete containing superplasticizers.

Attempts have made to correlate zeta potential and adsorption with rheological properties. It is generally found that both adsorption and zeta potential values increase as the concentration of superplasticizer added to cement paste is increased (Fig. 20).[28] It has been reported that generally, for the same cement and superplasticizer, the adsorption and zeta potential values show some correlation. This may not be so under all conditions.[43] Basile et al.,[44] for example, observed that with 0.4% SNF, the fluidizing effect determined by minislump technique was quite different for two cements even though they adsorbed the same amount of the superplasticizer. The differences were ascribed to the use of $CaSO_4$ in one cement and hemihydrate in the other.

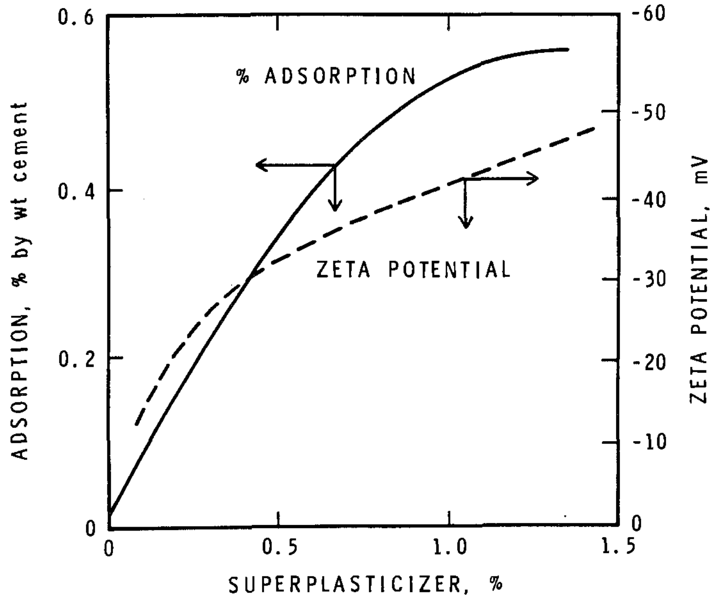


Figure 20. Changes in the zeta potential and adsorption values in the presence of superplasticizer.

3.4 Hydration and Microstructure

The rate of hydration of cement and cement compounds is influenced by superplasticizers. The hydration studies permit an understanding of setting and workability characteristics of cement pastes.

The reported results on the effect of superplasticizers on the hydration of C_3A and C_3A + gypsum systems are contradictory because of the variations in the materials used. The influence of superplasticizer depends on the water-solid ratio, the amount of superplasticizer, molecular weight of superplasticizer, the type of cation associated with it, the proportion of C_3A/gypsum, the type of sulfate, and temperature. There is a general agreement that superplasticizers based on SNF and SMF retard the hydration of C_3A.[18][45][46] Figure 21 compares the conduction calorimetric curves of C_3A hydrated in the presence of 2% SMF with that of C_3A hydrated in the absence of this admixture.[19] The results suggest that within a few seconds of contact with water, a rapid rate of heat development occurs with a peak at about 8–9 mins for the sample containing no admixture. In the sample containing SMF, the total amount of heat generated in the first 30 mins and the amplitude of the peak are lower in comparison with that without SMF.

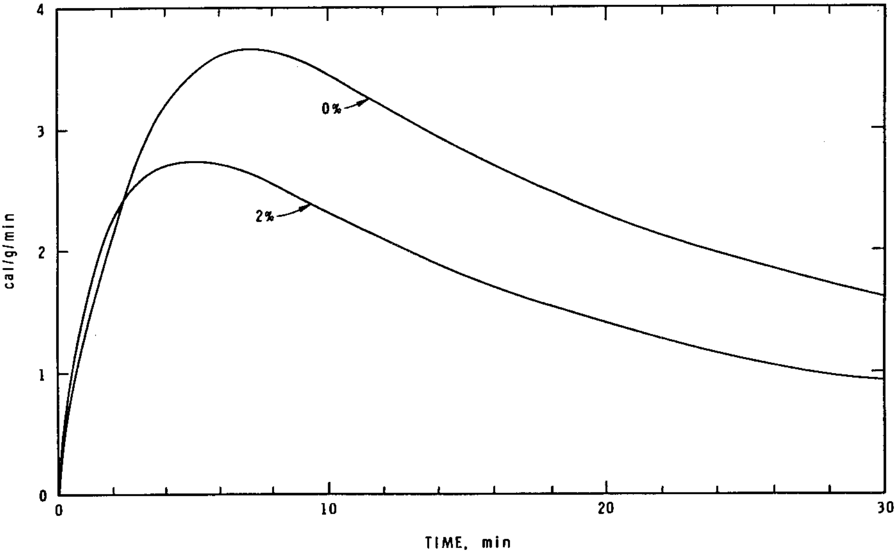


Figure 21. Conduction calorimetric curves of C_3A hydrated in the presence of SMF.

Opinions are divided on the kinetics of hydration of C_3A + gypsum mixtures in the presence of superplasticizers. All the three possibilities: acceleration, retardation, and neutral effects of superplasticizers, have been reported. The properties and proportions of the starting mixtures, the conditions of hydration, and the methods of examination are different and hence direct comparison cannot be made.[47]-[49] It is generally observed that the superplasticizers retard the conversion of ettringite to monosulfate. Figure 22 shows the conduction calorimetric curves of C_3A + 25% gypsum containing 0, 1, 2 and 4% SMF. The peaks appear at 20 hrs with 1% SMF, at about 23 hrs with 2% SMF, and at about 15 hrs with 4% SMF.[18] A continuous hump of lower amplitude is registered for the sample containing no admixture. The retardation effect of ettringite-C_3A reaction to produce low sulfoaluminate may be caused by adsorption of the superplasticizer on the hydrating C_3A surface.

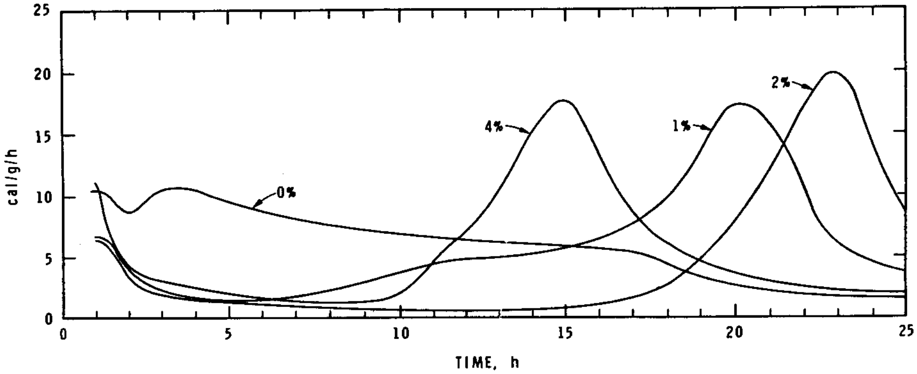


Figure 22. Conduction calorimetric curves for C_3A + gypsum + H_2O containing SMF.

Hydration of C_3S is retarded by superplasticizers.[19][49a][50] The retardation effects of various amounts of SMF on the hydration of C_3S are illustrated in Fig. 23.[19] By the addition of 1% SMF both the induction period and peak are shifted to higher temperatures, indicating a substantial retardation of hydration. At 2 and 4% SMF, further retardation of hydration becomes evident by the very low rate of heat development. There is evidence that the CaO/SiO_2 ratio of the C-S-H products is also changed. Addition of 2% SMF has been reported to change the CaO/SiO_2 ratio from 1.19 to 1.21.[50] In addition, the rate of hydration of the tricalcium silicate phase in the presence of superplasticizer has been carried out by estimation of calcium hydroxide formed at different periods of hydration.[51] Contrary to other investigations, it was reported that in alite containing 2–4% superplasticizer, there was no retardation. DTA and TGA were used in this study and details on the superplasticizers are not provided.

In cements, the hydration of C_3S is retarded but the extent of retardation is not as significant as with pure C_3S because part of the superplasticizer is adsorbed by the C_3A phase. Formation of ettringite may be accelerated or retarded depending on the amount of alkali sulfates in the cement.[5] The CaO/SiO_2 ratio of the C-S-H product in the hydrated cement is also affected. The retardation of the hydration the silicate phase in cement containing different amounts of SMF can be studied by conduction calorimetry (Fig. 24). The peak occurring at about 5 hrs in cement containing no SMF is reduced in intensity as the amount of SMF is increased.[19]

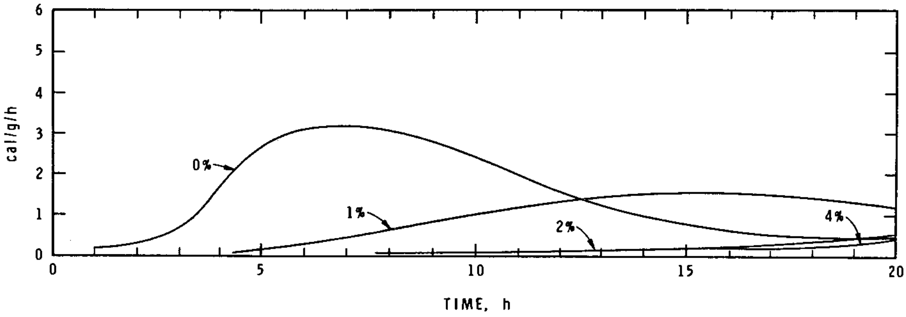


Figure 23. Influence of SMF on the conduction calorimetric curves of C_3S hydration.

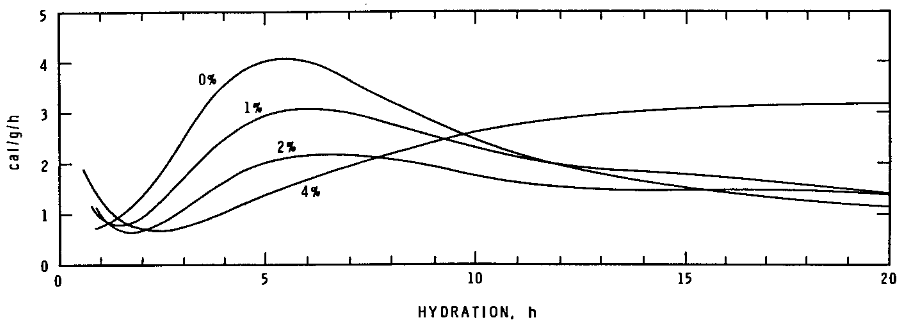


Figure 24. Conduction calorimetric curves of portland cement hydrated in the presence of SMF.

The estimation of calcium hydroxide formed at different times provides information on the effect of superplasticizers on cement hydration. Table 3 gives the amount of calcium hydroxide formed at different times in the presence of 1 or 2% SMF.[52] The early hydration is markedly reduced by 2% SMF up to 7 days. After seven days, the differences become negligible. One of the causes given for the alteration of the hydration rate is the release of Na from the adsorbed SMF. Several other investigations based on the rate of hydration, setting times, XRD estimation of the products, and conductivity measurements have confirmed that the hydration of cement is retarded by the superplasticizers.[53]-[56]

Table 3. Estimation of Calcium Hydroxide in Cement Paste Containing SMF

Mixture	3h	6h	9h	24h	3d	7d	14d	28d	90d
Cement (Ref)	2.3	6.8	8.0	13.7	17.8	19.3	19.8	20.2	20.8
Cement+1%SMF	2.1	6.4	7.3	13.1	17.6	19.4	19.6	19.9	20.5
Cement+2%SMF	1.9	3.3	4.0	12.9	17.1	18.8	19.4	19.4	20.4

Khalil and Ward,[57] using conduction calorimetry, studied the effect of different amounts of SO_3 on the hydration behavior of cement, with and without the superplasticizer. The heat effects were used to explain the workability loss. It was concluded that for cements cured at 25°C, the optimum SO_3 content with the superplasticizer was 1% higher.

Comparison of the effect of different types of superplasticizers on cement hydration is not easy because of the factors such as the amount and type of sulfate contained in the cement, and the molecular weight and its distribution, and the monomer contents of the superplasticizer. Regourd found that SMF is a stronger retarder than SNF but other reports suggest that SNF is relatively a stronger retarder than SMF.[43] In Figs. 25 and 26, the effect of different types of sulfates on the hydration of low and high alkali cements are given. In the cement containing high sulfate, the retardation is significant at 1% SNF when dihydrate and anhydrite are used, but is negligible when hemihydrate is used.[11] For the low alkali cement, independent of the sulfate form, no substantial retardation occurs unless a high dosage of SNF is added.

The relative retardation effect of superplasticizers depends on the fineness of cement. Aitcin and others[58] added 3.45% of SNF to three fractions of cement of particle sizes 72–30 µm, 30–4 µm and <4 µm. Type III cement was used. The conduction calorimetric curves in Fig. 27 show that the fine fraction rich in SO_3 and alkali is not retarded to any great extent, whereas the medium fraction is retarded substantially. The coarse fraction liberates low amounts of heat with or without the superplasticizer.

The relative retardation effects of superplasticizers seem to depend on the cation attached to the polymer. For example, the time to attain maximum heat effect in Type I cement using SNF containing varying cations such as NH_4, Co, Mn, Li, and Ni is 12.75, 11.50, 10.50, 10.25, 9.25 hrs respectively. The exact mechanism responsible for this variation is not understood.[59]

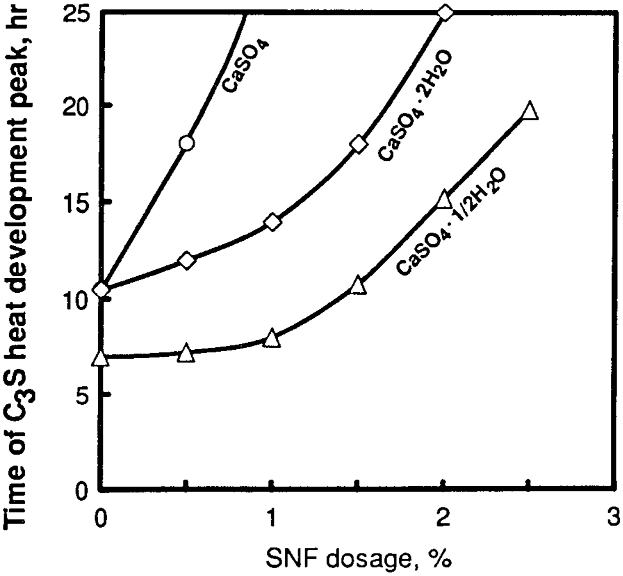


Figure 25. Effect of SNF on the hydration of tricalcium silicate in a high alkali cement.

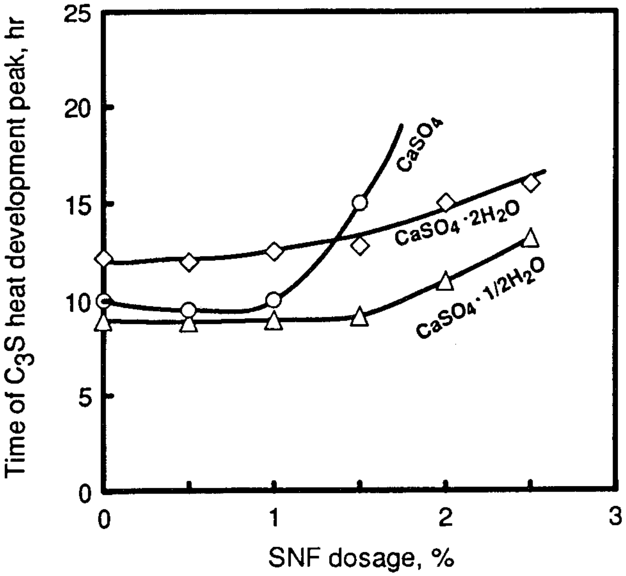


Figure 26. Effect of SNF on the hydration of tricalcium silicate in a low alkali cement.

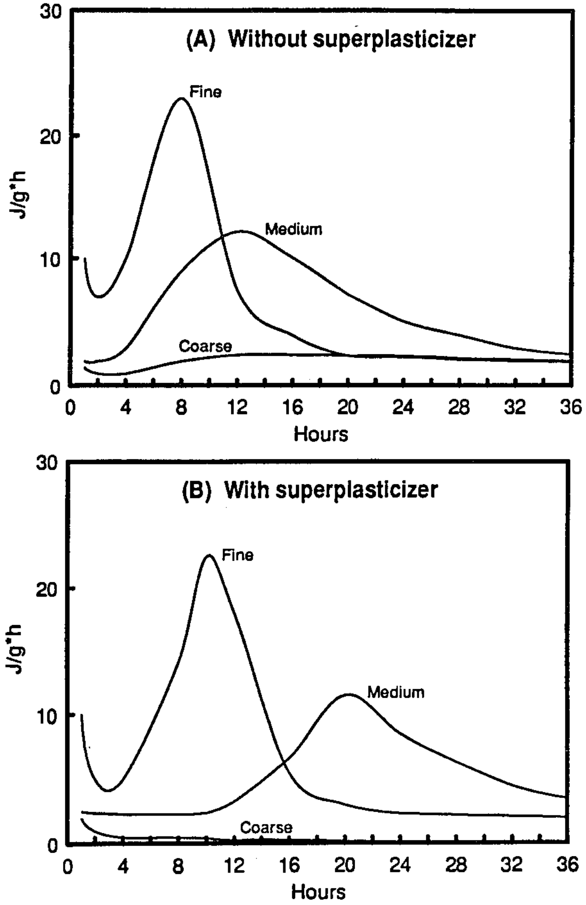


Figure 27. The effect of particle size of Type III cement on its hydration characteristics. *(Reprinted from* Cement Concrete Res., *17:995-999, P. C. Aitcin, et al., © 1987, with kind permission from Elsevier Science Ltd, The Boulevard, Langford Lane, Kidlington 0X51GB.)*

Most work on hydration aspects on cements pertains to ASTM Type I cement. The type of cement should play an important role in determining its physicochemical properties in the presence of superplasticizers. Contrary to expectations, Ramachandran et al.[60] found that concrete made with ASTM TypeV cement (water:cement = 0.5 and containing 0.6% SNF or SMF superplasticizer) developed lower strengths than the control. In concrete with Type I cement, the strengths did not show a decrease (Table 4). The strength data on the cement paste also showed the same effects. The conduction calorimetric curves in Fig. 28 for both Type I and Type V cements containing 0.6% SMF show differences. A more efficient retarding action occurs in Type V cement. The causes leading to the differences in strength development in these cements were explained by the lower porosities, and also very low rates of early hydration developed in Type V cements.

Table 4. Compressive Strength Development in Superplasticized Concrete Containing Type V Cement

W/C	Compressive Strength (MPa)				
	1day	3 days	7 days	28 days	90 days
Reference Concrete					
0.40	15.2	24.5	30.4	40.6	52.1
0.45	10.4	18.2	24.5	34.8	42.5
0.50	7.2	13.4	18.9	29.0	36.0
Superplasticized Concrete					
0.40	15.9	22.3	27.3	36.0	44.6
0.45	11.8	18.3	22.7	30.5	39.3
0.50	7.7	11.8	15.4	22.4	27.8

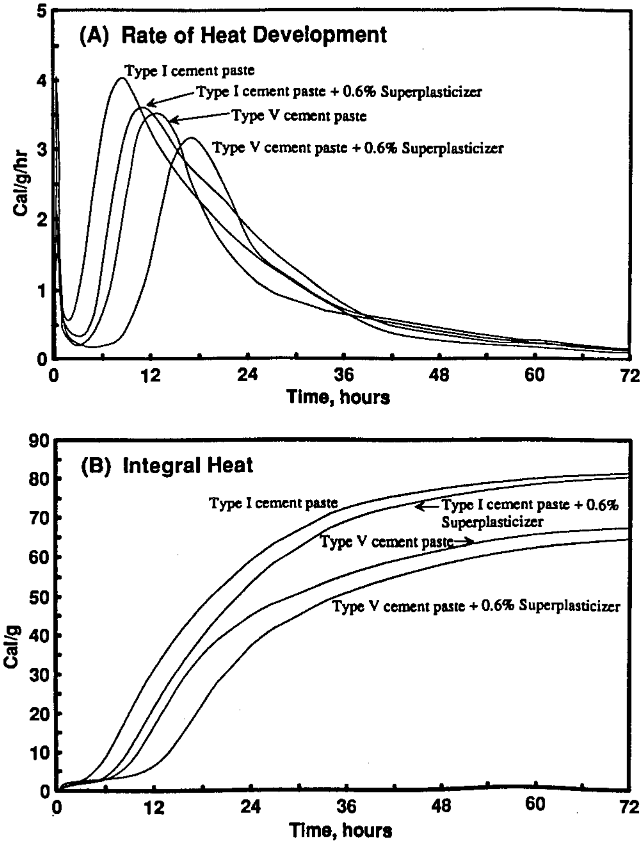


Figure 28. Conduction calorimetric curves for cements containing an SMF superplasticizer.

A limited amount of work has been carried out on the examination of the microstructure of cement containing superplasticizers. In C_3A-$CaSO_4 \cdot 2H_2O$-H_2O systems, a difference in the microstructure between that hydrated with and without 1% SNF was observed by SEM. At 30 mins in the absence of the superplasticizer, large fibrous ettringite bundles resulted. In the presence of superplasticizer, the ettringite was more needlelike. The former type of morphology may enhance interlocking and loss of workability.[49] Sakai et al. also observed changes in the microstructure of ettringite at 1 hour in the presence of superplasticizers.[47] Some differences in the morphologies have been observed in the products formed in C_3A-gypsum system containing SNF.[26] Well defined ettringite crystals formed in the reference samples, and in the samples with SNF products consisted of ill-defined ettringite laths, 3 µm long. Sarkar and Aimin[61] applied the ESEM technique that permits microstructural examination of cement paste samples under low vacuum, especially specimens containing moisture. They mixed C_3A_c (cubic) and orthorhombic C_3A_o (alkali-stabilized) with gypsum and investigated the morphologies from the first minute of contact of the solids with water. In the 5 minutes of hydration (without the SNF), the C_3A_c gave needlelike crystals of ettringite whereas C_3A_o showed elongated platy structure. At 20 minutes, large needles replace these platy crystals. In the presence of SNF, C_3A_c formed a dense microstructure. At 25 minutes, extremely short fibers resembling ettringite formed and this may cause retardation of reactions. The C_3A_o showed a different microstructure, forming a honeycomb structure up to 30 minutes.

Using the same w/c ratio of 0.6, a comparison of the SEM photographs of C_3S hydrated with or without SMF for 6 months shows differences. The hydrate formed in the presence of SMF has a more compact structure and seems to be less porous than the reference specimen.[29]

Although no substantial changes occur in the morphology of cement pastes hydrated with or without superplasticizers, the presence of finer particles and formation of a denser structure in cement paste hydrated with superplasticizers are known to occur. Recent work by Yilmaz and Glasser[62] has shown that morphological changes occur in the calcium hydroxide phase in the hydrated cement containing SMF. In the absence of SMF, pseudo hexagonal prismatic morphology predominated, but in the presence of 2% SMF, crystals were very thin and irregular and consisted of numerous stacked platelets.

3.5 Estimation

The estimation of admixtures in fresh, as well as in hardened, concrete is important from both theoretical and practical points of view. Sometimes problems that arise in practice may be attributed to the usage of excess, inadequate, or even a wrong type of admixture. In such cases, qualitative analysis and quantitative estimation of admixtures become very necessary.

The methods of estimation should rely on the complete extraction of the admixture and this is not always possible. In addition, there is always the possibility of interferences from other constituents. In view of this, the following procedures for the estimation of superplasticizers can be considered as a guide.

The SNF, SMF, and MLS types of admixtures can be estimated by extraction with 10% sodium carbonate. After filtration and centrifuging, the solution is subjected to analysis in the UV spectrophotometer. The wavelengths used for estimation are 340, 220, and 250 nm for MLS, SMF, and SNF respectively. The sulfonates may also be estimated by extracting with NaOH and measuring the absorbance at 520 nm.

Much interest has been shown in recent years in applying various techniques to identify or estimate superplasticizers. Techniques include wet chemical analysis, thermo-analytical techniques, HPLC, spectrofluorometry, chromatography, infrared analysis, and UV.

Yilmaz and others have suggested the application of spectrofluorometry as an alternative to UV for quantitative analysis of SNF and SMF-based superlasticizers.[63] In the quantitative estimation of SMF by the UV method, they found that the OH ions interfered with the determination. Spectrofluorometry was claimed to yield more accurate results and the effect of pH interference was negligible when this method was used.

The IR spectroscopy has been used for estimating superplasticizers. For SNF, characteristic bands for sulfonate occurred at 1200 cm^{-1}, and other bands situated between 1330 and 1540 cm^{-1} were also recorded.[64] The SMF gave a characteristic band at 820 cm^{-1}. Bensted made a systematic characterization of SNF by IR. Several typical bands were obtained for OH and CO stretching frequencies, including frequency bands typical of aromatic structure.[65] The applicability of TG/DTG and Fourier Transfer Infrared Spectroscopy has also been assessed to characterize some SNF-based admixtures.[66] The DTG exhibited some differences in the thermograms. FTIR although showing similar spectra for most samples, had different intensity values due to the molecular weight differences.

Methods are needed to determine the molecular weight distribution of laboratory-synthesized superplasticizers. The gel permeation chromatography has been successfully applied to determine the monomer and low molecular contents of SNF.[67] By applying this technique, up to twenty different molecular weight fractions of SNF could be analyzed.

Thermal analysis methods such as DTA, DTG, TG, and EGA have been applied in the estimation of superplasticizers. Gupta and Smith[68] tested DTG for differentiating sodium salts of SNF from those of SMF. In SMF there was a loss of weight at about 400°C and the loss in SNF occurred at about 800°C. In the evolved gas analysis technique, organic gases and vapors are determined. A quantitative assessment of superplasticizers has been made utilizing this technique.[69]

A deflocculation method has been developed by Verhasselt and Pairon to quickly differentiate the normal plasticizer from the superplasticizer.[70] The technique also determines the minimum active dosage required for a given cement, and also the relative effectiveness of various types of superplasticizers.

4.0 FRESH CONCRETE

4.1 Workability

The workability of concrete is measured by means of slump, flow table spread, compacting factor, or modified flow table method. These methods are not satisfactory for the concrete of flowing consistency. The slump test, although used extensively, reaches its practical limit at about 220–250 mm. The ability of the superplasticizers to increase the slump of concrete depends on the type, dosage, and time of addition of the superplasticizer, w/c ratio, nature and amount of cement, aggregate, temperature, etc. Generally, the superplasticizers are used at higher dosages than are conventional water reducing admixtures.

The chemical nature of the superplasticizer determines its effectiveness in increasing the slump. For example, to obtain a slump of about 260 mm from an initial value of 50 mm, it may be necessary to add 0.6% SMF or MLS-based superplasticizer, whereas this could be accomplished with only 0.4% SNF.[71] Lassard obtained data on the relative amounts of SMF and SNF needed to attain the same slump value.[72] For example, to obtain a slump of 185–190 mm (w/c = 0.3), the dosage required for SMF and SNF were 14.9 L and 9.3 L, respectively. Also for obtaining a slump of 230–240 mm at a w/c ratio of 0.22, the corresponding dosages were 20.3 L and 13.6 L. These results show that SNF outperforms SMF by increasing the slump at a given dosage. Similar conclusions were drawn by Zakka et al.[73] Some work has indicated that the Ca salt of polystyrene sulfonate, at a dosage of only 0.1%, increases the slump from 8 cm to 18 cm whereas 0.15% Na salt of SNF would be needed to achieve the slump gain.[42]

The dosage required to obtain a required slump depends on the initial slump: low slump mixes require higher dosages. At any particular initial slump, the slump value increases as the amount of superplasticizer is increased[6][74] (Fig. 29). The effectiveness, however, does not continue beyond a particular dosage. The superplasticizer permits manipulation of a wide range of workability within a narrow range of initial water to cement ratios.

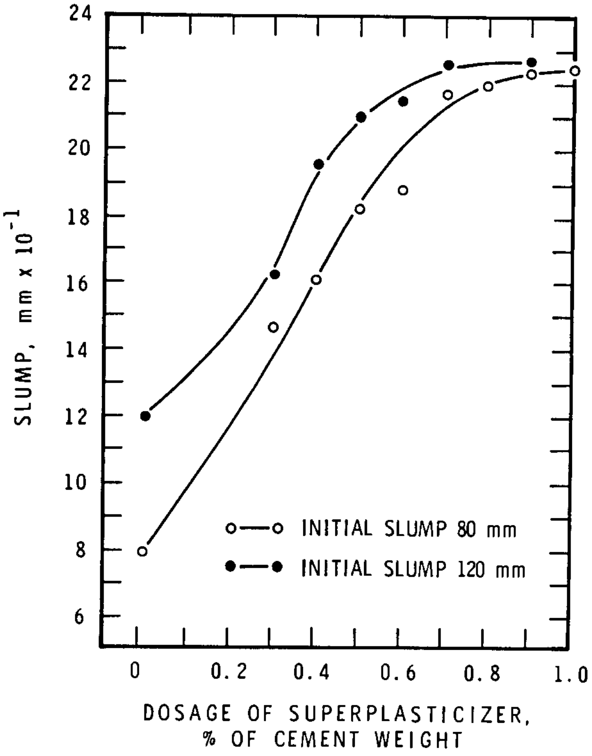


Figure 29. Effect of dosage of superplasticizer on slump of concrete.

The time when the superplasticizer is added to concrete affects the slump values. By adding the superplasticizer with the mixing water, the slump value is increased considerably. Even higher slump values are possible by the addition of the admixture a few minutes after the concrete is mixed with water. In the period from 5 minutes to 50 minutes after the concrete is in contact with water, addition of superplasticizer generally results in decreased slump values (Fig. 30).[6][75]

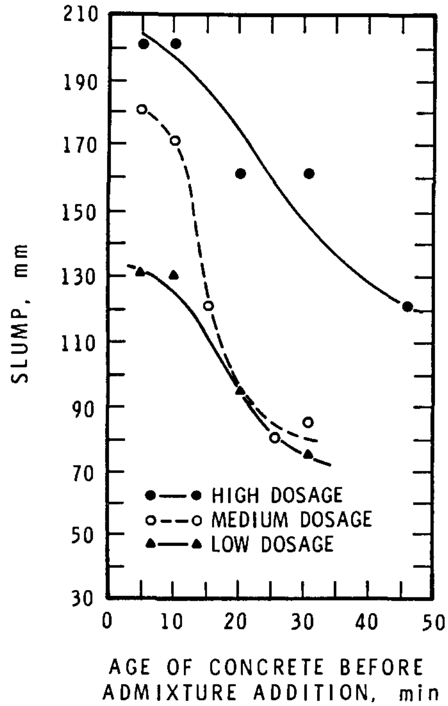


Figure 30. Effect of delayed addition of superlasticizer on the slump of concrete.

Many types of portland cement show an increase in workability by the addition of a superplasticizer. For example, by incorporating 1.5% SMF in concretes containing Types I, II, and V cements, the initial slump of 76 mm is increased to 222, 216, and 229 mm, respectively;[76] but it is necessary to carry out preliminary tests if a cement other than Type I cement has to be used. The cement content is also a factor that determines the slump values.

Concretes containing 237, 326, and 415 kg/m^3 of cement, exhibit slumps of 203, 222, and 254 mm, respectively, when using an SMF-type admixture.[76] This trend is expected because, even in cement without an admixture, the mix becomes more fluid as the cement paste content is increased.

In the temperature range of 5–30°C, there is no drastic difference in the slump values attained by the addition of a superplasticizer.

4.2 Water Reduction

The amount of water reduction (15–35%) achievable with a particular superplasticizer depends on the dosage and the initial slump (Table 5).[77] There is evidence that, beyond a particular dosage, further water reduction is not possible. In all types of portland cements, water reduction occurs, but to different extents. Generally, water reduction increases with the increase in the cement content. It has been reported that, for equal water reductions, more SMF than SNF type admixture is required.[12] The water reduction also depends on the type of superplasticizer and the type of cation associated with the superplasticizer. Popescu et al.[55] investigated the water reduction capabilities of ammonium salt of SNF, sodium-based SMF, and a mixture of lignosulfonate and alkyl aryl sulfonate. Compared to the w/c ratio of 0.25 for the reference, the values for the above admixtures were 0.21, 0.23, and 0.23 respectively.

Table 5. Water Reductions in Concrete with an SNF Superlasticizer

Dosage	w/c ratio	water reduction	slump
Reference	0.60	0	100
Double	0.52	15	100
Normal	0.57	5	100
Triple	0.48	20	100
Reference	0.55	0	50
Normal	0.48	13	55
Double	0.44	20	50
Triple	0.39	28	45

4.3 Slump Loss

Higher than normal workability of concrete containing a superplasticizer is maintained generally for about 30–60 minutes, and this rapid decrease in slump is termed *slump loss*. Factors that determine slump loss include the initial slump value, type and amount of superplasticizer, type and amount of cement, time of addition of the superplasticizer, humidity, temperature, mixing criteria, and the presence of other admixtures in the mix.

In order to control the slump loss, the superplasticizer may be added at the point of discharge of concrete. It is more desirable, for control purposes, to add the superplasticizer at the ready mix operations.

The rate of slump loss depends on the type of superplasticizer. At 0.6% SMF, SNF, or modified lignosulfonate, the rate of loss may be the highest with SMF.[71] The loss in slump is also a function of the temperature. Table 6 shows the effect of temperature on the loss of slump of concrete containing an SNF type of admixture.[31] The loss of workability is lower at lower temperatures.

Table 6. Effect of Temperature on Slump Loss in SNF-Based Concrete

Time (hrs)	Slump (mm)		
	4°C	21°C	42°C
0	220	220	210
0.5	205	200	195
1.0	210	195	185
2.0	210	200	150
4.0	185	140	30

The mechanism responsible for the slump loss may involve chemical and physical processes. According to Hattori and Izumi,[78] the loss of consistency in cement paste during the dormant stage is mainly attributable to the physical coagulation of the cement particles rather than to chemical processes. In the period during which the slump loss is occurring, the tricalcium aluminate phase reacts with gypsum. The product develops into a crystalline structure and is distributed in the mass. It is thus possible that the reaction of the aluminate phase will have an important effect on the workability of concrete. It has been shown that the addition of superplasticizer enhances the reaction between the aluminate phase and gypsum.[18] The rate of this reaction is also enhanced by the presence of increased amounts of sulfate. Young carried out work on the individual cement phases.[79] Slump loss of tricalcium aluminate + 30% gypsum, tricalcium silicate + tricalcium aluminate + gypsum and tricalcium silicate systems in water were examined (Fig. 31). Slump loss did not occur in the C_3A + gypsum system. The slump loss was related to the C_3S phase. For a given slump gain, higher amounts of the silicate phase were required, and this also was related to greater slump loss. It appears, therefore, that hydrate coatings restore charge interactions between the C_3S grains, thereby restoring tendencies for flocculation. Re-dosing with the superplasticizer neutralizes these charges and restores the fluidity, but continued hydration will lead to slump loss. The retarders that retard the C_3S hydration are expected to delay the onset of rapid slump loss.

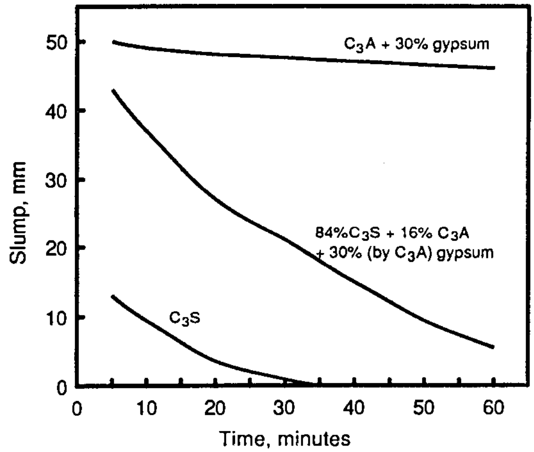


Figure 31. Slump loss in cement compounds containing gypsum.

Hanna et al.[80] have developed a procedure with a rheopump to test the fluidity characteristics of cements in the presence of SNF. An equation describes the fluidity in terms of the aluminate phases in the cement pastes, as follows:

$$\text{Fluidity Factor } (F_f) = \alpha\ C_3A + C_4AF$$

The factor α is related to the fineness and is allotted values 1, 2, or 3. It was found that the higher the F_f value, the lower the fluidity retention. Good fluidity levels for grouts were obtained for $F_f < 20$ while those with $F_f > 30$ showed poor fluidity retention.

Several methods have been adopted to extend the slump retention such as addition of higher amounts of superplasticizer, use of a retarder, redosing with superplasticizer at different time intervals, use of coarser grained admixture, blends of admixtures, water soluble polymer, etc. Figure 32 shows how adding an SMF superplasticizer at different times can restore the slump value.[81] Similar results have also been obtained using SNF.

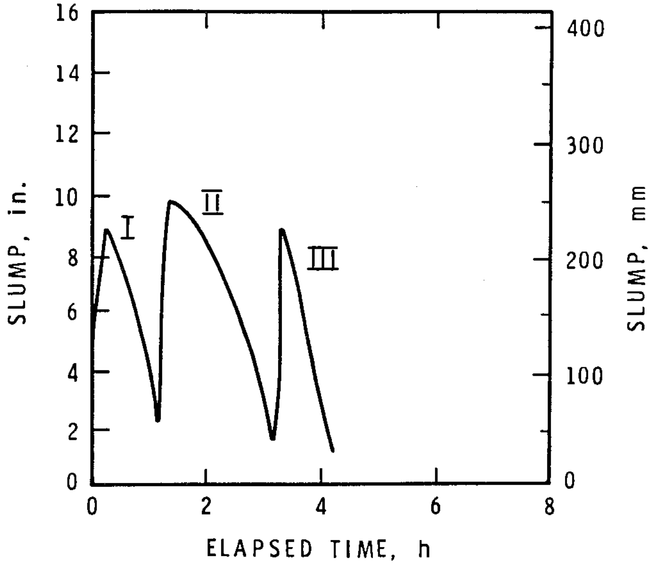


Figure 32. Effect of repeated dosages of SMF on slump of concrete. I: 1st dosage; II: 2nd dosage; III: 3rd dosage.

The effect of w/c ratios on the retempering has been examined on four types of concrete at w/c ratios of 0.5, 0.6, 0.7, and 0.8.[82] The concretes contained 0.5% superplasticizer by weight of cement. Figure 33 gives the slump loss as a function of time. The effect of retempering is more pronounced in terms slump increase at lower w/c ratios. Although the rate of slump loss is similar for the samples, slump retention is higher for low w/c ratio concretes. It was also found that low w/c ratio concretes had higher strengths than those which were not retempered.

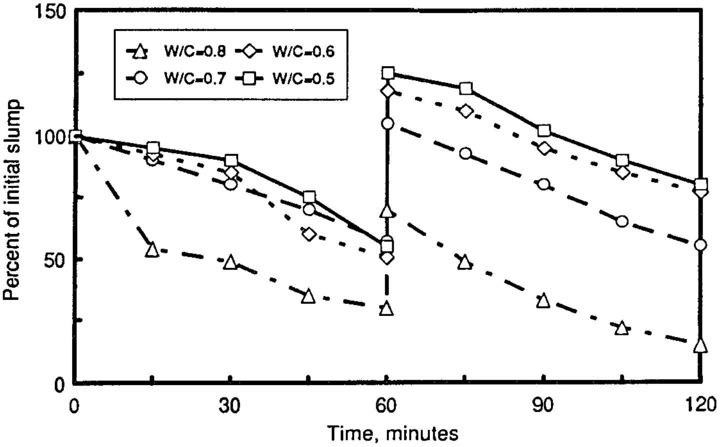


Figure 33. Retempering of concrete at different w/c ratios.

Another method of extending the slump in superplasticized concrete is to use blended admixtures.[83] Various commercial superplasticizers containing mixtures of admixtures were subjected to tests involving slump loss measurements.[83] Some results are plotted in Fig. 34. The designations FN-I, FM-2, FB-I, and FX-I are as follows: FN-I is a blend of Na and K salts of lignosulfonate and SNF; FM-I contained a blend of SNF, SMF and a salt of hydroxycarboxylic acid; FB-I contained a blend of SNF and lignosulfonate; and FX-I was a Na salt of copolymer of unsaturated carboxylic acid and a hydroxy alkyl ester of the acid. C-I refers to concrete containing only air entrainment. All the admixed concrete, although showing high slump of about 8", loses slump with time. The *flow life,* representing the time required for concrete slump to revert to that of the same concrete prior to addition of the superplasticizer, is used to determine the relative effectiveness of the formulations. In most cases, it exceeds one hour and is greatest for concrete containing FX-I admixture. Park et al.[84] have attempted to use an SNF-lignosulfonate condensate and found that the slump was retained well, but there was a substantial increase in the setting times and bleeding. It is evident that extended slump retention with 2 or 3 repeated dosages of superplasticizers may result in extra bleeding and segregation. Sometimes setting may occur only after 24 hrs.[85]

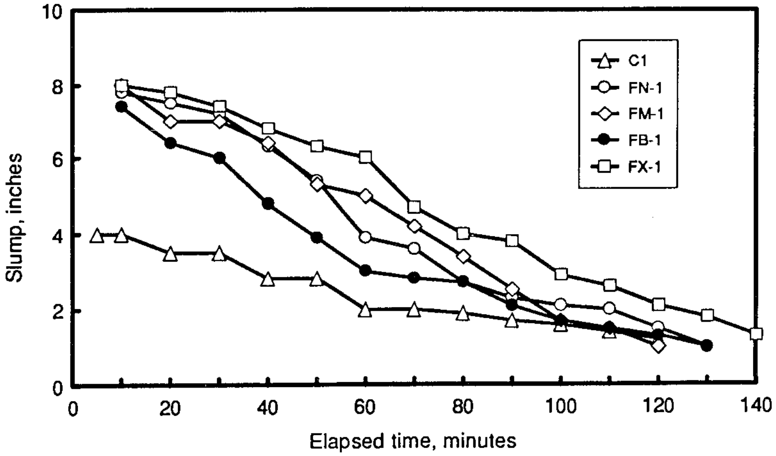


Figure 34. Slump loss in concretes containing blends of admixtures. *(© ASTM, reprinted with permission.)*

Slump control is especially critical in hot climatic conditions. Retempering at temperatures of 30 or 60°C has not been found to be detrimental to the quality of fresh and hardened concrete.[86] The effect of retempering at 3 w/c ratios are shown in Fig. 35. The retempering was done at 30 minutes and 70–80 minutes. The quantity of superplasticizer for the second retempering was considerably higher than that for the first retempering. For example, concrete prepared at a w/c ratio of 0.4 had an initial slump of 65 mm which increased to 95 mm on first retempering with 14 mL of the admixture. At the second retempering stage, the initial slump had fallen to 5 mm and it needed an addition of 374 mL of admixture to increase the slump to 85 mm.

By repeated addition of dosages of superplasticizers, both adsorption and zeta potential values are increased and viscosity is decreased. Inclusion of some retarders in the superplasticizer formulation retards slump loss. In Fig. 36, the slump loss of concrete containing no admixture is compared with that containing 0.3% SMF or Na gluconate or a mixture of SMF and Na gluconate.[87] The admixture containing a combination of gluconate and superplasticizer, in addition to increasing the initial slump, also retards the slump loss.

The cement content is another important factor that determines slump loss, the higher cement content reduces the rate of slump loss.[81]

In addition to the work described above, several examples of recent work on the methods of controlling slump loss in concrete are given in Ch. 4.

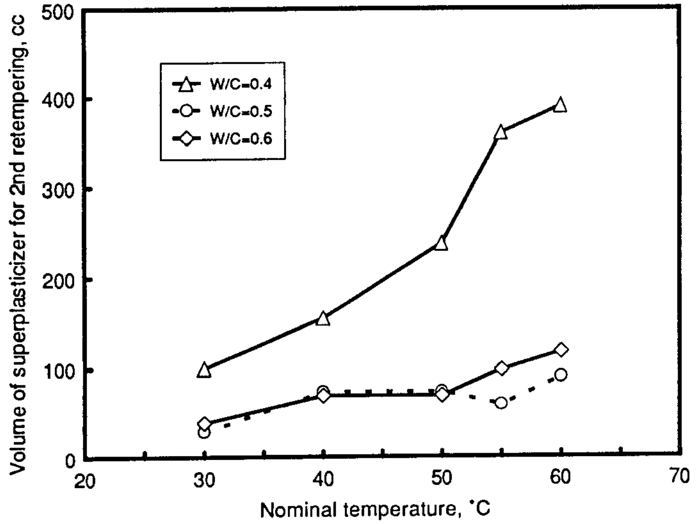


Figure 35. Amount of superplasticizer needed for retempering at various temperatures.

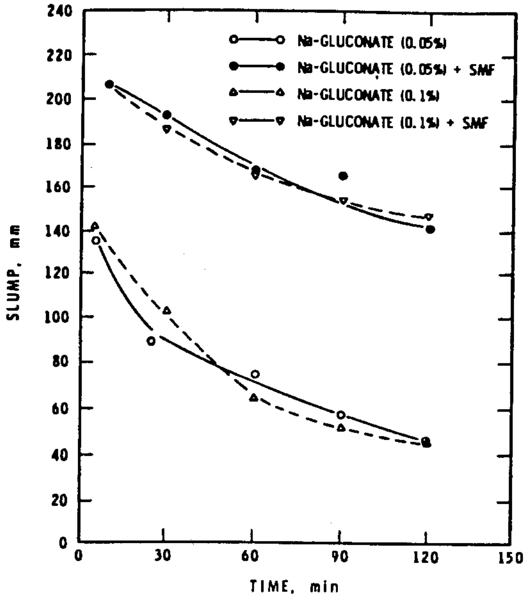


Figure 36. Effect of Na gluconate and its mixture with SMF on slump loss.

4.4 Bleeding and Segregation

Segregation is the separation of the components of the mix because of differences in their size and specific gravity. Bleeding is a particular form of segregation in which some of the mixing water raises to the surface of fresh concrete. Normal bleeding occurring as a uniform seepage (within limits) is not undesirable. In a water-reduced superplasticized concrete, no undue segregation or bleeding occurs. Generally, the bleeding decreases because of the decreased w/c ratio. This has been verified for Types I, II, and V (ASTM) cement concretes.

Bleeding and segregation may occur in flowing concrete if precautions are not taken. When repeated dosages of superplasticizers are used to control the loss of slump, bleeding and segregation may occur if the repeated dosing exceeds two or three times. The amount of bleeding depends on the type of superplasticizer. For example, the addition of both Na-based SNF and Ca-based polystyrene sulfonate increases bleeding. The bleeding period is an hour longer in concrete containing Ca-polystyrene sulfonate than in Na-SNF. However, the total amount of bleeding is almost equal.[42] When excessive bleeding occurs, stabilizing agents may have to be used.[88] Overdosage of superplasticizers promotes segregation and formation of a deposit containing lime, calcium sulfate, and calcium carbonate. This is called *chemical segregation* and can be solved by the addition of extra cement into the mix.[15]

In concrete mixes with flowing consistency, the mix must have sufficient fines. According to the Canadian Association Guidelines (A 266.5M 1981), in conventional mixes modified to flowing consistency containing aggregates of maximum size 40 mm, 20 mm, and 14 mm, the recommended minimum amount of combined fines passing 300 μm sieve is 400 kg/m^3, 450 kg/m^3, and 500 kg/m^3, respectively.

4.5 Air Content

Superplasticizers based on SNF and lignosulfonates entrain some air in concrete. In fluidized concrete, the superplasticizer facilitates escape of some air. Typically 1–3% of air is lost. Repeated dosage of a superplasticizer will accentuate this effect. At a w/c ratio of 0.42 using SNF, the initial air content of 4.9% is decreased to 3.8, 1.7, and 1.5% after the 1st, 2nd, and 3rd dosages respectively. In the presence of lignosulfonate-based admixture, the air content may actually increase.[88] Superplasticizers may also coalesce the air bubbles to some extent. The air loss from concrete is also a function of the type of superplasticizer. In concrete containing Na-based SNF, the loss was found to be 2%, but in the presence of Ca-salt of polystyrene sulfonate, the loss was only 0.6%.[42]

Incorporation of SNF admixture sometimes leads to the phenomenon called *bubbling concrete* or *champagne effect.*[15] During mixing, large air bubbles are entrapped and sparkle like champagne. Some of these bubbles may remain entrapped in the hardening concrete even after good vibration.

4.6 Setting Times

Generally, superplasticizers retard the setting of concrete. The extent of retardation depends on the temperature, type of cement, and the type and dosage of the superplasticizer. Investigating three types of superplasticizers, Popescu et al.[55] found that the setting times increased by 15 mins to 2 hr 30 mins, depending on the admixture. In an investigation of several superplasticizers, another work[89] has reported that the maximum delay in the initial setting time was 2 hr 30 min and in the final setting time, 1 hr 45 mins. Excessive retardation may result by accidentally overdosing with the superplasticizer or with certain cement compositions. For example, with double the normal dosage, the retardation with Type V cement may be excessive but it may be acceptable in Type I cement.[60] In combination with a retarder, the superplasticized concrete may show a synergistic effect, i.e., the value may exceed that obtained by adding the retardation effects of the individual admixtures.[83]

Figure 37 shows the penetration resistance results for samples containing three types of superplasticizers.[81] There is generally a retardation effect, except for SMF, which shows a slight acceleration effect that may be caused by the low w/c ratio used. The setting times may be retarded or accelerated when superplasticizers are used in combination with other admixtures. Figure 38 shows the setting times in mortar containing SMF with various types of retarders. The initial setting times of retarder-SMF combinations are higher than those with retarders only.[87]

The setting times are also influenced by the temperature. The initial and final setting times of cement containing 1% SMF are given for three temperatures: 20, 40, and 55°C. The setting times are increased by the incorporation of superplasticizer. The difference tends to decrease as the setting temperature is increased (Table 7).[52]

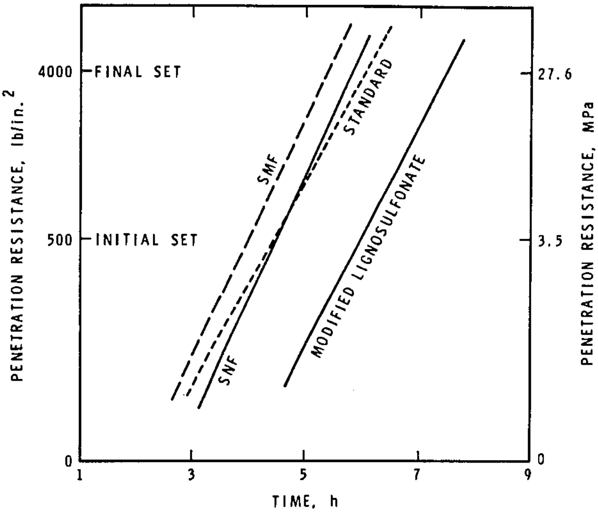


Figure 37. Effect of superplasticizers on the setting property of concrete.

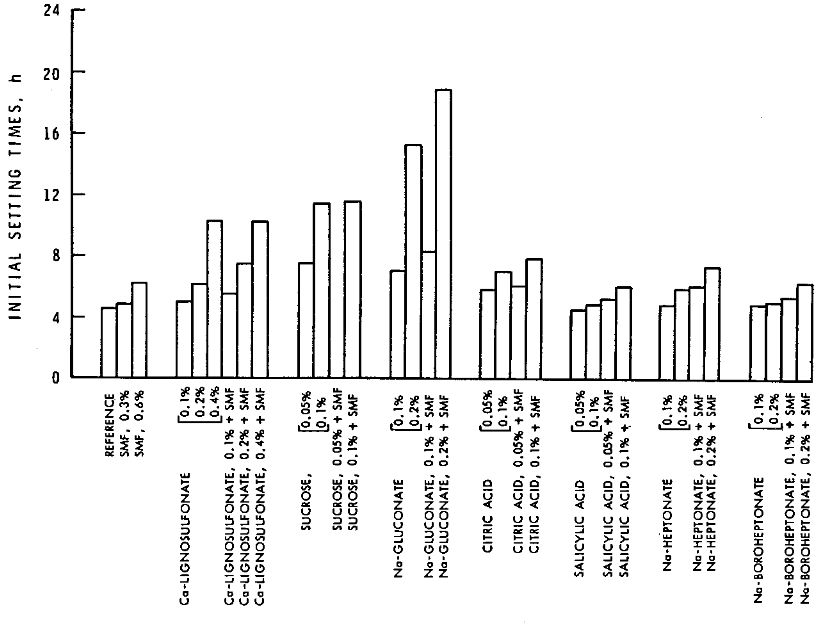


Figure 38. Effect of retarders and their mixtures with SMF on initial setting times for mortar.

Table 7. Influence of SMF on the Setting Times of Cement at Different Temperatures

Temperature, °C	Initial Setting (mins)		Final Setting (mins)	
	Ref.	SMF	Ref.	SMF
20	225	283	257	330
40	134	157	159	181
55	100	113	125	139

4.7 Compatibility

Some of the problems arising out of the use of superplasticizers with other admixtures have been discussed. Generally retarders, water reducers, accelerators, and air-entraining agents have been found to be compatible with superplasticizers. In some instances, the resulting effects are synergistic. It is, however, essential that each admixture combination should be evaluated before it can be practically utilized. With air-entraining agents, attainment of sufficient air with adequate bubble size distribution and spacing may not be easy to achieve. The superplasticizers have been shown to be very compatible with many types of fly ashes.

Problems could arise if higher than normal dosages are used with Type V cement. It has been found that, with normal cement concrete, the use of 0.6% SMF or SNF results in strengths equal to those of the reference specimens. However, with Type V cement concrete, the strengths are decreased significantly with 0.6% superplasticizer addition.[60] Figure 39 demonstrates the low strengths attained with the use of cement pastes containing the superplasticizer. The low strengths are attributable to the development of higher porosity and a more efficient retardation of hydration in the Type V cement. High dosages of admixtures may also result in undesirable effects. Johnston[90] attributed the low strengths and excessive retardation in some concretes to the use of high dosages of lignosulfonate and a superplasticizer in Type V cement concretes.

The behavior of concrete in the presence of superplasticizers is related to the amount and type of sulfate added to the clinker. The rheological and setting behaviors are changed depending on whether the sulfate is added as anhydrite, hemihydrate, or gypsum. The differences are explained by the different rates of dissolution of these sulfates. They are discussed in Sec. 3.1.

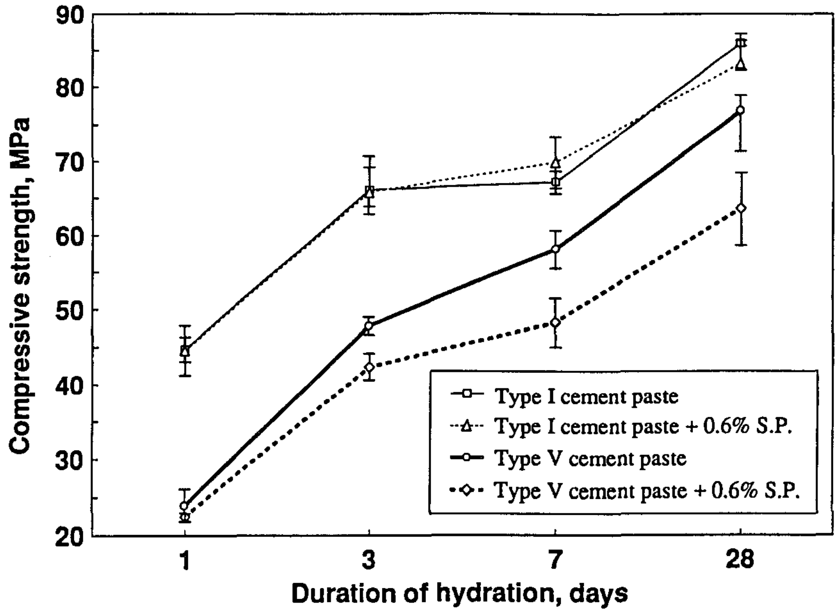


Figure 39. The effect of sulfonated melamine formaldehyde superplasticizer on the compressive strength development in ASTM Type I and V cements.

It is also important to note that all admixtures belonging to the same generic type may not behave similarly in concrete because of the variations in the molecular weight, cations associated with them, chain length, etc. Similarly, the same type of cement generically may be different in mineral, alkali and sulfate contents, and fineness.

4.8 Standards and Commercial Products

Standards. The ASTM standards C 494-92 and C 1017-92 provide information on the specifications for superplasticizers. Two types of superplasticizers, Type F water-reducing, high range, and Type G water-reducing, high range, and retarding, are described. The requirements for these admixtures are as follows: The water requirement (% max of control) for both types is 88%, whereas it is 95% for normal water reducing admixtures. The setting times for Type F admixture are as follows: The initial setting time (deviation from control) should not be more than 1 hr earlier nor 1 hr 30 min later, and the final setting time, not more than 1 hr earlier nor 1 hr 30 min later. The corresponding values for Type G admixture are 3 hrs 30 min later for both initial and final setting times; however, the added stipulation is that for Type G admixtures, the initial setting time should at least be 1 hr later. The compressive strength requirements are also different but only at 1 day; the minimum value, as a percentage of the control, is 140% and 125% for Type F and Type G respectively. The compressive strength values required for both admixtures are 125, 115, 110, 100, and 100% of the control at 3 days, 7 days, 28 days, 6 months, and 1 year respectively. The minimum flexural strengths should be 110% of the control at 3 days. The durability and length changes are similar to all chemical admixtures.

The ASTM C 1017-92 on *Flowing Concrete* describes Type I plasticizing and Type II plasticizing and retarding admixture. The flowing concrete is defined as a concrete that is characterized as having a slump greater than 7½ inches while maintaining a cohesive nature. Type G and Type II have similar setting time requirements except the initial setting time for Type II should not be more than (at least) 1 hr later than the reference. The setting time values for both Type I and Type F admixtures are similar. The increase in slump for both these admixtures should be at least 3.5 inches. The compressive strength as a minimum of the reference at 3 days to 1 year for both types is 90%. The flexural strengths are also expected to be 90% of the reference from 3 days to 28 days. The proportioning of concrete mixtures is carried out according to ACI 211.1-81.

The Canadian Standards Association published a preliminary standard A 226.5-M 1981 on *Guidelines for the Use of Superplasticizing Admixtures in Concrete.* This standard discusses types of admixtures, their function, mix proportioning, compatibility with other admixtures, addition method, placement, and principal effects on fresh and hardened concrete. The Canadian Standards CAN 3-A 266.6-M 85 deals with *Superplasticizers in Concrete.* The superplasticizers are divided into four types: SPN and SPR (non-flowing types) and SPN and SPR (flowing types). The minimum water requirement for the non-flowing type is 88% of the control, whereas there is no requirement for the flowing types. There is also a requirement for the slump retention. The slump retention of the mix after 20 minutes should at least be 50% of the initial slump. The initial set (a minimum difference with respect to the control) is 1 hr 20 min for both SPN types and 1 hr for both SPR types. The maximum values are 1 hr 20 mins for SPN and 3 hrs for SPR. For the flowing type admixtures the compressive strength should be the same as the reference specimen from 1 day to 1 year. The SPN (non-flowing) concrete should have a minimum compressive strength (with respect to the reference) at 1 day, 3 days, 7 days, 28 days, 6 months, and 1 year, of 150, 130, 125, 120, 100, and 100%, respectively. The corresponding figures for SPR (non-flowing) are 130, 130, 125, 120, 100, and 100%. The air void spacing (maximum) should be 0.23 mm. The relative durability factor defined as T/R x 100 x 1.10 should be a minimum of 100 for all superplasticizers. T and R are respectively test and reference samples.

The American Concrete Institute *Manual of Practice* covers superplasticizers in ACI Manual Part I, 212-3R-93. Chapter 5 deals with the admixtures for flowing concrete. Information is provided on the materials, evaluation, application, performance criteria, proportioning of concrete, effects on fresh and hardened concrete, and quality assurance. The procedure for proportioning and adjusting concrete mixtures are covered under ACI 211.1. The fine-aggregate/coarse-aggregate ratio may require adjustment to assure that fines are present to allow a flowing consistency without excessive bleeding or segregation. It also may be necessary to increase the cement content or add other fine materials such as pozzolan or slag. The ACI committee report No. ACI 212.4R pertains to the *Guide for the Use of High Range Water-Reducing Admixtures (Superplasticizers) in Concrete.* It includes information on general uses, effects on fresh and hardened concrete, typical applications, and quality control. Typical applications such as high strength concrete, prestressed concrete, architectural concrete, parking structures, rapid high-rise projects, industrial slabs, and massive concrete are described.

Commercial Products. In this section, a few of the commercial products produced/supplied in North America are described. The products Daracem-100, WRDA-19, and a mid-range water reducing admixture (Daracem-55) are manufactured by W. R. Grace Construction Products. Daracem-100 is an aqueous solution of chemical dispersants. The slump retention of concrete is extended from 25–45 minutes to 50–90 minutes by the use of this admixture. The normal dosage is 5–10 ozs per 100 lbs (325–1300 mL per 1000 kg). This admixture meets the ASTM C 494 for Type F water reducing high range admixture. For proper air entrainment Daracem-100 should be used in combination with Vinsol resin or a tall oil derivative air entrainer. Daracem-100 is available in 55 gal (208 L) drums. It does not contain flammable ingredients. It will freeze at 0°C and can be used after thawing and agitation. However, it should preferably be maintained at a temperature above 4°C for storage and dispensing purposes. WRDA-19 is also an aqueous solution and is based on sulfonated naphthalene formaldehyde. It does not contain chloride. It conforms to ASTM C 494 Type A or Type F admixture. The normal addition rate is 6 to 20 fl ozs per 100 lb of cement. It is compatible with Vinsol resin and also with most Type A or Type D admixtures. In combination with retarders, excessive retardation occurs at higher dosages. For dispensing and storage, it should be kept above the freezing point.

Masters Builders produce several types of admixtures which increase the flowability of concrete. Polyheed 997 is a liquid that satisfies the ASTM specification for 494 Type A or F admixture. Some of the advantages in using these admixtures are: increased workability, pumpability, reduced segregation, and superior finishing characteristics in concrete. At a dosage of 3–6 ozs/cwt, it behaves as the ASTM Type A admixture. At 8 fl oz/cwt, it conforms to the requirements of ASTM Type F admixture. It is supplied in drums. Rheobuild 1000 is a high range-water reducing admixture and is used as ASTM Type A or Type F admixture. The plasticity range of concrete could be increased up to 11 inches (200–280 mm), slump is extended, time of set and segregation are controlled by this admixture. The recommended dosage is 10–25 fl oz per 100 lbs (0.65–1.6 liters/100 kg). If the admixture is frozen, it should be thawed at 7°C and agitated mildly. Conchem SPN is a high range water reducing admixture conforming to ASTM C 494 Type F admixture. It is used for high slump, high water reduction, rapid strength gain and normal setting characteristics. Rheobuild/MB-SF in concrete develops superior strengths and permits easy placement and improves finishing characteristics. It contains silica fume.

Fritz Admixture Company supplies three types of superplasticizers. They are Supercizer 6, Supercizer 5 and Supercizer 1. The Supercizer 6 is claimed to reduce water requirements by 40% and to increase the strength of concrete within 6–24 hrs. Supercizer 5 produces a flowing concrete and reduces water requirement by 25%. Supercizer 1 produces a highly flowable concrete with a slump of 6 inches.

Axim Concrete Technologies produces superplasticizers called Catexol 1000SP-MN and Catexol 2000-SP MN. The superplasticizer 1000-MN reduces water content by 30%. It contains a mixture of sulfonated-naphthalene formaldehyde, -melamine formaldehyde, and other proprietary ingredients. It is effective in concrete containing pozzolanic materials. It should be added at the end of the mixing cycle. It maintains the slump of concrete up to 90 minutes depending on the environmental conditions. It meets the ASTM C 494-92 Type A and Type F or CSA A 266 specifications.

Catexol 2000 SP-MN is formulated for the precast and piping industries. It provides denser concrete and higher early strengths. The recommended dosage is 65–200 mL/100 kg.

Handy Chemicals produces a highly active superplasticizer called Disal and Durasar. Disal is a salt of sulfonated naphthalene formaldehyde. It is capable of maintaining the slump of concrete for 1 hr at 20°C. It is supplied in drums. Storage at room temperature is recommended. A direct contact with the eye may cause irritation. Durasar is a non-alkaline superplasticizer with low a sulfate content. Reduction of water up to 50% is claimed for this admixture. Both admixtures are used at a dosage of 500–1000 mL/100 kg.

5.0 HARDENED CONCRETE

5.1 Methods of Using Superplasticizers

There are three possible ways in which superplasticizers may be used in concrete:

a. *To produce concrete with very low water-to-cement ratio.* To achieve high strength concrete, water content of the mixture is reduced while maintaining the same cement content. The reduced workability is compensated for by incorporating superplasticizers. By this method, water reductions of up to 30% can be achieved and concretes with water-to-cement ratios as low as 0.28 have been successfully placed.

b. *To produce concrete with reduced cement content.* Superplasticizers can be used to produce concretes with reduced cement contents while the water-to-cement ratio is maintained constant. As in method *(a)*, the decrease in workability of concrete is compensated by incorporating superplasticizers.

c. *To produce flowing concrete.* Superplasticizers have been used to produce self-compacting, self-leveling flowing concretes. In this application, no attempt is made to reduce either the water-to-cement ratio or the cement content. Instead, the aim is to increase the slump up to 75–200 mm without causing any segregation so that the concrete can be placed in heavily steel-reinforced sections.

5.2 Strength Properties

For flowing concretes, when superplasticizers are added to concrete at the manufacturer's recommended dosages, the 28-day compressive strengths of test cylinders cast from the superplasticized concrete are equal to or greater than the corresponding strengths of cylinders cast from the reference mixture. This is true for cylinders cast with and without compaction by vibration, implying that concrete incorporating superplasticizers can be placed in forms without the need for mechanical compaction, resulting in considerable savings of time and money. Notwithstanding the above, it is always desirable to use some vibrating during placement to ensure good bond between reinforcement and concrete, especially for structural slabs.

It has been mentioned already that water reductions of up to about 30% can be achieved in the manufacture of concrete when superplasticizers are incorporated in concrete as water reducers. Figure 40 illustrates one such instance.[90a] The increase in mechanical properties, i.e., compressive and flexural strength and modulus of elasticity is generally commensurate with reductions in water-to-cement ratio, although some exceptions have been noted.[91] The ability of superplasticizers to reduce water and achieve very high strengths is of special importance for the precast concrete industry where high early strengths are needed for rapid turnover of formwork. Figure 41 and Table 8 present strength data for flow and water-reduced concretes respectively made with three types of cement.[90a][92]

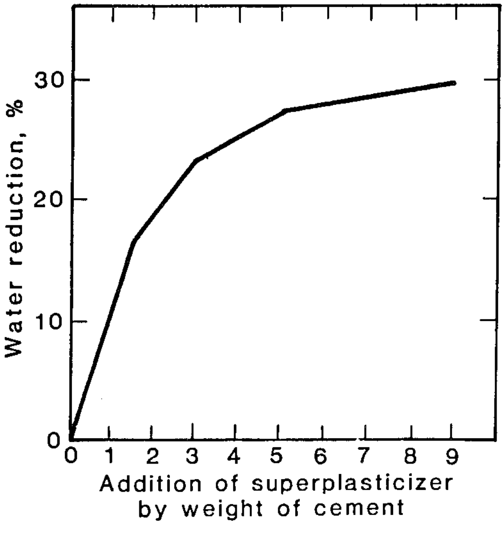


Figure 40. Water reduction obtained by adding a superplasticizer.

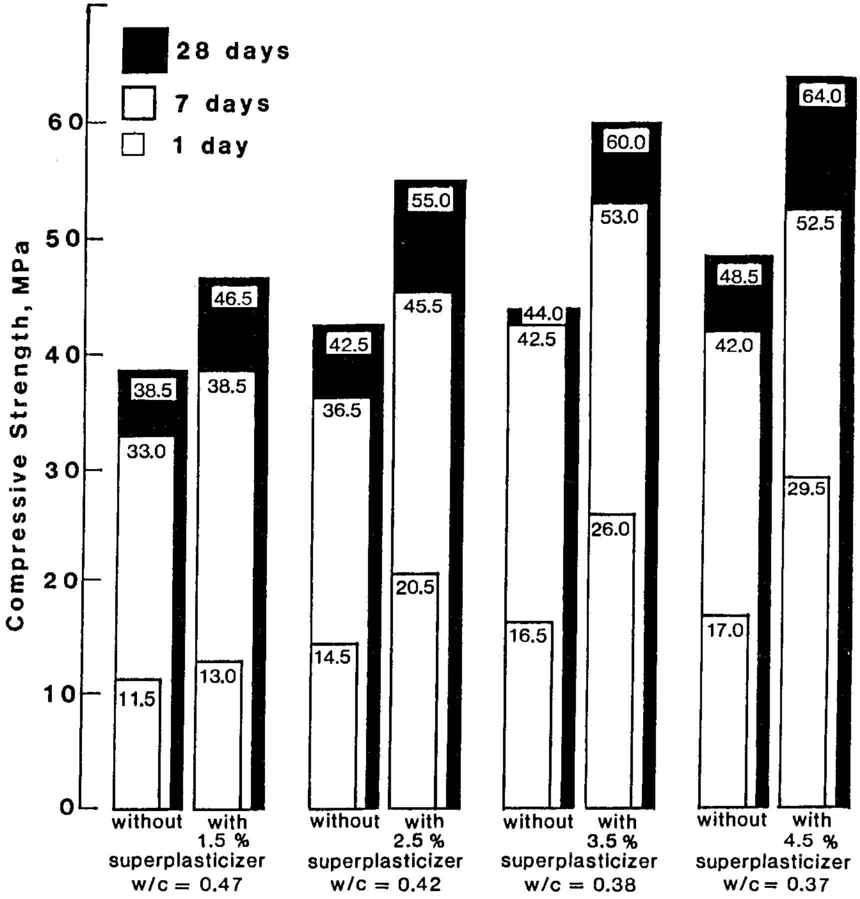


Figure 41. Strength development of high strength flowing concrete containing melamine-based superplasticizer compared to concrete made with 400 kg of normal portland cement per cm^3 in the stiff to soft workability ranges (25–100 mm slump).

Table 8. Mixture Proportions and Properties of Fresh and Hardened Concrete (Water Reduced)[92]

		Mixture Proportions and Properties of Fresh Concrete					Properties of Hardened Concrete				
							Compressive strength of 150x300 mm cylinders (MPa)			Flexural Strength of	
Mix Series	Type of Concrete	Water Content (kg/m^3)	W/C Ratio	Entrained Air (%)	Slump (mm)	Density (kg/m^3)	7 days	28 days	91 days	90x100x40 mm prisms (MPa)	Modulus of elasticity (MPa x 10^{-4})
1	Reference (Type I cement)	147	0.49	5.2	75	2348	26.8	32.8	37.8	6.1	3.2
2	Type I cement and SP-M	120	0.40	5.6	80	2362	37.3	44.0	48.5	7.0	3.7
3	Type I cement and SP-N	120	0.40	6.0	70	2350	35.5	39.3	47.6	7.0	3.7
4	Type I cement and SP-L	120	0.40	5.6	80	2360	36.3	42.6	49.9	6.6	3.6
5	Reference (Type II cement)	147	0.49	4.9	85	2354	25.6	36.6	42.4	6.0	3.2
6	Type II cement and SP-M	120	0.40	5.6	90	2362	36.3	47.6	55.0	6.9	3.7
7	Type II cement and SP-N	121	0.40	5.3	75	2377	36.9	47.6	55.8	7.2	3.7
8	Type II cement and SP-L	121	0.40	4.8	75	2385	35.0	47.6	55.8	7.3	3.6
9	Reference (Type V cement)	144	0.48	5.4	90	2352	19.1	32.2	38.0	5.0	3.2
10	Type V cement and SP-M	117	0.38	5.4	75	2364	31.9	40.3	46.2	6.2	3.6
11	Type V cement and SP-N	118	0.38	5.3	80	2381	33.0	42.0	48.5	5.7	3.5
12	Type V cement and SP-L	118	0.38	5.2	85	2379	32.8	42.4	50.3	6.2	3.5

1. Coarse aggregate was crushed limestone with a maximum size of 19 mm. Fine aggregate was natural sand. Air-entraining agent was sulfonated hydrocarbon.
2. SP-M, SP-N, and SP-L refer to melamine, naththalene and lignosulfonate type superplasticizers (SP) respectively.

5.3 Shrinkage and Creep

The shrinkage of superplasticized concrete is comparable to, or is less than, that of the reference concrete, although there are exceptions. Generally, the shrinkage of test prisms is well below the maximum requirement of ASTM C494.[93] The shrinkage data for flowing concrete are compared with those of conventional concrete in Fig. 42. The relationship between moisture loss and shrinkage for water-reduced superplasticized concrete is shown in Fig. 43.[92] For the same amount of moisture loss, the superplasticized concrete exhibits a larger shrinkage; this may be related to the larger dispersion of cement and cement hydrates.

Several investigators have published data on creep of superplasticized concrete. However, in each case, different concrete, loading, and moisture conditions have been used, thus making direct comparison rather difficult. The general consensus appears to be that concretes made with superplasticizers have approximately the same creep as the reference concrete, although there are exceptions. Data on creep measurements for control and water-reduced superplasticized concrete obtained by Ghosh and Malhotra[92] are shown in Table 9.

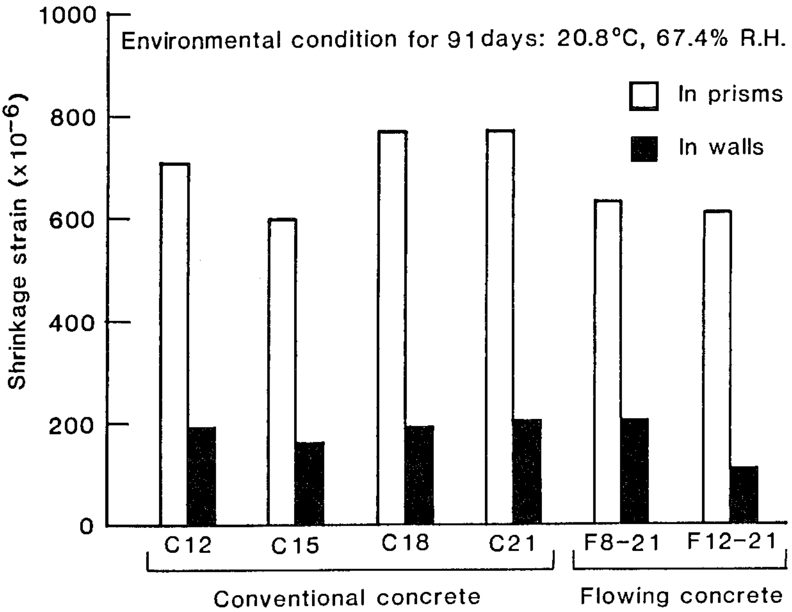


Figure 42. Shrinkage strains in each finished model wall compared with prisms at 91 days.

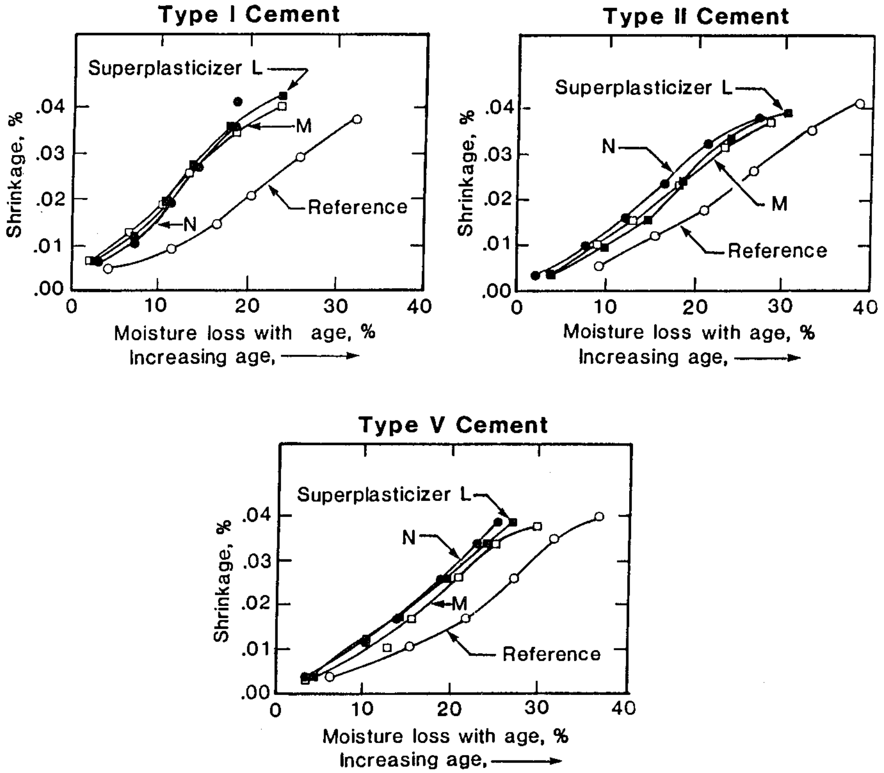


Figure 43. Shrinkage vs moisture loss for reference and superplasticized concretes. L = modified lignosulfonate, M = melamine and N = naphthalene.

Table 9. Data on Creep Measurements for Control and Water-Reduced Superplasticized Concrete[92]

………. Admixtures ……….			……… Mixture Proportions ………				Properties of Fresh Concrete			Creep Measurements on 150 x 300 mm Cylinders				
Superplasticizer type	Superplasticizer	AEA*	W/C ratio by Weight	Type I Cement	F.A.	C.A.	Entrained air	Slump	Density	f'c at 28 days	f'c at 63 days	Stress Applied	Stress/Strength Ratio	Total Creep Strain**
	. (ml/kg of	Cement) .		(kg/m^3)	… (kg/m^3)	…	(%)	(mm)	kg/m^3	…… (MPa)		……		(in./in x10^{-6})
Control	-	0.31	0.49	298	817	1,082	5.3	80	2,344	34.3	37.4	15.2	0.44	1,101@338 d
Melamine	23.6	1.18	0.40	304	835	1,106	5.4	75	2,365	45.2	50.8	19.6	0.43	1,085@324 d
Naphthalene	9.1	3.15	0.40	303	832	1,102	6.0	80	2,357	47.4	51.1	20.3	0.43	1,107@345 d
Lignosulfonate	25.6	0.34	0.40	305	839	1,111	5.4	40	2,377	46.0	48.7	19.8	0.43	1,157@339 d

*Air-entraining agent

**Total creep strain is obtained by subtracting shrinkage and elastic strain at loading from the strain readings

5.4 High Strength Semi-Lightweight Concrete

By the use of superplasticizers, semi-lightweight concrete having compressive strengths of the order of 30 to 40 MPa at one and three days respectively can be made.[95] In one investigation, the coarse fraction of the aggregate in the mixture consisted of 19-mm crushed lightweight aggregate manufactured by bloating extruded clay pellets in a rotary kiln. The unit weight and specific gravity of the coarse fraction were of the order of 740 kg/m^3 and 1.60, respectively. The fine fraction used was natural sand with a specific gravity of 2.70. The unit weight of the fresh concrete ranged from 1835 to 1961 kg/m^3. Table 10 gives a summary of mechanical properties of air-entrained, superplasticized, semi-lightweight concrete containing different cement contents.[95]

5.5 Effect of Repeated Dosages

To overcome the problem of rapid slump loss with time, a number of researchers have shown that large increases in slump of superplasticized concretes can be maintained for several hours by additional dosages, the amount of second and third dosage being the same as the initial. Figure 44 shows the effect of repeated dosages of superplasticizers on slump, air content, and 28-day compressive strength of concrete. As can be seen from Fig. 44, the strength of concrete is not impaired by the use of repeated dosages. The changes in the strength values are a direct reflection of the changes in the entrained air content. The concept of repeated dosages is especially suited for hot climates where rapid slump loss can occur during transportation.

5.6 Superplasticized Concrete Containing Fly Ash

Reports are available on the use of superplasticizers in concrete incorporating a large amount of fly ash.[96] The purpose of one such study has been to determine the following:

1. Whether high strengths could be achieved with concrete mixtures incorporating a large percentage of fly ash as a replacement for portland cement.
2. Whether strength values thus achieved could be further increased by reducing the water content of the concrete mixtures by 20 per cent. The loss in slump of the concrete was to be restored by using superplasticizers.

Table 10. Summary of Compressive and Flexural Strengths[95]

Mixture Series	Mixture No.	Cement Content	.... Compressive Strength of 102 x 203 mm Cylinders (MPa)											28 Day Flexural St of 89 x 102 x 408 Pri (MPa)
			1 Day	3 Days	7 Days	28 Days		180 Days		270 Days		365 Days		
		(kg/m^3)	*	*	*	*	**	*	**	*	**	*	**	
A	5	422	27.1	31.9	36.6	43.5	43.5	49.0	49.8	46.9	48.6	47.7	50.1	-
	6	431	34.1	36.3	40.3	47.0	46.0	51.5	46.3	46.4	47.0	48.7	50.5	-
	7	445	35.0	42.8	44.4	49.6	50.7	49.7	53.1	54.7	53.1	51.9	54.7	-
B	8***	393	36.0	41.6	41.7	47.6	-	53.6	-	49.4	-	50.7	-	5.6
	9***	420	38.2	43.8	43.9	48.5	-	53.9	-	53.1	-	52.0	-	6.4

*Moist-cured.

**Submerged in water.

***Mixture No. 8 and 9 also contained 60 and 30 kg/m^3 of fly ash.

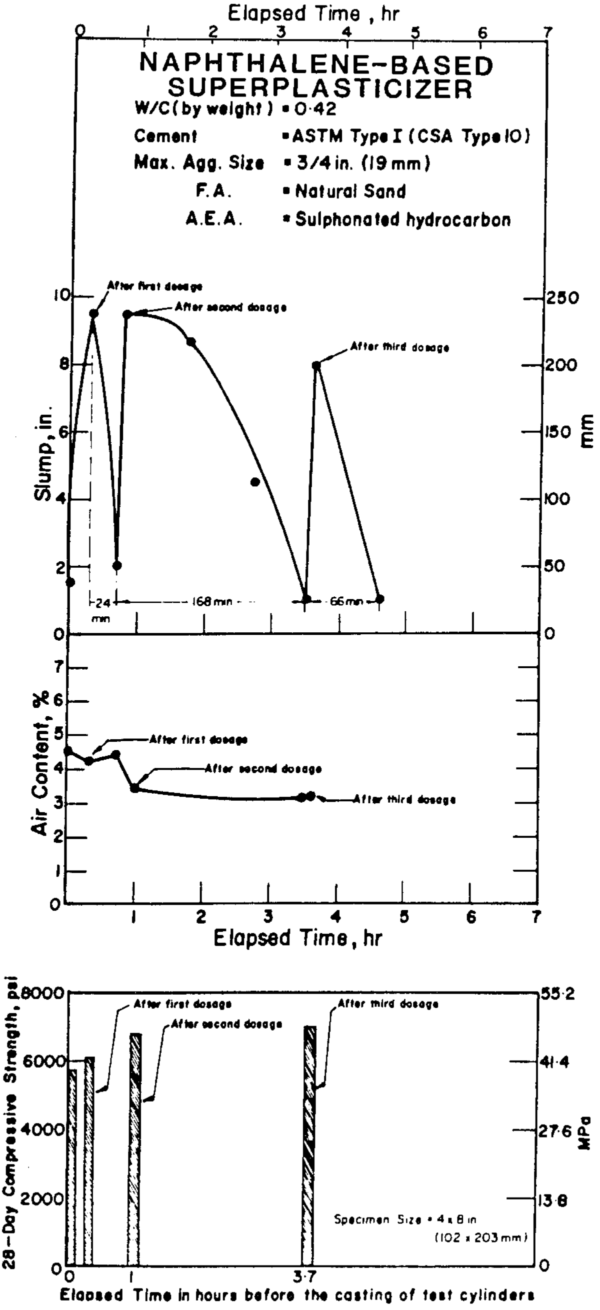


Figure 44. Effect of repeated dosages of superplasticizers on slump, air content and 28-day compressive strength.

In the above investigation, the concrete mixture had a water-to-(cement + fly ash) ratio of 0.28, cement and fly ash contents of 390 and 230 kg/m^3, respectively, and a larger than recommended dosage of superplasticizer. The 28-day compressive strength of 152 x 305-mm cylinders ranged from 51.0 to 53.8 MPa, and the 28-day flexural strength was in the order of 8 MPa. Table 11 and Fig. 45 give additional detailed data. Somewhat similar results have also been reported in another work.[97]

5.7 High-Volume Fly Ash Concrete Incorporating Large Dosages of Superplasticizers

In 1985, CANMET in Canada, developed the concept of high-volume fly ash concrete. Briefly, this type of concrete has low amount of cement content (about 150 kg/m^3), large volume of ASTM class F fly ash (about 225 kg/m^3), and a very low water content (about 115 (kg/m^3). The "flow" slumps are achieved by the use of large dosages of superplasticizers. These types of concretes have considerable economic and environmental impact, and are discussed in detail in Ch. 12.

5.8 High-Volume Slag Concrete Incorporating Large Dosages of Superplasticizers

The mixture proportion of these concretes are similar to those of the high-volume fly ash concretes that are discussed in Ch. 12.

5.9 Durability

Resistance to Repeated Cycles of Freezing and Thawing. It is well known that for satisfactory freezing and thawing durability of concrete, the cement paste should be protected by incorporating air bubbles through the addition of an air entraining admixture. Adequate air protection requires that the spacing factor, an index related to the maximum distance of any point in the cement paste from the periphery of an air void, should not exceed 200 µm (0.2 mm). Investigations in North America and Japan have indicated that in concretes incorporating superplasticizers, the above value is generally exceeded.[91][92][93][98]-[105] This is especially so for melamine and naphthalene-based superplasticizers. In spite of the increased bubble spacing however, the freezing and thawing durability of concrete when tested in accordance with ASTM Standard C666, Procedure A (freezing in

Table 11. Properties of Hardened Concrete Containing Fly Ash and a Superplasticizer

				Properties of Hardened Concrete										
				Compressive strength (MPa)										
Mix No.	Batch No.	W/C+F	Type of super plasticizer *	7 Days	28 Days	56 Days	91 Days	183 Days	365 Days	MPa 28 Days	28d MPa $x10^4$	Dry storage (d)	Shrinkage (%)	Moisture loss
1	1	0.35	-	-	41.0	-	51.8	-	-	6.3	3.17	-	-0.0441	-1.81
	2	0.35	-	28.8	37.9	51.9	51.5	-	-	-	3.43	-	-	-
	3	0.35	-	25.0	-	41.4	-	-	-	6.8	-	448	-0.0453	-1.84
	4	0.35	-	-	-	-	-	53.4	57.3	-	-	-	-	-
2	1	0.28	M	-	53.3	-	65.2	-	-	8.3	3.48	-	-0.0413	-1.19
	2	0.28	M	36.1	52.5	61.8	65.6	-	-	-	3.46	448	-	-
	3	0.28	M	36.1	-	57.7	-	-	-	8.0	-	-	-0.0399	-1.13
	4	0.28	M	-	-	-	-	70.0	69.8		-	-	-	-
3	1	0.28	N	-	52.5	-	66.9	-	-	8.0	3.48	-	-0.0467	-1.07
	2	0.28	N	36.8	53.8	61.7	67.1	-	-	-	3.46	448	-	-
	3	0.28	N	36.8	-	63.2	-	-	-	7.4	-	-	-0.0427	-1.08
	4	0.28	N	-	-	-	-	66.3	74.7	-	-	-	-	-
4	1	0.28	L	-	51.0	-	62.7	-	-	7.8	3.45	-	-0.0455	-1.19
	2	0.28	L	35.4	51.0	59.5	62.5	-	-	-	3.47	448	-	-
	3	0.28	L	34.1	-	59.0	-	-	-	8.1	-	-	-0.0451	-1.26
	4	0.28	L	-	-	-	-	63.4	62.5	-	-	-	-	-

Note: All Tests results are for individual specimens only. M is melamine; N is naphthalene ; L is lignosulfonate

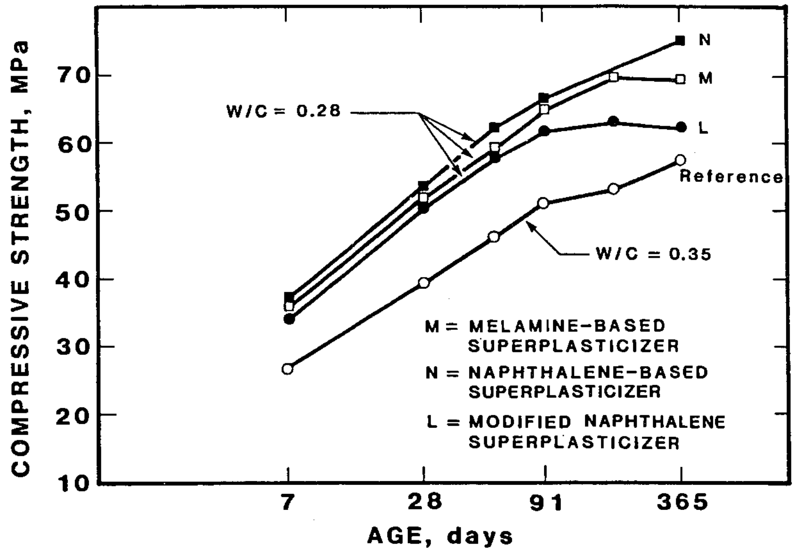


Figure 45. Compressive strength as a function of the age of the reference for water-reduced superplasticized concretes.

water and thawing in water) or Procedure B (freezing in air and thawing in water) is not impaired. Some test results are shown in Tables 12, 12a, 13 13a, and 14. Unexplained minor exceptions have been reported. In order to take the above into account, the new edition of Canadian Standard A 23.1 has stipulated a value of 230 μm (0.23 mm) for the bubble spacing factor. Implications in the use of air-entraining admixtures in concrete are discussed in Ch. 8.

Effect of Dosage Rate of Superplasticizer on $\bar{L}$ Figure 46 shows the effect of dosage rate of ß-NSFHC (naphthalene-sulfonate based) on the bubble spacing factor $(\bar{L})$ of concrete; the concrete was made with a water-cement ratio of 0.52, a cement factor of 300 kg/m^3, and an air content of 4.0 ± 0.5%. Malhotra investigated concrete with an air content of 4.8 to 5.0%, and that investigated by Goto et al. had an air content of only 3%. The figure shows that $\bar{L}$ increases with an increasing dosage of the superplasticizer, reaching a maximum value near the dosage rates of 0.40 to 0.50% by weight of cement, after which it decreases. Thus, correct dosage of a superplasticizer appears to be essential to obtain adequate bubble spacing factor.

Table 12. Relative Dynamic Moduli of Elasticity and Durability Factors after 300 Cycles of Freezing and Thawing[105]

				... ASTM C 666, Procedure A ...			... ASTM C 666, Procedure B ...		
Mix No.	**Water to Cement Ratio (by wt)**	**Air Content (%)**	**Void Spacing Factor (mm)**	**Freezing and Thawing Cycles**	**Relative Dynamic Modulus Pc(%)**	**Durabili-ty Factor**	**Freezing and Thawing Cycles**	**Relative Dynamic Modulus (%)**	**Durabili-ty Factor**
1	0.65	3.1	0.72	32	19	2	48	76	12
2	0.70	2.8	0.78	32	9	1	19	*	*
3	0.70	6.5	0.16	300	101	101	300	98	98
4	0.70	8.2	0.25	300	97	97	300	97	97
5	0.50	2.2	1.01	17	63	4	21	25	2
6	0.50	6.5	0.13	300	100	100	300	96	96
7	0.50	7.8	0.17	300	101	101	300	97	97
8	0.35	202	0.81	110	85	31	300	95	95
9	0.35	5.5	0.16	300	102	102	300	98	98
10	0.35	4.9	0.15	300	100	100	300	98	98

*Prisms completely distintegrated

Table 12a. Air-Void Determinations on Hardened Concrete[105]

.... Properties of Fresh Concrete				Air-Void Determinations on Hardened Concrete			
Mix No.	Water to Cement ratio (by wt)	Nature of Mix	Air Content (%)	Paste Content (%)**	Voids in Concrete (%)	Specific Surface Area (mm)	Void Spacing Factor (mm)
1	0.65	plain	3.1	24.7	2.8	8.340	0.72
2	0.70	plain	2.8	23.9	4.1	8.360	0.78
3	0.70	air entrained	6.5	20.7	6.8	22.876	0.16
4	0.70	air entrained and superplasticized*	8.2	20.7	8.1	13.657	0.25
5	0.50	plain	2.2	26.9	2.9	6.038	1.01
6	0.50	air entrained	6.5	23.2	6.3	29.889	0.13
7	0.50	air entrained and superplasticized*	7.8	22.6	8.3	20.996	0.16
8	0.35	plain	2.2	33.5	1.9	9.883	0.81
9	0.35	air entrained	5.5	29.8	6.3	27.335	0.16
10	0.35	air entrained and superplasticized*	4.9	29.0	5.9	30.377	0.15

*A melamine based superplasiticizer.

**Calculated from paste content.

Table 13. Relative Dynamic Moduli of Elasticity and Durability Factors after 300 Cycles of Freezing and Thawing[105]

				.... ASTM C 666, Procedure A			.... ASTM C 666, Procedure B		
Mix No.	Water to Cement Ratio (by wt)	Air Content (%)	Void Spacing Factor (mm)	Freezing and Thawing Cycles	Relative Dynamic Modulus Pc(%)	Durability Factor	Freezing and Thawing Cycles	Relative Dynamic Modulus (%)	Durability Factor
1	0.70	2.4	0.62	9	43	1	16	1	1
2	0.70	6.2	0.23	300	91	91	300	98	98
3	0.70	6.7	0.26	300	91	91	300	98	98
4	0.50	2.2	0.59	15	39	2	48	20	3
5	0.50	6.8	0.13	300	96	96	300	100	100
6	0.50	6.5	0.18	300	95	95	300	98	98
7	0.35	2.0	0.73	12	78	3	300	90	90
8	0.35	5.7	0.14	300	94	94	300	100	100
9	0.35	5.0	0.23	300	95	95	300	98	98
10	0.50	6.0	-	300	98	98	300	98	98

Table 13a. Air-Void Determinations on Hardened Concrete[105]

.... Properties of Fresh Concrete				Air-Void Determinations on Hardened Concrete**			
Mix No.	Water to Cement ratio (by wt)	Nature of Mix	Air Content (%)	Paste Content (%)***	Voids in Concrete (%)	Specific Surface Area (mm)	Void Spacing Factor (mm)
1	0.70	plain	2.4	24.6	2.4	10.299	0.620
2	0.70	air entrained	6.2	21.2	9.0	14.511	0.226
3	0.70	air entrained and superplasticized*	6.7	20.9	9.4	12.341	0.259
4	0.50	plain	2.2	27.0	2.0	12.129	0.591
5	0.50	air entrained	6.8	23.2	7.7	28.302	0.129
6	0.50	air entrained and superplasticized*	6.5	23.2	7.1	21.305	0.178
7	0.35	plain	2.0	34.1	1.4	12.711	0.732
8	0.35	air entrained	5.7	31.2	6.0	31.930	0.139
9	0.35	air entrained and superplasticized*	5.0	30.7	4.8	22.801	0.228

*A naphthalene based superplasiticizer was used at a dosage rate of 0.75% by weight of cement.

**Data supplied by Ontario Hydro.

***Calculated from paste content.

Table 14. Effect of Melamine-Based Superplasticizers on Freezing and Thawing Resistance of Air-Entrained Concrete[100]

Series No.	.. 100 kg of Cement .. Dosage of Admixture per: Melamine based superplasticizer	AEA* (ml)	Cement (ASTM Type I) (kg/m^3)	Water (kg/m^3)	Entrained Air (%)	Slump (mm)
A	4,564ml	60.6	308	118	5.5	64
	0.667kg	57.4	309	138	5.4	57
B	4,565ml	75.0	306	121	8.1	118
	0.667kg	69.1	306	148	7.7	197

Series No.	...... Air Void Systems** ...... A (%)	 $\propto cm^{-1}$	 L(μm)	... Durability*** Factor (%) ... DF	 RDF
A	4.45	142	323	90	99
	5.13	185	241	91	100
B	6.41	176	193	91	101
	7.40	210	157	90	100

*AEA = air entraining agent.

**Air Void Systems = modified point count (ASTM C457).

***Durability Factor = by Procedure A of ASTM C666.

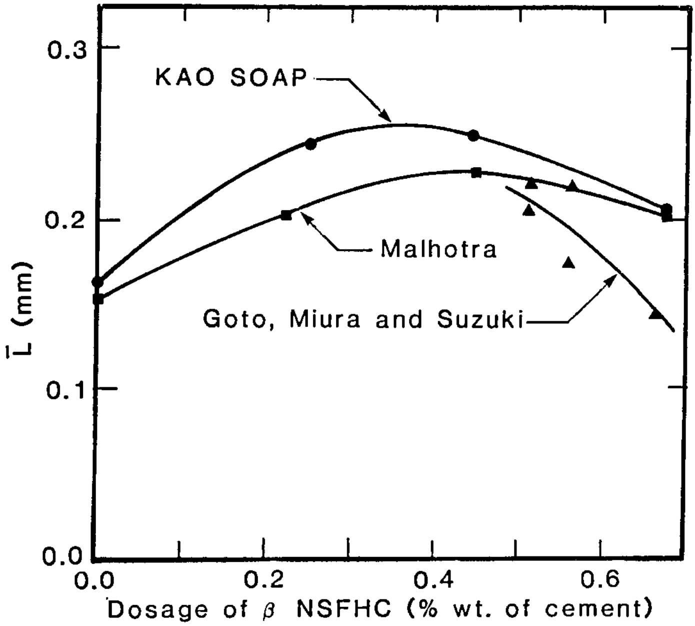


Figure 46. Effect of ß-NSFHC on spacing factor.

Resistance to Sulfate Attack. The resistance of superplasticized concrete to sulfate attack is comparable to non-superplasticized concrete. Brooks et al. have investigated the performance of superplasticized concrete exposed to magnesium sulfate solution.[106] The concentration of the sulfate solution was maintained at a nominal 3% SO_3 content. A naphthalene-based superplasticizer was used and the test specimens, 100 x 100 x 500-mm prisms, were exposed to sulfate solution for 3 days. The durability was monitored by determining changes in weight, length, and dynamic modulus of the specimens. The investigation indicated (Fig. 47 and 48) that the performance of the superplasticized concrete was no different than that of the control specimens. Similar results have been reported by Collepardi et al.[107]

Resistance to Salt Scaling. Superplasticized concretes appear to have satisfactory resistance to salt scaling. Mukherjee and Chojnacki[101] have obtained limited data on salt scaling tests in which a 3% sodium chloride solution was used. All test slabs were exposed to 50 cycles of freezing and thawing in water. After each of the five cycles, the salt solution and the deteriorated concrete were removed from the slab and stored in a watertight container.

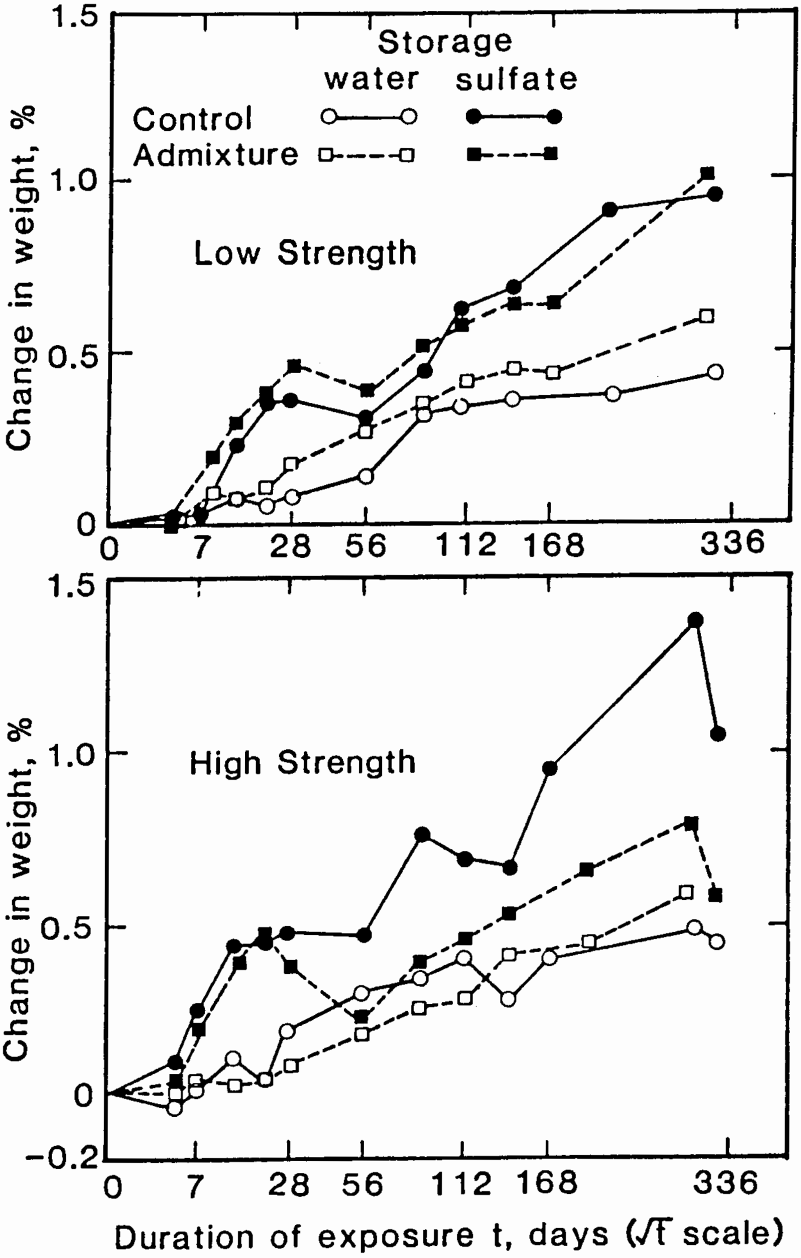


Figure 47. The effect of admixture on the change in weight of water- and sulfate-stored specimens.

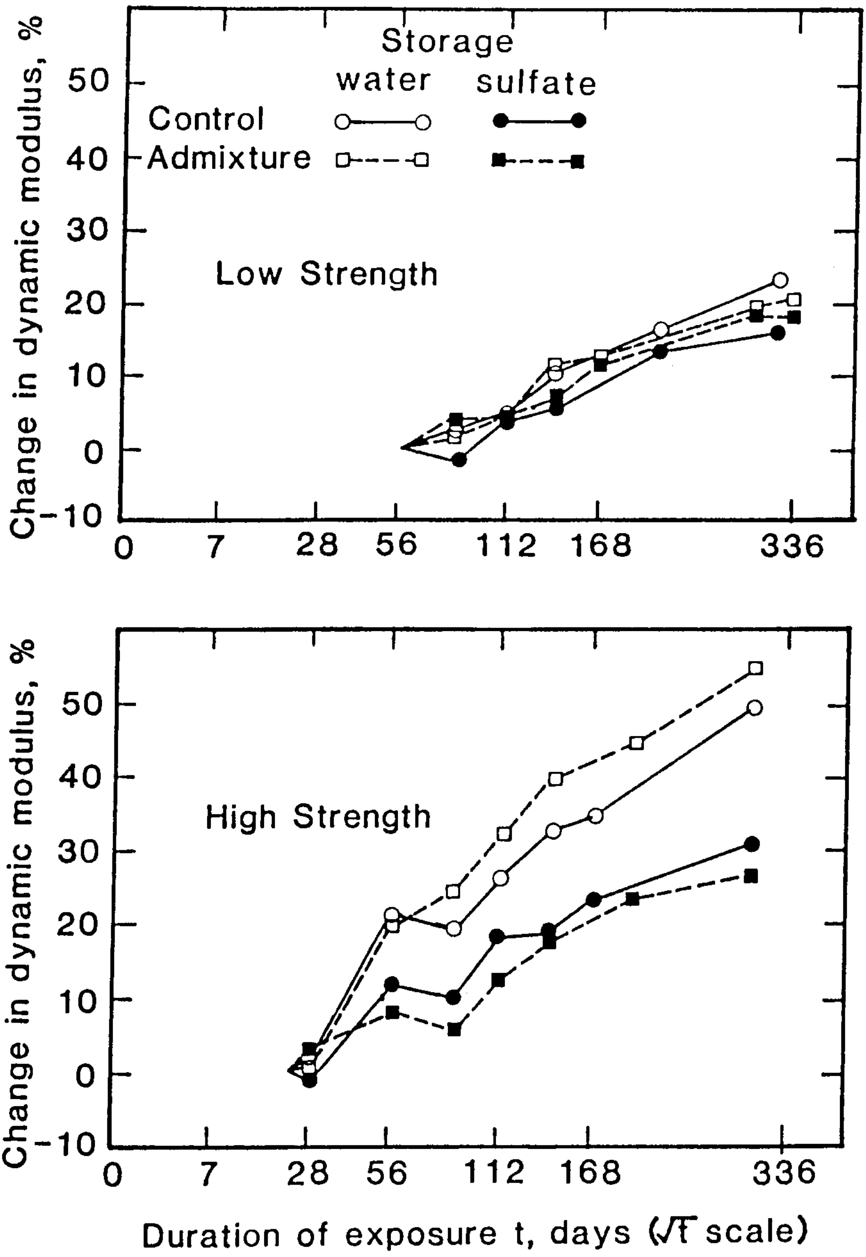


Figure 48. The effect of the admixture on the change in dynamic modulus of elasticity of water- and sulfate-stored concretes.

The solution was then strained through a filter and the residue dried at 105°C to constant weight. The weight of the residue was cumulatively determined after each of the five cycles and reported as the loss of weight per unit of exposed slab area. The test results indicated that the performance of concrete slabs incorporating a melamine-based superplasticizer compared well with that of the reference slabs. The maximum weight loss of 0.05 g/cm^2, shown in Fig. 49, is below the maximum allowed limit of 0.08 g/cm^2.[101]

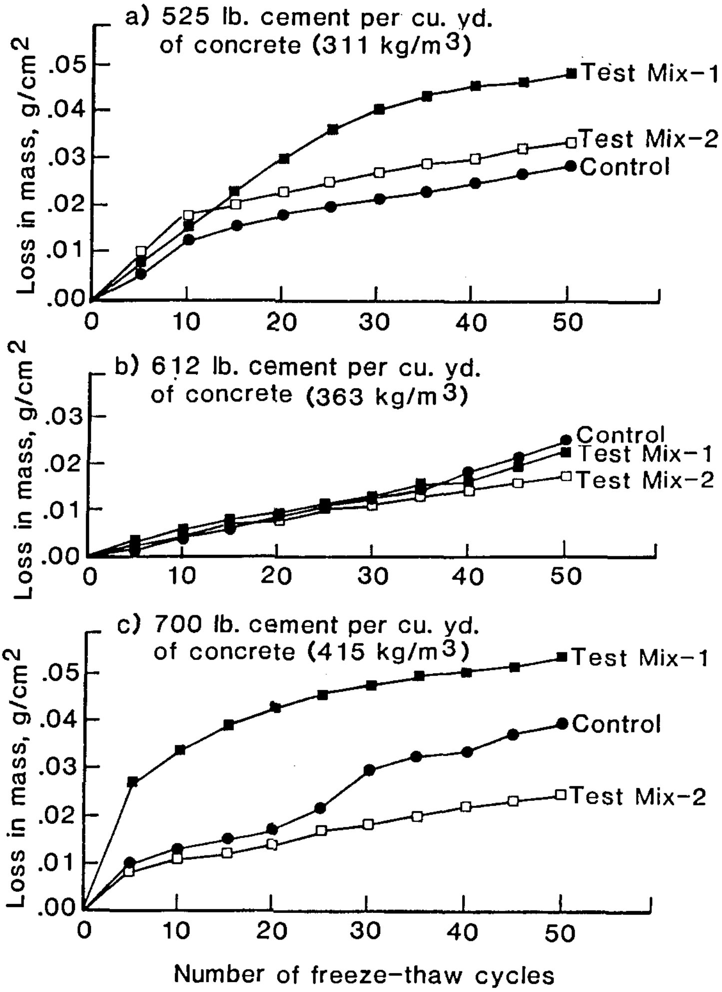


Figure 49. Salt scaling tests.

5.10 Corrosion of Reinforcement

Hattori has investigated the corrosion of reinforcement in superplasticized concrete, and has shown that the incorporation of a naphthalene-based superplasticizer in concrete does not lead to any significant rust formation on reinforcement. In his investigation, a series of reinforced concrete piles of 300-mm outer diameter, 70-mm wall thickness and 2300 mm in length was prepared. The effect of three types of admixtures, including a superplasticizer, was investigated. The reinforcement consisted of four steel bars. The piles were made by centrifugal forming and prestressing, followed by steam curing.

The piles were then exposed to water for one year and left outdoors for four years. At the end of this period, the reinforcing rods were taken out for evaluation of rusting. The test data are shown in Table 15.

The table indicates that, whereas reinforcement in superplasticized concrete showed only traces of rust, the reinforcement in concrete incorporating calcium chloride has a high percentage of rust.

Table 15. Data on Rusting of Reinforcement Embedded for Five Years in Concrete Piles

Type of Admixture	Dosage % by wt of cement	Rust Coverage
None	-	0.25
Superplasticizer	0.6	trace
Lignosulfonate	0.25	0.1
$CaCl_2$	0.05	0.3
$CaCl_2$	0.5	0.6
$CaCl_2$	1.0	11.7
$CaCl_2$	2.0	19.6
$CaCl_2$	4.0	75.0

5.11 Influence of Superplasticizers on Concrete-Steel Bond Strength

Collepardi and Corradi[107] have published data on the influence of superplasticizers on concrete-steel bond strength. The incorporation of a superplasticizer in concrete improves the adhesion between steel and concrete for both normal and lightweight concretes (Table 16). For example, for normal concrete, the addition of a superplasticizer raised the steel-concrete bond strength at 7 days from 1.2 to 3.5 MPa for smooth bars, and from 15.0 to 27.5 MPa for twisted bars. Similar improvements were observed for lightweight concrete.

Table 16. Data on Concrete-Steel Bond Strength[107]

Type of Concrete	Type of Admixture	Cement Brand	Cement Content	Slump
Normal weight	none	Type I, Brand 1	400	100
Normal weight	Superplasticizer	Type I, Brand 1	400	220
Lightweight*	None	Type I, Brand 2	500	100
Lightweight*	Superplasticizer	Type I, Brand 2	500	210

	.... Bond Strength, kg/m^2 (MPa)			
	.... 7 Days		...... 28 Days	
Type of Concrete	**Smooth Bars**	**Twisted Bars**	**Smooth Bars**	**Twisted Bars**
Normal weight	12 (1.2)	150 (15)	13 (1.3)	152(15.2)
Normal weight	35 (3.5)	275 (27.5)	40 (4.0)	285 (28.5)
Lightweight*	4 (0.4)	66 (6.6)	6 (0.6)	92 (9.2)
Lightweight*	9 (0.9)	142 (14.2)	21 (2.1)	210 (21.0)

*1,800 kg/m^3

5.12 Architectural Prestressed and Precast Concrete Applications

The superplasticizers are being used increasingly by the precast concrete industry for the following principal reasons:

1. To produce concrete products that achieve compressive strengths of the order of 40 MPa in 8 to 18 h.
2. To reduce fuel costs associated with the use of heat in accelerated curing of precast concrete products.

3. To reduce the high cement contents.
4. To optimize vibration energy and to reduce noise levels. Figures 50 and 51 show the effects of superplasticizers on the strength of concrete at early ages.[108][109]

LaFraugh[108] has indicated that significant energy savings may be realized by the use of superplasticizers. High-early strength can be attained at lower curing temperatures and/or curing times than are currently used in the industry. Figure 50 illustrates the effect of curing temperature on the 18-hour compressive strength for three superplasticized mixtures and one control mixture with an ordinary water-reducer. Results show that lower curing temperatures can be used to achieve satisfactory early-age strengths.

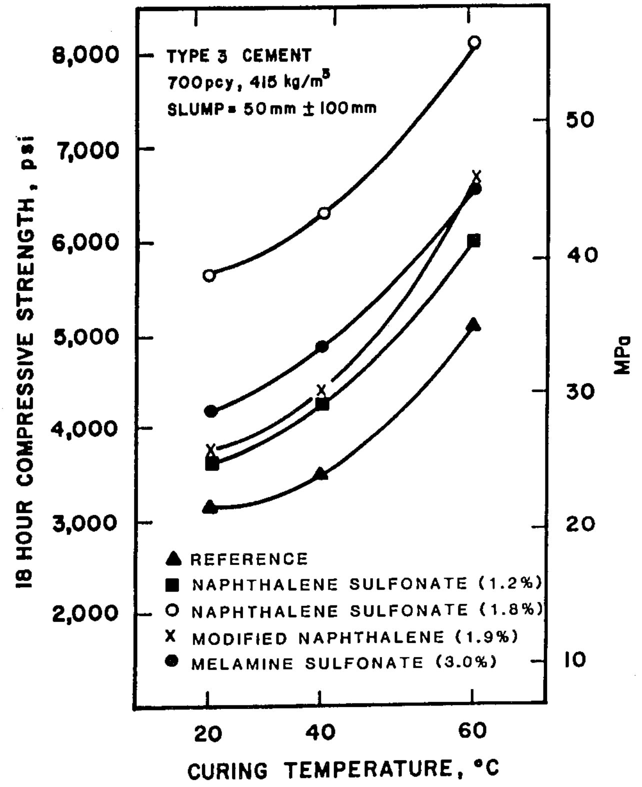


Figure 50. Effect of curing temperature on 18 hour compressive strength of superplasticized concrete.

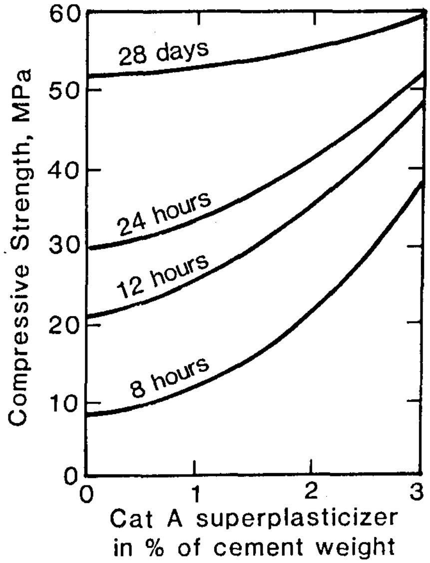


Figure 51. Relation between compressive strength after 8, 12, and 24 hours and 28 days; and concentration of Category A (melamine-based) superplasticizer.

Hester[110] has published guidelines for mixture consolidation, and uniform mixture coloration and concrete surface texture architectural prestressed and precast concretes when using superplasticizers. These are reproduced below:

A. Guidelines for *Mix Consolidation*

1. Depending upon the maximum aggregate size, use dynamic consolidation devices with a high rate of acceleration. An acceleration effort of at least 100 g, where g = 386"/sec^2 (9800 mm/sec^2), is highly effective with both low and high slump concrete.
2. Provide enough superplasticizing admixture to furnish both the desired mix water reduction and enhance the consolidation effort.
3. Use a high-slump, flowing concrete when casting units with constricted dimensions or limitations on the amount of consolidation effort which may be applied.

B. Guidelines for Uniform Mix Coloration and Concrete Surface Texture

1. Use an "optimal" admixture dosage (i.e., that dosage which provides the desired mix setting times and strength properties).
2. Consider the fact that naphthalene type superplasticizers may slightly discolor white or other lightly colored concretes.
3. Recognize the fact that reduced mix water-cement ratio achievable with superplasticizers will probably not result in a permanent discoloration or darker shading of the concrete.
4. The appearance of unusually large amounts of air voids, or *bugholes,* on the surface of superplasticized concrete may be minimized by reducing dosage.

The first significant precast concrete project where superplasticizers were used in North America was the Montreal Olympic Stadium, an outstanding example of segmental precast construction.[111]

The main part of the Stadium structure consists of 34 freestanding column-arches (consoles) which together with 4 ribs of similar construction cantilevering from the mast, carry the upper seating slabs, and all floors (Fig. 52). The design compressive strength was 42 MPa at 28 days with the proviso that the release strength (removal from the mould) was not less than 21 MPa. The heavy reinforcement of the precast units (Fig. 53) required a slump of at least 150 mm for the fresh concrete. The above slump and strength requirements were achieved using superplasticized concrete with mix proportions shown in Table 17.

5.13 Shrinkage Compensating Concrete

In the USA, expansive cements are used to produce shrinkage-compensating concretes, whereas in Italy and Japan suitable amounts of expansive agents are added as admixtures at the time of mixing concrete. The two types of expansive agents usually used are based on calcium sulfoaluminate or calcium aluminate and calcium oxide.

Figure 52. A general view of the Olympic Stadium in Montreal, Canada.

Figure 53. A general view of the high density steel reinforcement used in the voussoir elements.

Table 17. Superplasticized Mix Proportions for Structural Concrete for Montreal Olympic Stadium[111]

	...... Quantities	
Material	**Kilograms**	**Pounds**
Cement Type 30 (ASTM Type III)	353	780
Concrete sand (FM = 2.6)	566	1,250
Crushed limestone 9.5 to 16 mm (3/8" to 5/8")	852	1,880
Water	852	280
Melamine based superplasticizer (20% solid)	10	22
Density	2,497*	4,212**

*Per cubic meter.

** Per cubic yard.

The use of superplasticizers, through decrease of water:cement and increase in early compressive strength allows the production of shrinkage-compensating concretes containing lower amounts of an expansive agent.[112] Table 18 gives mixture proportions and characteristics of shrinkage-compensating (A) and superplasticized shrinkage-compensating (B & C) concretes. In concretes B and C, increased compressive strength, decreased shrinkage values, and low requirements of the expansive agent are a result of the incorporation of a superplasticizer.

5.14 Pumpability

Kasami et al.[74] have investigated the pumpability of superplasticized concrete under field conditions. In one experiment, about 200 m^3 of normal and lightweight aggregate concrete, involving fourteen mixes with and without superplasticizers, was pumped horizontally. The pumping distance was 109 m and the line diameter was 125 mm. The dosage of the naphthalene-based superplasticizer was in the range of 0.4 to 0.7% by weight of cement, and concrete mixing was done in ready-mixed agitator-type trucks. After the addition of superplasticizer, the mixer was rapidly agitated for one minute. Following this, the concrete was pumped at rates of 10, 20, 30, 40, 50, and 60 m^3/h. Pump pressure and line pressure were measured at each pumping rate. The slump, air content, and other properties of fresh and hardened concrete were measured on all reference superplasticized and pumped concretes. The test data indicated that pumping pressure and line pressure loss for normal weight concrete were reduced by about 30%, whereas those for lightweight concrete were reduced by no more than 10%. The increase in pumping resistance with the increase in pumping rate was less than that for conventional concrete. Data on slumps of conventional and superplasticized pumped concretes are shown in Fig. 54. Line pressure distribution is shown in Fig. 55.

Table 18. Mixture Proportions and Characteristics of Shrinkage-Compensating (A) and Superplasticized Shrinkage-Compensating (B and C) Concretes[112]

Concrete Mixture	**A**	**B**	**C**
Slump, mm			
After Mixing	150	150	150
After 1 hour	100	50	120
Type I cement content, kg/m^3	333	339	338
Water content, kg/m^3	200	153	152
Superplasticizer type	-	Accel.	Retard.
Superplasticizer content,kg/m^3	-	4.07	3.38
(% by weight of cement)	-	(1.2%)	(1.0%)
Water/cement	0.60	0.45	0.45
Aggregate/cement	5.2	5.6	5.6
Compressive strength			
1 day	6	10	8.0
28 days	31	47	48.0
Shrinkage at 2 years, 10^{-6}	790	460	450
ASTM restrained expansion, 10^{-6}	840	480	470
Expansive agent, kg/m^3	78	27	34
(% by weight of cement)	(23%)	(8%)	(10%)

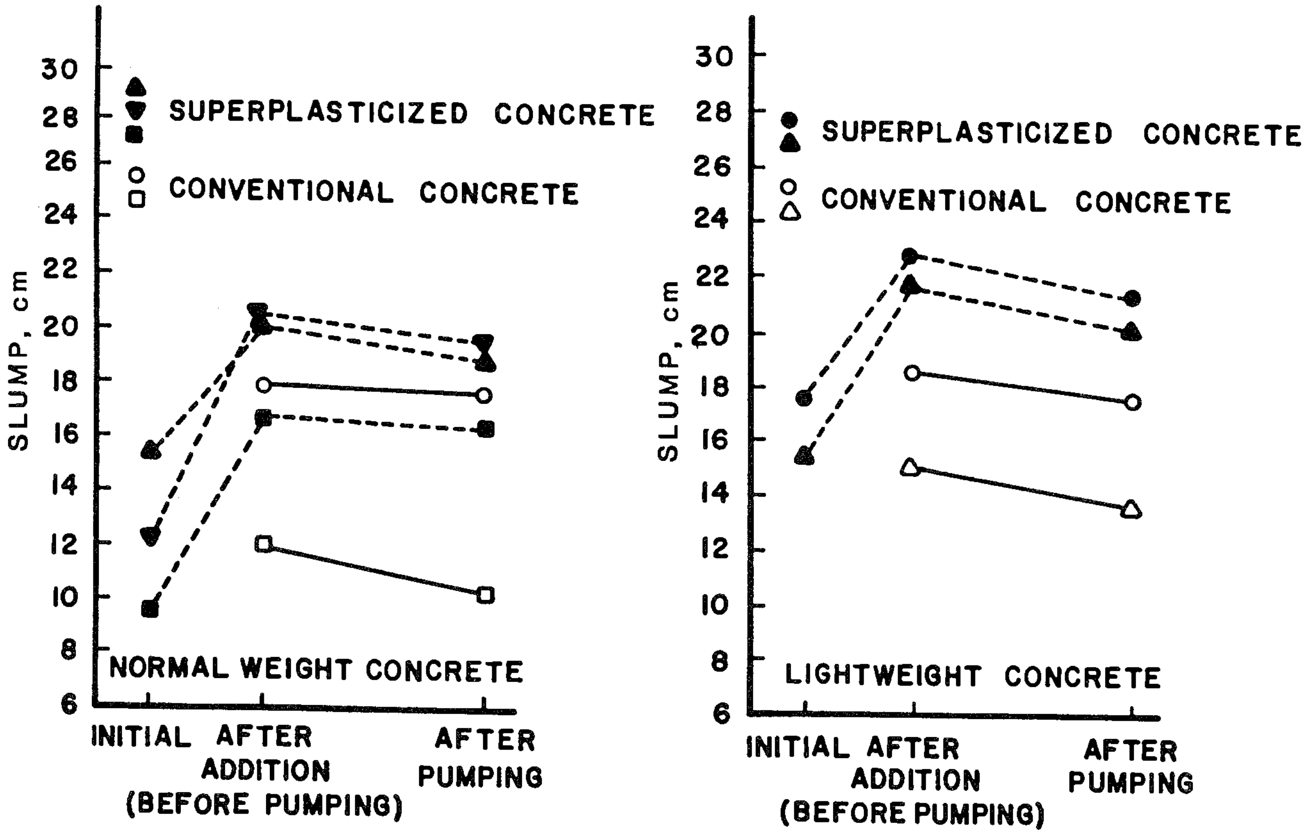


Figure 54. Slump of conventional, superplasticized and pumped concrete

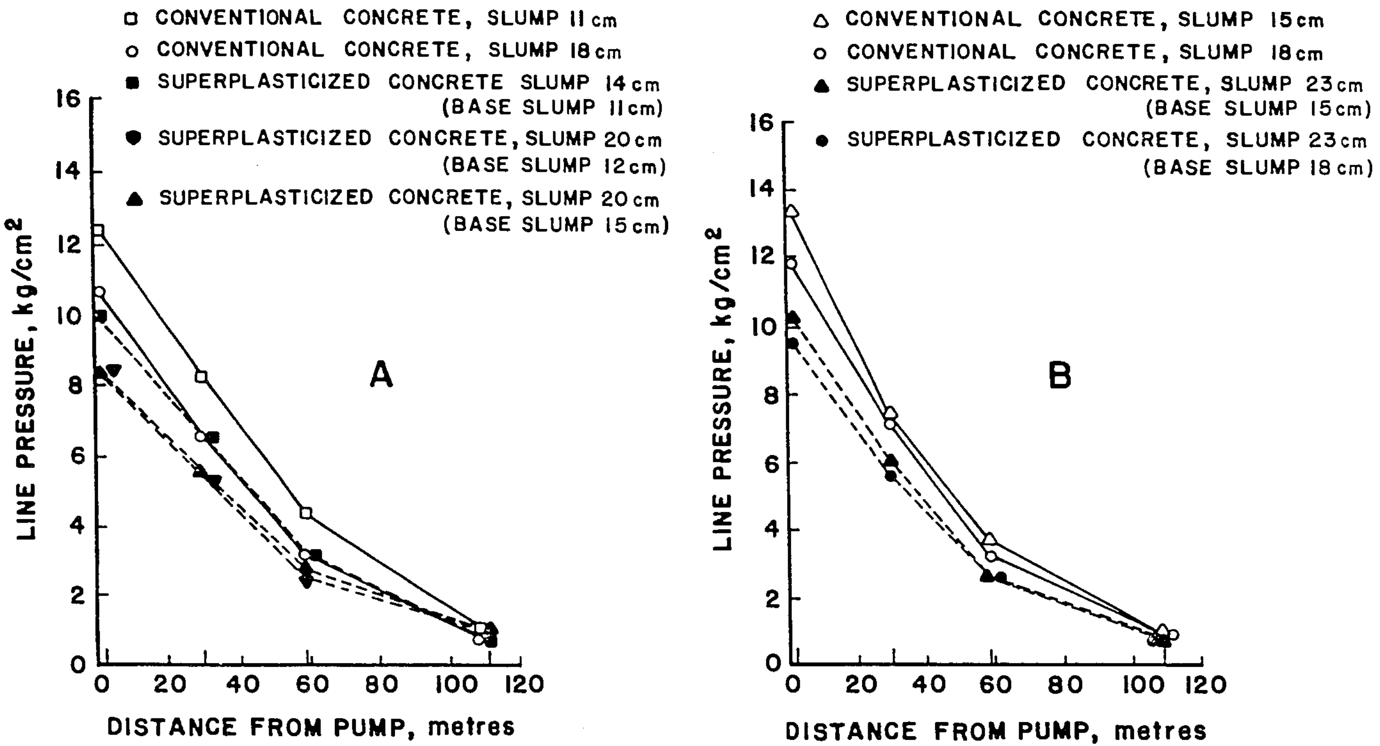


Figure 55. Line pressure distribution in concrete: *(A)* normal weight concrete, and *(B)* lightweight concrete.

5.15 Performance of Steel-Fiber Reinforced Concrete

Ramakrishnan et al.[113] have investigated the performance for steel-fiber reinforced superplasticized concrete. The carbon steel hooked fibers used were glued together side by side into bundles with a water soluble adhesive. The fibers had a nominal length of 51 mm and a diameter of 0.5 mm. When used in a concrete, the glue dissolves and the fibers are separated into individual pieces with an aspect ratio of 100 (the ratio of length-to-diameter of the wires). The fiber content of the mixtures varied from 32.62 to 50.41 kg/m^3; the corresponding water-to-cement ratios (by weight) ranged from 0.36 to 0.32. Test data indicated that the use of superplasticizers can overcome the serious drawbacks of fiber-reinforced concrete exhibiting reduced workability. However, slightly higher dosages of superplasticizer are needed to achieve the same workability as can be obtained with a corresponding superplasticized concrete without fibers. Figure 56 shows the relationship between slump and flow table spread and Fig. 57 gives a comparison of load deflection curves for concrete mixtures with different fiber contents.

5.16 Role of Superplasticizers in Concrete Incorporating Condensed Silica Fume

Silica fume, an active pozzolan, is a by-product resulting from the reduction of high purity quartz with coal in electric arc furnaces in the manufacture of ferro silicon and silicon metal. The condensed fume, which has a high content of amorphous silicon dioxide consists of very fine spherical particles (average diameter about 0.1 µm), and is collected by filtering the gases escaping from the furnaces.

The specific surface of silica fume is of the order of 20,000 m^2/kg. Because of the extreme fineness, the water demand of mortars and concretes incorporating silica fume increases with increasing amounts of silica fume.[114] For example, at 30% cement replacement for concrete at a water-to-cement ratio of 0.64, the water demand has been found to increase by almost 30% (Fig. 58). This problem of high water demand has been overcome by the use of superplasticizers. The strength development characteristics of silica fume concrete are shown in Fig. 59 and 60.

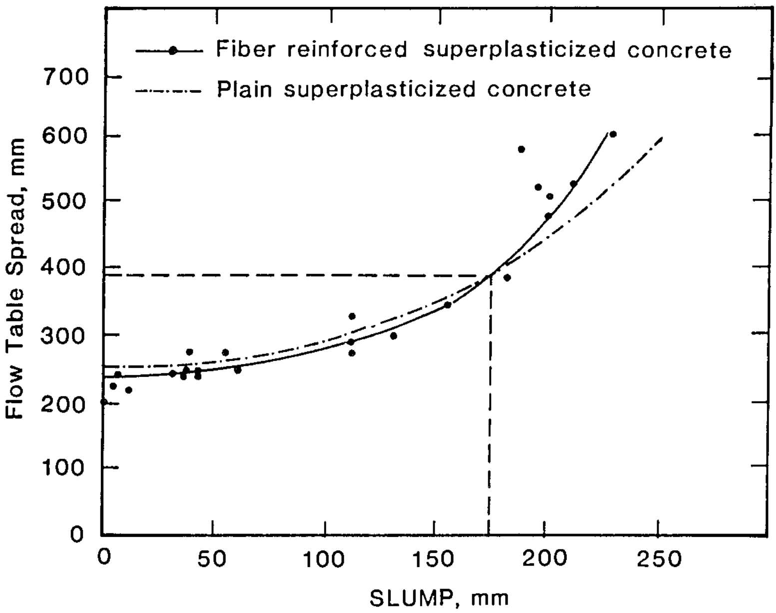
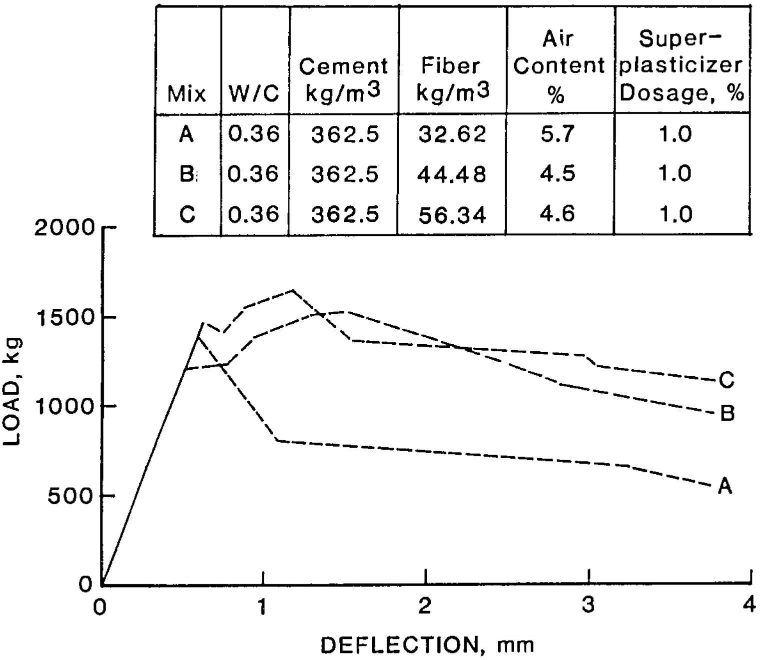


Figure 56. Relationship between slump and flow table spread.



Mix	W/C	Cement kg/m3	Fiber kg/m3	Air Content %	Super-plasticizer Dosage, %
A	0.36	362.5	32.62	5.7	1.0
B	0.36	362.5	44.48	4.5	1.0
C	0.36	362.5	56.34	4.6	1.0

Figure 57. Comparison of load deflection curves of mixes with different fibers.

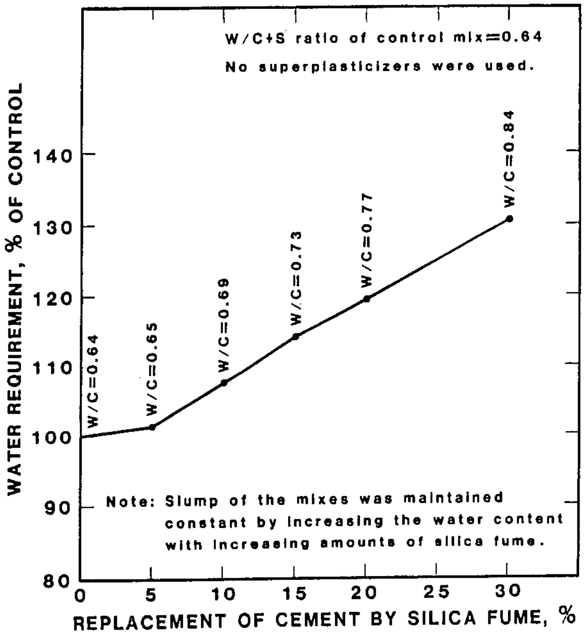


Figure 58. Water requirements for silica fume concrete.

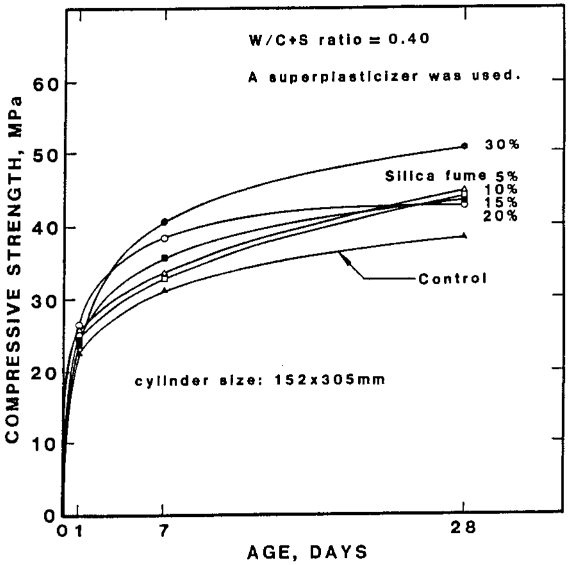


Figure 59. Rate of development of strength in superplasticized concrete fabricated at a water/cement + silica fume ratio of 0.40.

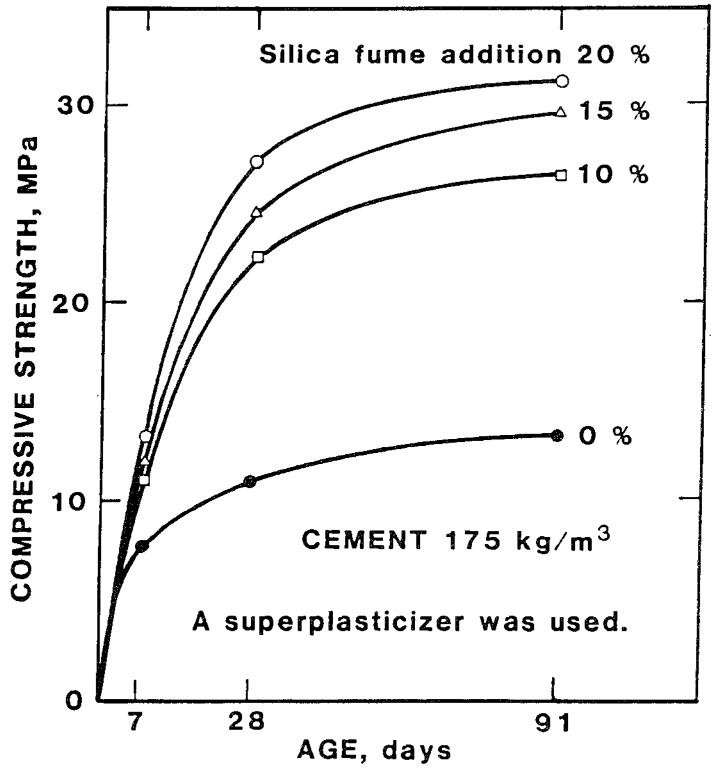


Figure 60. Strength development in superplasticized very lean concrete.

5.17 Development of Ultra High-Strength Concrete

The introduction of superplasticizers has made it possible to develop ultra high strength concretes. Bache[115] has reported development of superplasticized concretes with strengths of the order of 150 MPa at 100 days incorporating a superplasticizer (typically 1 to 4% of the weight of the cementitious materials + silica fume). Mixture proportions of one such type of concrete are shown in Table 19, and strength development with age is shown in Fig. 61.

By using stronger aggregates, Bache[115] has been able to achieve considerably higher strengths. Some data are shown in Table 20 from which it can be seen that the high-strength mortars and concrete are 3–5 times stronger than normal concrete.

Table 19. Compressive Strength Test Results for High Alumina Concretes[116]

Mixture Number	Type of Superplasticizer and Dosage in Percent by Weight of Cement	.... Compressive strength				
		10 Hours	1 Day	2 Days	7 Days	180 Days
1	Control	53.6	59.1	62.1	65.8	82.1
2	Naphthalene (retarded) 2%	-	42.7	50.8	58.9	84.5
3	Naphthalene (retarded) 4.6%*	-	33.6	43.1	53.7	72.3
4	Lignosulfonate 3%	32.6	42.9	49.9	60.1	83.7
5	Lignosulfonate 4.1%	33.3	41.6	46.7	54.8	76.0
6	Melamine 3%	40.6	44.8	54.8	58.3	83.4

*Repeated Dosage

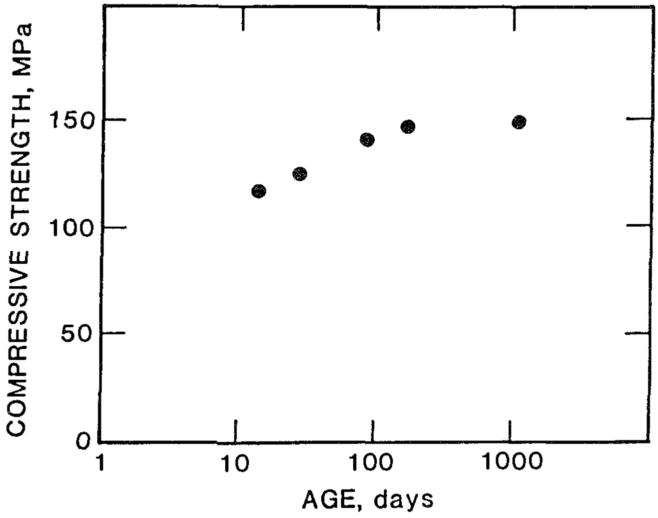


Figure 61. Compressive strength of high strength concrete cured at 20°C in water.

Table 20. Mechanical Properties of Soft Cast Mortar and Concrete Water-Cured for 4 Days at 60 to 80°C[115]

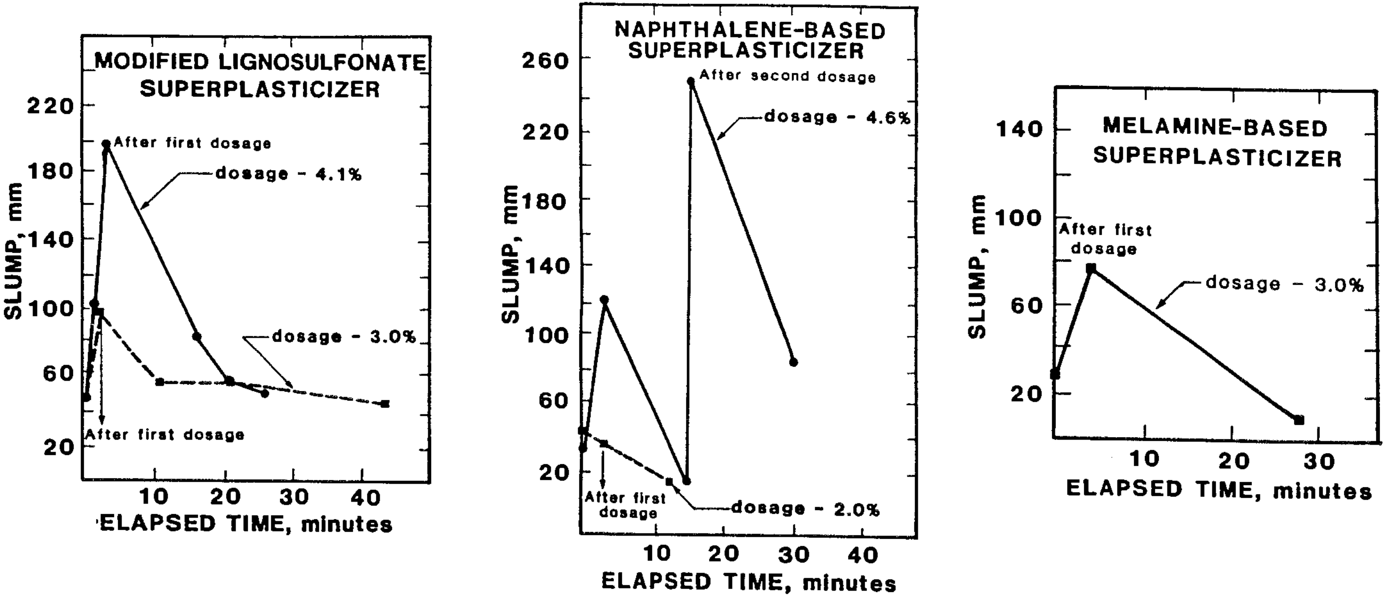
Type of Concrete or Mortar (max. size aggregate)	Density (kg/m^3)	Compressive Strength (MPa)	Sound Velocity m/sec	Dynamic modulus of Elasticity MPa	Stress Density Ratio m^2/sec^2
16 mm granite	2,500	124.6	5,200	68,000	49,840
16 mm diabas	2,666	168.1	4,890	65,000	63,050
10 mm calcined bauxite	2,878	217.5	6,150	109,000	75,573
4 mm calcined bauxite	2,857	268.3	6,153	108,000	93,910

5.18 High Alumina Cement Concrete

It is well known that for satisfactory performance of concrete made with high-alumina cement, it must be proportioned to have a water-to-cement ratio of not greater than 0.40 and a cement content of not less than 400 kg/m^3 of concrete. If the above precautions are not taken, the concrete may show major losses in strength at later ages, a phenomenon resulting from the conversion of metastable monocalcium aluminate decahydrate ($CaO \bullet Al_2O_3 \bullet 10H_2O$) to a more stable tricalcium aluminate hexahydrate ($3CaO \bullet Al_2O_3 \bullet 6H_2O$). However, at the very low water-to-cement ratios of 0.40 or less, the concrete mixtures have poor workability and create problems in handling, placing, and finishing. The introduction of superplasticizers may offer the possibility of obtaining high-alumina flow concrete at very low water-to-cement ratios. However, superplasticizers perform poorly when incorporated in high-alumina cement concrete.[116] Even at the very high dosage rates, the concrete does not achieve "flow" characteristics and reverts back to the original slump in less than 20 minutes (Fig. 62). Furthermore, at the age of up to two days, the compressive strength of superplasticized high-alumina cement concretes is considerably lower than that of the control concrete. At 180 days, the strengths of the superplasticized and control concretes are comparable (Table 21). The rate of conversion of high-alumina cement is not affected in the presence of the superplasticizers.

5.19 Blast Furnace Slag/Portland Cement Concrete

In recent years, the pelletized and granulated blast furnace slags are being used increasingly as a part of the cementitious material in concrete. In one investigation, a naphthalene-based superplasticizer was used in concretes in which up to 65% of portland cement was replaced by pelletized slag.[117] It has been shown that blast furnace slag–portland-cement concretes require about 10% less superplasticizer than reference portland cement concrete for the same consistency. Furthermore, at 25% cement replacement level and at water-to-cementitious materials ratios of 0.46 and 0.56, the compressive strength of air-entrained and superplasticized concrete is higher than the corresponding strength of the air-entrained concrete; at higher cement replacement levels, the strength of two types of concretes are about the same (Table 22). On the contrary, at 0.38 water-to-cementitious materials ratio and regardless of the percentage of the slag used, the compressive strengths of air-entrained superplasticized concrete are lower than the corresponding strength of air-entrained concrete. No explanation has been offered for this reversal in strength behavior.



(A) (B) (C)

Figure 62. Loss of slump with time in high alumina concrete: *(A)* lignosulfonate-type superplasticizer, *(B)* naphthalene-type superplasticizer, and *(C)* melamine-type superplasticizer.

Durability studies indicate that regardless of the water-to-cement plus slag ratio, air-entrained superplasticized concrete performs satisfactorily in freezing and thawing tests (ASTM C666 Procedure B, freezing in air and thawing in water) with minor exceptions.[117]

5.20 Accelerated Strength Testing

The incorporation of superplasticizers in concrete does not affect the relationship between the accelerated and 28-day compressive strengths.[91][118][119] The probable rationale is that most of the action of superplasticizers takes place in the first several hours and the specimens are placed in the boiling water tanks 24 hours after casting (modified boiling test, ASTM C684, Procedure B). Selected data are shown in Table 23 and Fig. 63.

Table 21. Compressive Strength Tests Results for High Alumina Concretes[116]

Mix No.	Superplasticizer (% by wt. Cement)	Compressive Strength (MPa)				
		10 Hr	1 Day	2 Days	7 Days	180 Days
1.	Control	53.6	59.1	62.1	65.8	82.1
2.	Naphthalene(retarded) 2%	---	42.7	50.8	58.9	84.5
3.	Naphthalene(retarded) 4.6%*	---	33.6	43.1	53.7	72.3
4.	Lignosulfonate 3%	32.6	42.9	49.9	60.1	83.7
5.	Lignosulfonate 4.1%	33.3	41.6	46.7	54.8	76.0
6.	Melamine 3%	40.6	44.8	54.8	58.3	83.4

* Repeated Dosage

Table 22. Compressive and Flexural Strength at Various Ages—Mix Series B, C, and D[117]

Mix Series	Mix No.	Type of Mix	W:C+S Ratio*	Compressive Strength of 102x203 mm Cylinders (MPa)					Flexural Strength of 89x102x406 mm Prisms (MPa)	Splitting-Tensile Strength of 102x203 mm Cylinders (MPa)	
				1 Day	2 Days	28 Days	91 Days	365 Days	14 Days	28 Days	91 Days
B	5	Control + AEA	0.38	25.5	38.1	47.9	53.6	60.7	8.1	4.1	4.6
	6	Control + AEA + SP		28.3	38.3	44.5	53.6	56.5	8.0	4.1	4.1
	7	25% slag + AEA		17.2	34.1	43.3	50.0	54.4	7.8	3.9	4.5
	8	25% slag + AEA + SP		21.2	33.8	40.6	46.1	49.8	7.5	3.2	4.0
	9	45% slag + AEA		10.6	32.2	39.9	45.9	50.1	7.5	4.5	4.1
	10	45% slag + AEA + SP		10.2	31.2	36.6	42.5	46.5	6.8	3.7	4.0
	11	65% slag + AEA		6.7	29.6	35.1	41.8	47.5	6.7	4.0	4.1
	12	65% slag + AEA + SP		5.6	26.1	31.8	40.3	44.3	6.5	3.3	3.9
C	13	Control + AEA	0.46	16.6	28.4	36.7	43.1	49.9	5.4	3.7	4.1
	14	Control + AEA + SP		17.9	29.2	35.9	44.4	51.3	6.0	3.7	4.5
	15	25% slag + AEA		11.0	27.0	35.9	41.5	46.4	6.1	3.7	4.7
	16	25% slag + AEA + SP		12.4	27.1	37.8	44.0	47.7	5.9	3.9	4.6
	17	45% slag + AEA		8.2	23.5	34.0	41.4	44.8	6.1	3.7	4.2
	18	45% slag + AEA + SP		8.0	23.4	36.4	40.2	47.2	6.8	3.2	4.5
	19	65% slag + AEA		2.9	17.4	29.6	35.6	40.6	5.5	3.5	3.2
	20	65% slag + AEA + SP		3.1	18.8	29.3	34.1	39.2	5.6	3.4	3.3
D	21	Control + AEA	0.56	11.1	23.4	29.1	31.4	36.0	4.7	3.0	3.9
	22	Control + AEA + SP		13.7	22.8	28.4	36.1	42.9	5.2	3.3	4.3
	23	25% slag + AEA		8.2	20.0	27.0	32.0	36.8	5.5	3.3	3.7
	24	25% slag + AEA + SP		8.9	20.9	28.7	34.0	41.1	5.9	3.6	4.1
	25	45% slag + AEA		4.6	16.3	27.1	30.1	32.8	5.5	3.4	3.7
	26	45% slag + AEA + SP		4.1	20.7	26.2	35.3	38.8	6.0	3.8	3.5
	27	65% slag + AEA		1.8	13.8	26.2	28.4	31.3	5.4	3.4	3.3
	28	65% slag + AEA + SP		1.8	13.1	23.7	27.0	32.5	4.3	3.2	3.5

Table 23. Comparative Compressive Strength of Accelerated and 28-Day Cured Superplasticized Concrete (SPC)[114]

Sample	Compressive Strength		f'acc/f'28 x 100
	f'acc (accel) MPa	f'28 (28-Day) MPa	
Control	18.3	36.2	50.5
SPC	16.6	36.9	45.0
Control	7.7	18.9	40.7
SPC	12.6	23.7	53.2
Control	12.0	26.1	46.0
SPC	18.3	34.3	53.4
Control	11.1	24.2	45.9
SPC	11.0	26.3	41.8
Control	13.9	28.1	49.5
SPC	13.1	26.6	49.2
Control	13.0	28.4	45.8
SPC	12.4	24.1	51.5
Control	13.8	26.0	53.1
SPC	5.3	8.8	60.2
Control	10.1	27.0	37.4
SPC	10.9	27.2	40.1
Control	11.6	24.8	46.0
SPC	12.6	26.1	48.3
Control	17.5	37.5	46.7
SPC	11.9	23.6	50.4
Control	14.6	32.3	45.2
SPC	10.0	20.6	48.5
Control	15.9	33.4	47.6
SPC	11.9	23.7	50.2

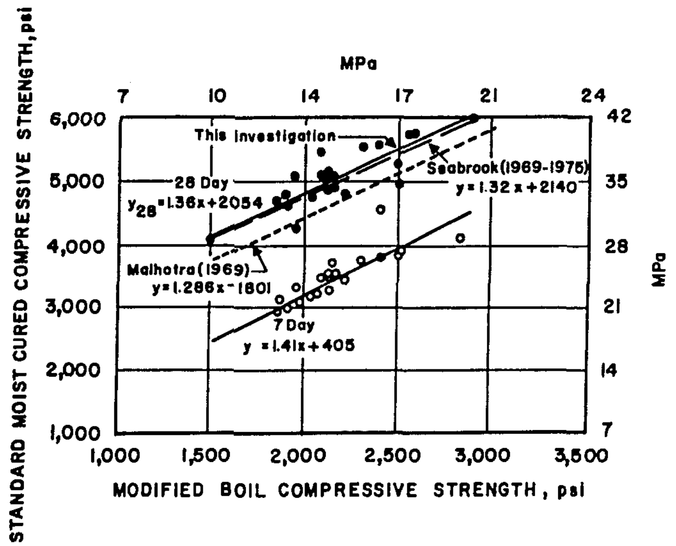


Figure 63. Relationship between accelerated 7-day and 28-day compressive strengths of superplasticized concrete.

5.21 Durability of In-Place Superplasticized Concrete

Under the USA National Co-operative Highway Research Program (NCHRP) project 10-32, *Durability of In-Place Concrete Containing High-Range Water-Reducing Admixtures,* Construction Technology Laboratories, Inc., of Skokie, USA, conducted a study of concrete placed with high-range water reducing admixtures.[120]

Existing concrete bridges and highway pavement and cores from these structures were examined to assess the relationship between durability and air-void characteristics. Although these admixtures have not been in use for very long, the study identified factors that appeared to influence the production of high quality durable concrete. The authors of the above study concluded as follows:

1. High-range water-reducing (HRWR) admixtures, in themselves, have no significant deleterious effects on the surface durability of portland cement concrete exposed to freeze-thaw environments and de-icing agents. Behavior in these environments is similar to "control" concretes prepared without HRWR admixtures.
2. Those qualities that lead to durable conventional concretes also apply to concretes containing HRWR. Properly air-entrained, low w/c ratio concretes that are workable and easy to finish will, in general, be durable even under severe environmental conditions. Factors that impact negatively upon these qualities, such as additions of water at the job site, difficulty in consolidation, overfinishing, or other poor construction practices, will result in a concrete of questionable durability, with or without the inclusion of HRWR.
3. Those variables having the greatest effects on scaling of concrete surfaces in this study include the w/c ratio of the concrete, the proportional amount of entrained air removed from the surface zone, and the spacing factor, $\bar{L}$, in the concrete as a whole.
4. By themselves, characteristics of the air-void system in concrete, as measured by standard (ASTM C 457) and novel techniques, show little correlation with durability of concrete surfaces. Although spacing factors and

specific surfaces in many HRWR concretes fail to meet minimum guidelines established by the American Concrete Institute, other factors, namely the w/c ratio and amount of entrained air removed from the near surface zone, have a greater influence on durability than do air-void characteristics measured in the bulk of the concrete.

5.22 Biological Effects

Limited or no data have been published on the biological safety of superplasticizers. Some organic materials such as urea formaldehyde foam are known to evolve formaldehyde gas that poses health hazards. Superplasticizers contain formaldehyde in their structure but they are strongly bound with the hydrated cement and hence no adverse effects may result.

6.0 CONCLUDING REMARKS

In 1980, Malhotra's concluding remarks in a paper published by the American Concrete Institute paper were as follows:[121] "There have been very few major developments in concrete technology in recent years. The concept of air entrainment in the 1940's was one; it revolutionized concrete technology in North America. It is believed that development of superplasticizers is another major breakthrough which will have a very significant effect on the production and use of concrete in years to come."

The above statement is equally valid today.

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The American Concrete Institute has also published another document, SP-148, in 1994, that contains 18 papers dealing with different aspects of superplasticized concrete.

8

Air-Entraining Admixtures

William L. Dolch

1.0 INTRODUCTION

Air entrainment is the process whereby many small air bubbles are incorporated into concrete and become part of the matrix that binds the aggregate together into the hardened concrete. The air bubbles are dispersed throughout the hardened cement paste but are not, by definition, part of it. This effect is accomplished by the use of an air-entraining agent that is called an admixture if it is added with the other ingredients at the mixer or an addition if it is interground with the cement.

Air entrainment was discovered accidentally in the late 1930's. It was observed that concrete pavements made with certain cements were more durable than others and survived the ravages of freezing exposure comparatively well. A check of the records showed the more durable cements had been manufactured with grinding aids that included beef fat, calcium stearate, and fish oil, which acted apparently as air-entraining agents.[1] A better story, although probably apocryphal, is that the air entrainment was imparted because the bearings of the grinding mill were defective and leaked grease into the charge of cement.

Air entrainment has come to be regarded as essential for the durability of concrete that will become wetted and then exposed to freeze-thaw conditions. Because of the benefits imparted in other ways as well, an argument can be made that all concrete should be air entrained, whether it will be frozen or not, except where high strength is required.

Air entrainment improves the workability and consistency of plastic concrete and reduces its bleeding and segregation. Air-entrained concretes should be proportioned to take advantage of these changes by using less water and sand. The strength of the hardened concrete is decreased unless the effects are offset by the proportioning changes, as is usually the case. The other main effect of air entrainment is the great improvement of the durability of the concrete to freezing exposure. Any concrete not air entrained and that contains freezable water is potentially in danger from such exposure. Air entrainment does not, however, protect concrete from the type of freeze-thaw failure that originates in the coarse aggregate; it protects only the paste.

Air entrainment is reviewed by Klieger,[2] in the ACI Manual of Concrete Practice,[3] in the PCA manual,[4] and in books by Powers,[5] Rixom and Mailvaganam,[6] and Dodson.[7]

Air entrainment can be carried beyond the several percent of air required for the effects mentioned above and into the realm of lightweight and foamed concretes used for insulating purposes. This subject will not be treated in this chapter.

2.0 COMPOSITION AND MANUFACTURE

2.1 Properties of Surfactants

Air-entraining agents are *surfactants,* which are materials whose molecules are adsorbed strongly at air-water or solid-water interfaces. That is, the molecules are abstracted from the solution phase and concentrated at the surface. Such molecules are termed *amphipathic.* They have a dual nature, one portion of the molecule being polar and the other being markedly nonpolar. These are sometimes termed the polar *head* and the nonpolar *tail.* The details of these portions can vary enormously. Surfactants are extremely important commercially, the whole list of detergents being only one subgroup, and there are dozens of classes of compounds and thousands of individual examples.

The polar portion of the molecule can be one of three types. If it is negatively charged, the substance is an anionic surfactant. Examples are carboxylates (COO^-) formed from the neutralization of carboxylic acids, sulfonates (SO_2O^-) from sulfonic acids, and sulfate esters (SO_3O^-). If the head is positively charged, the surfactant is cationic. The most common example is substituted ammonium ion (RNH_3^+). If the polar portion is uncharged, the material is a nonionic surfactant. The most common examples of soluble nonionic surfactants are polyoxyethylenated compounds in which the polarity and solubility are derived from a $(CH_2CH_2O)_x$ structure, with x being about 15 for products used in concrete.

The nonpolar tail of the molecule is frequently a straight or branched chain hydrocarbon group of perhaps eight to twenty carbon atoms, alkyl (8–15 carbons) benzene groups, or larger polymeric structures. This portion must be comparatively large for there to be significant surface activity; a short chain will not do.

When a surfactant molecule is adsorbed at an interface, the nature of the molecule allows its two different portions to arrange themselves so as to be in the phase each prefers, or excluded from the phase it dislikes. At an air-water interface, the polar head is in the water phase, while the nonpolar tail is excluded from the water and more or less sticks out into the air phase. Thus the molecule can satisfy both aspects of its dual nature, and this ability is the reason for its strong adsorption at the interface and its surface activity. One consequence of this adsorption is a lowering of the surface tension; the higher the concentration of surfactant in solution, the lower the surface tension.

It should be noted that many, if not most, surfactants—the whole host of soaps and detergents and wetting agents—could probably serve as air-entraining agents for use with concrete. Not all are equally good, and the critically important properties of the entrained air system depend on the nature of the surfactant used. The agents used in commerce are the inexpensive ones that experience has shown to be reliable. There has been little work on the relationship between the molecular structure of the surfactant and the important details of the resulting air bubble system in the concrete, so the time of "molecular engineering," when desirable properties can be tailor-made by a choice of surfactant, has not yet arrived.

2.2 Types of Air-Entraining Agents

The air-entraining agents used commercially make up a comparatively small group of surfactants. They have been categorized[8] as follows:

1. Salts of wood resins
2. Synthetic detergents
3. Salts of sulfonated lignin
4. Salts of petroleum acids

5. Salts of proteinaceous materials
6. Fatty and resinous acids and their salts
7. Organic salts of sulfonated hydrocarbons

Group 1, salts of wood resins, is probably the most widely used type of air-entraining agent, and for practical purposes one can read this as *neutralized vinsol resin (NVR).* Vinsol is the insoluble residue left after distillation and extraction of pine stumps to obtain other materials. It is a complex mixture of phenolics, carboxylic acids, and other substances. Neutralization with sodium hydroxide renders it soluble, and such a solution is the air-entraining agent of commerce, on which many formulations are based.

Group 2, synthetic detergents, refers mostly to alkyl aryl sulfonates, a common class of surfactants. Usually the alkyl groups are complex petroleum residues that are condensed with benzene, and the product is then sulfonated and neutralized to obtain the soluble salt.

Group 3, salts of sulfonated lignin, are by-products of the paper industry. They are comparatively poor air-entraining agents and are not much used for that purpose, but are used widely as water reducers and retarders. They are treated elsewhere in this volume.

Group 4, salts of petroleum acids, are the by-products of petroleum refining. The sludge left after treatment of petroleum with sulfuric acid to produce white oils contains water-soluble sulfonates that are then neutralized, usually with sodium hydroxide. If the neutralization is done with triethanolamine, one obtains agents of Group 7, organic salts of sulfonated hydrocarbons.

Group 5, salts of proteinaceous materials, are products of the animal-processing industries. They consist of salts of a complex mixture of carboxylic and amino acids. Comparatively few air-entraining agents are of this type.

Group 6, fatty and resinous acids and their salts, are produced from various materials. They can be the soaps that result from the saponification of animal tallow, but the calcium salts of these surfactants are insoluble, which renders them of less value for air entrainment in concrete, since the aqueous phase becomes saturated with calcium hydroxide soon after mixing. Vegetable oils, such as coconut oil, are also used. Another starting material is tall oil, which is a by-product of the paper industry and consists of a mixture of about half fatty acids and half rosin acids related to abietic.

Owing to the low cost of all these materials, it is unlikely that more expensive substances will be used in concrete until research shows specific reasons why they are superior to the existing agents.

3.0 USE IN CONCRETE

Air-entraining agents should be added as solutions, dissolved in the mixing water of the concrete. If other admixtures are also used, the air-entraining agent should be added separately, because sometimes there are reactions between materials that could result in a decrease in the effectiveness of the air-entraining agent.

These materials are used (and usually supplied) as comparatively dilute solutions with specific gravities less than about 1.1. The usual dosage rate is between about 0.3 and 1.0 ml/kg of cement, which corresponds to about one half to one and a half ounces per US bag of cement. This rate is roughly equivalent to 0.01 percent solid admixture substance to cement. The proper dosage rate can vary considerably, according to various conditions of the concrete.

The alternate way of using air-entraining agents is to intergrind them with the cement at the time of its manufacture. One thereby obtains a so-called *air-entraining cement.* Such cements are designated with a capital A after the appropriate ASTM number, e.g., Type IA, according to ASTM C 150 or C 595.[9] An air-entraining cement is distinguished from a non-air-entraining cement by the use of ASTM C 185,[9] in which a mortar is prepared and its density is determined by weighing a cupful. The air content of the mortar is calculated from the mixture proportions and known densities of the ingredients.

The advantage of using air-entraining cements is that difficulties which sometimes occur when an admixture is used, such as forgetting to add it to the mixture, can be avoided. The disadvantage is that one may get a concrete with either less or more air than desired, since the amount depends on things other than the amount of agent present. Under such circumstances, additional agent, or possibly even an air-detraining admixture, may be needed. Only a small amount of the cement produced in the US is air-entraining.

It is estimated that in the US about two thirds of the concrete produced is air entrained. The cost of air-entraining agents is small, and the cost of air-entrained concrete is virtually the same as that of non-air-entrained concrete. Most air-entraining agents have a shelf life of at least a year, and are not harmed by freezing. Air-entraining agents are not dangerous, and no special safety precautions are usually needed for their use, but manufacturer's cautions should be followed.

Air-entraining agents can be used with cements other than portland. When used with blended cements, a larger amount of agent may be required to obtain the desired air content of the concrete.

4.0 EFFECT ON CEMENT HYDRATION AND HYDRATION PRODUCT

Air-entraining admixtures have no appreciable effect on the rate of hydration of cement or on the heat evolved by that process. Even if they possess retardant properties, as the lignosulfonate salts do, they are used in such small amounts that such effects are negligible. Apparently they also have no effect on the chemical composition of the hydration products. The pore structure of the hardened cement paste was found to be the same, with or without air entrainment.[10] The only effect of these agents on cement paste seems to be the inclusion of the air bubbles.

5.0 EFFECTS OF AIR ENTRAINMENT ON PLASTIC CONCRETE

5.1 Mechanism of Air Entrainment

The air bubbles in concrete are generated by the mixing action. All the air-entraining agent does is stabilize the bubbles that are formed; it does not generate them. The details of the air-entrainment process have been analyzed by Powers[5] and reviewed by Dodson.[7]

In the mixing action, two processes apparently are at work. One is an infolding of air by a vortex action, as can be seen in the stirring of any liquid. The air is drawn into the vortex and then dispersed and broken up into smaller bubbles by the shearing action. In pan type mixers, the vortices are created by the passage of the mixing blades through the mass. In drum mixers, the vortices exist primarily at the ends of shelves where the mass tumbles down. For vortices to occur, the mass must be more or less fluid, but for dryer mixes, a sort of kneading action is postulated to cause an infolding of the air with much the same effect.

A second process involves the fine aggregate, which acts as a so-called *three dimensional screen* to entrap and hold air bubbles within its network of particles as the masses fall and cascade on each other during the mixing. This effect is thought to be responsible for the influence of the fine aggregate on the entrained air.

These processes are responsible for the inclusion of air in the plastic concrete during mixing, and they operate much the same whether or not an air-entraining agent is present. A concrete without an agent is a *non-air-entrained* concrete, but even so it will contain a small amount of air. This air is termed the *entrapped* air, and is distinguished from the *entrained* air that is present if an air-entraining agent is used. The word *entrapped* is probably unfortunate, since the air is all entrapped in the literal meaning of the word. But if an air-entraining agent is present, more air is incorporated and its bubble size is small, so that the effects are noticeable and important with respect to the properties of the plastic and hardened concrete. Also, a distinction is frequently made between these kinds of air and larger and more irregular volumes, the honeycombing that is the result of the failure to consolidate the concrete properly.

The action of the air-entraining agent is to stabilize the smaller bubbles and to ensure that they remain in the concrete. The agent does this in several ways. These processes have been the subject of considerable research, but the details are still obscure. Important results are described and analyzed in Refs. 5, 7, 11, and 12.

Without an air-entraining agent, the bubbles incorporated in the concrete by the mixing are lost relatively easily. They coalesce and form larger bubbles when they are brought near each other, then the larger bubbles come to the surface when the mixing action brings them relatively close, and there they burst and are lost.

One stabilizing action of the air-entraining agent is the result of its adsorption at the bubble surface. The adsorbed molecules form a film and are oriented with their polar heads in the water phase. If the molecule is charged, the bubble will acquire this charge, so when two bubbles approach each other during the mixing, they experience an electrostatic repulsion that keeps them separate when they would otherwise coalesce. The action is much the same as that by which an emulsifying agent stabilizes and prevents the breaking of an emulsion.

A second type of action is the orientation of a layer of water around the bubbles, probably several molecules thick, a so-called *hydration sheath* that also serves to separate the bubbles and stabilize and deflocculate the system.[13] This type of action is thought also to be operative in the case of adsorbed layers of nonionic agents that cannot change the potential of the bubbles. It may be significant in this connection that nonionic agents seem to result in poorer air entrainment and larger bubble sizes, compared with ionic agents.

One consequence of the lowering of surface tension caused by the surfactant is to stabilize the bubbles against mechanical deformation and rupture by means of the so-called *Marangoni effect.*[14] This effect depends on a local dynamic change in surface tension owing to the deformation of the bubble. The result is an opposing action that tends to offset the deformation. A similar mechanism operates to stabilize foams.

A second mode of action of an anionic air-entraining agent seems to be related to the extent to which it is precipitated by the components of the aqueous phase of the concrete. For practical purposes, this means the extent to which its calcium salt is insoluble, since the concentration of calcium ion in solution increases rapidly as hydration of the cement progresses, and becomes supersaturated with respect to calcium hydroxide after only a few minutes. So if the calcium salt of the agent is insoluble, it should be precipitated from solution. If the anionic molecules are adsorbed and concentrated at the surfaces of the bubbles, it is logical that such precipitates should form there in especially large amounts. Mielenz et al.[15] postulated that such films form at the bubble surfaces and are of sufficient thickness and strength to help stabilize the bubbles and prevent coalescence. They showed photographs of such films. The matter is discussed by Dodson,[7] who pointed out that there is a contrary action by which the agent is precipitated out of solution by the calcium ion and becomes unavailable for air-entraining action. He postulated that a long mixing period would tend toward the latter action.

The mode of action of these *precipitate* films may essentially be that of a protective colloid that maintains dispersion and prevents coalescence by a *steric* effect of preventing the bubbles from approaching each other too closely. Such effects occur in many systems.[16] Foamed concretes of low unit weight are stabilized by the addition of animal products that probably form similar films around the bubbles.

It should be remembered that many air-entraining agents are complex mixtures, portions of which might produce insoluble precipitates leaving other components in solution to become adsorbed at bubble surfaces and lower the surface tension.

It is known that cationic and nonionic surfactants, which cannot form insoluble precipitates in the concrete system, do cause air entrainment.[7][17][18] Also, anionic agents whose calcium salts are soluble, such as the sulfonates, are good as air entrainers. So it would seem that the insoluble film mechanism, while apparently important to the process, is not essential.

Another way in which air-entraining agents are supposed to stabilize the bubble system is by adsorption onto the cement. When the particles of cement come in contact with the water, they rapidly become coated with a hydration product that is a finely-divided calcium silicate hydrate. This hydration product bears a positive surface charge, due probably to the adsorption of calcium ions. It is postulated that the air-entraining agent is adsorbed onto this surface by an electrostatic bond between the positive surface and the negative ion of an anionic surfactant, with the nonpolar portion of the molecule protruding out into the water. This action is said to render the cement particle *hydrophobic* and to result in the attachment of the cement particles to the air bubbles. Since the particles are mostly smaller than the bubbles, the result is a coating of the cement particles on the bubbles that helps to anchor them in the mass and prevent their ascension and coalescence. The action has many aspects in common with the flotation of minerals that is used to concentrate ores. Bruere[19] used such a flotation test to evaluate air-entraining agents in cement pastes, and concluded that bubble attachment to the cement particles was important. On the other hand, it is difficult to see how this mechanism can apply to cationic or nonionic agents. Adsorption of air-entraining agent and superplasticizer molecules onto cement surfaces was demonstrated by Andersen[20] using electrophoretic methods.

Once the bubbles are formed and stabilized against loss, a further action takes place that influences their final form in the hardened concrete. This process is a dissolution of air from the smaller bubbles and a diffusional transfer from one bubble to another.

The pressure inside a bubble is greater than that outside, and the difference is called the capillary pressure. The magnitude of the capillary pressure is inversely proportional to the size of the bubble. Since the solubility of a gas in a liquid is proportional to the pressure of the gas, air will dissolve out of the small bubbles and form a more concentrated solution around them than exists around the larger bubbles. Therefore, a transfer will take place by diffusion along the concentration gradient, and the net result will be a transfer of air from the small bubbles to the larger ones and a corresponding coarsening of the bubble size distribution. Practically, the result is that the smallest bubbles disappear. A rough calculation shows that the bubbles smaller than about four micrometers in diameter should disappear, and it does seem that microscopical examination of the hardened concrete shows an absence of the smallest air bubbles.

This mechanism was postulated[15] and defended[11] by Mielenz. Some contrary evidence was reported by Bruere.[21] If this mechanism is valid, and it seems on theoretical grounds that it must be, then any barrier to the passage of air through the bubble wall, such as might be provided by adsorbed films or colloidal precipitates, would tend to offset this effect. The permeability of the bubble walls to the passage of air was measured, and the agents that gave the lowest permeability resulted in the smallest bubbles in concrete, as would be expected.[17]

5.2 Factors Influencing the Amount of Entrained Air

As will be discussed later, the total air content of the concrete is not the most significant parameter with respect to the protection of the concrete against frost damage. Nevertheless, the total air content is the only quantity that can be measured on the fresh concrete. In what follows, the influence of several significant variables on the air content will be discussed. Some of these also influence the spacing factor of the air bubbles in the hardened concrete, which is the most important parameter of the air system. The effects of these variables on that parameter will be discussed later.

Agent Dosage. The more air-entraining agent that is used in the mixture, the higher will be the air content. For most agents, this effect is parabolic and tends to more or less level off at higher dosages.

Slump. The higher the slump of the concrete, the higher will be its air content, until high slumps are reached, when the air content drops off somewhat. An increase in slump of about three inches will result in an increase of air content of about one percent. A typical relationship is shown in Fig. 1. The increased water will result in a more fluid mixture into which the air can be incorporated more easily by the mixing action. The additional water also bulks the sand and creates more space for the bubbles. This influence was discussed by Powers.[5] At higher slumps, in the region of seven inches, the increased fluidity of the mix results in an easier loss of air during handling and placing, so the value decreases slightly.

It is difficult to entrain air in a very dry, low-slump, concrete. Whiting[22] showed that with some agents, a tenfold dosage was required for such concretes, while with others, a proper air system could not be obtained even so.

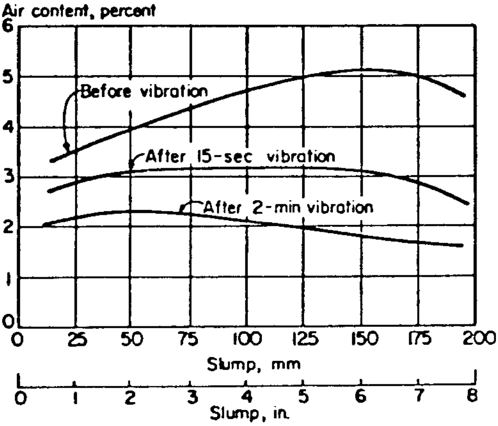

Figure 1. Relationship between slump and air content of concrete.

Coarse Aggregate. As the maximum size of the coarse aggregate increases the air requirement of the concrete decreases. The ACI proportioning method[3] calls for 7.5 percent air with 3/8-in aggregate but for only 5.0 percent with 2-in aggregate. This effect is indirect, because the maximum size of the coarse aggregate determines the fraction of the concrete that is mortar; the larger the maximum size, the smaller the mortar fraction. The requirement for durability has been shown by Klieger[23] to be an air content of the mortar fraction of about 9 or 10 percent, which is obtained if the specified values for the air content of the concrete are met.

Fine Aggregate. The fine aggregate is the portion of the mixture that serves as a "screen" to trap the air during the mixing. The fine aggregate provides interstices that contain paste and air bubbles, so it generates the air efficiently. The greater the proportion of sand in the total aggregate, the greater the air content of the concrete. The effect is shown in Fig. 2. But beyond the mere proportion, there seems to be an effect of size and grading, especially in leaner mixes. The critical factors seem to be the amount of interparticle space that the grading contains (which serves as the locus of air bubbles) and the size of that space.

The conventional wisdom[4] is that the middle sand sizes, from about the 600 μm (No. 30) to the 150 μm (No. 100), are most efficient in entraining air bubbles. The interstices of groups of particles in this size range are of the size of a large proportion of the desirable bubbles in air-entrained concrete, and this may be the reason for the importance of this size fraction. For richer mixes, the influence of the aggregate is less important.

Sometimes the sand seems to have an influence that is difficult to understand. In some instances when difficulty was experienced in obtaining the required air content, a change of the sand source solved the problem. Hollon and Prior[24] refer to the sand as the "most important single factor...in air entrainment" and emphasize the need for control of uniformity of the sand. Occasionally sands have become contaminated with either natural or industrial materials that have served as either air-entraining agents or sometimes as air-detraining agents.

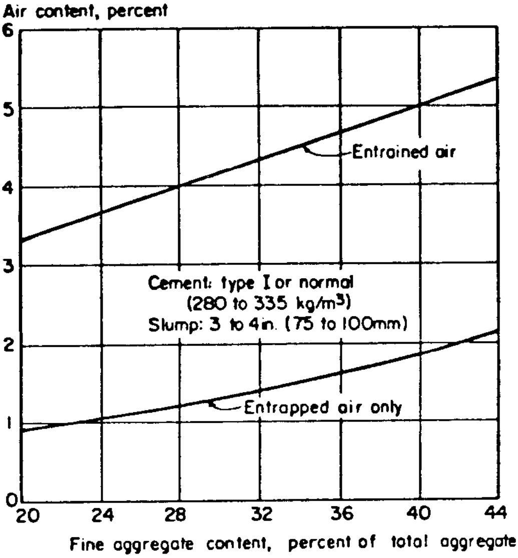

Figure 2. Relationship between percentage of fine aggregate and air content of concrete.

Finely-Divided Materials. The presence of finely-divided materials causes a reduction in the air content of concrete and an increase in the required dosage of air-entraining agent. Such substances as fly ash, other mineral admixtures, carbon black, the finest sand fractions, and the cement itself have all been implicated.

The effect is probably twofold. Fine fractions tend to "bind" more of the mix water because of the requirement that it coat their larger surface areas. The water can then not be a part of the air bubble generating and stabilizing process. In addition, increased solid surface area may adsorb molecules of the agent and render them unusable in the air-entrainment process. This action is thought to be the reason that fly ashes with high ignition losses, which is to say a large amount of unburned carbon particles, cause an especially large reduction in air content and therefore require additional air-entraining agent. Klieger and Gebler[25] reported tests on a large number of both Class F and Class C fly ashes. The ashes that required more air-entraining agent in order to obtain the required air also caused a greater instability and more rapid loss of that air in the plastic concrete.

Excessive fines or "dirt" in the sand can also cause this problem. So can crusher dust on a manufactured sand. The use of such a *stone sand* may require several times the amount of agent that would normally be expected.[24]

A richer mix with its high cement content will also cause a reduction in the air content, especially if the fineness of the cement is high. A Type III cement may require half again as much air-entraining agent as a Type I.[24]

Dodson[26] devised a test to show the efficacy of the air-entraining agent and the influence of such factors as finely divided materials, cement composition, etc. This foam index test is performed by titrating a slurry of the cement and mineral admixture with a solution of the agent. The resulting foam index is the amount of titrant needed to establish a stable foam after shaking the mixture. The smaller the value, the more efficient the admixture.

Temperature. A higher temperature of the concrete results in a lower air content, and vice versa. This is true even if the water content has been modified to keep the slump constant. Powers[5] contends that the reason is that, at a higher temperature, there is less water "available for bubble formation," but the details are unclear and have not been investigated. Probably, it is a complicated matter of the effect of temperature on the amount of the agent adsorbed at the bubble surface, the thickness of the electrical double layer that is formed, and the surface tension and viscosity of the liquid phase.

The effect is more important at higher slumps. At a 7-inch slump, a temperature rise of 15°C will cause a decrease in the air content of about one percent; at a slump of 1 inch, the effect is negligible. Typical behavior is shown in Fig. 3.

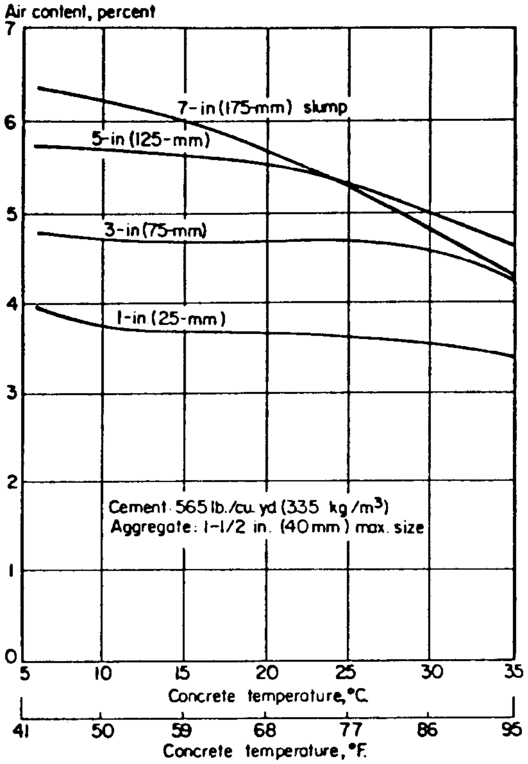

Figure 3. Relationshp between temperature and air content of concrete.

Other Admixtures. When lignosulfonate water reducers or retarders are also used in the concrete, less air-entraining agent is required than would otherwise be needed, presumably because the lignosulfonate has a moderate air-entraining capacity by itself. According to Rixom and Mailvaganam,[6] this effect is also valid for the hydroxycarboxylic acid type of retarders, although alone they do not act as air-entraining agents. Authorities seem to differ on the effect of calcium chloride on the air content of concrete,[3][7] but it seems to be small.

Chemical Composition of the Cement. Cements with a high alkali content entrain air more easily than do low-alkali cements. Less agent is required for high-alkali cements; they lead to a lower foam index.[7] Some work[27] showed alkalis to increase the spacing factor and, therefore, to degrade the quality of the bubble system, but other results[28] pointed to sulfate as the influential factor.

It is possible for the cement to be accidentally contaminated with oils or other substances that can act as air entrainers or as air detrainers.[29] Possibly for these reasons, considerable variability has been observed in the air content of concretes made with a variety of cements, but otherwise of identical nature.[6][30] Some cements seem to be "sensitive" with certain agents for reasons that are poorly understood, and difficulty can sometimes be eliminated by a change of the cement or of the admixture.

Mixing. A higher mixing speed gives a higher air content, which is only expected. A longer mixing time will cause a small increase in the air content, but still longer mixing causes it to decrease.[4][30] The time at which the maximum air is entrained is earlier the lower the initial slump. This effect is shown in Fig. 4. Worn mixer blades or a buildup of hardened concrete on the blades results in a decrease in the air content. Overloading the mixer also lowers the air.

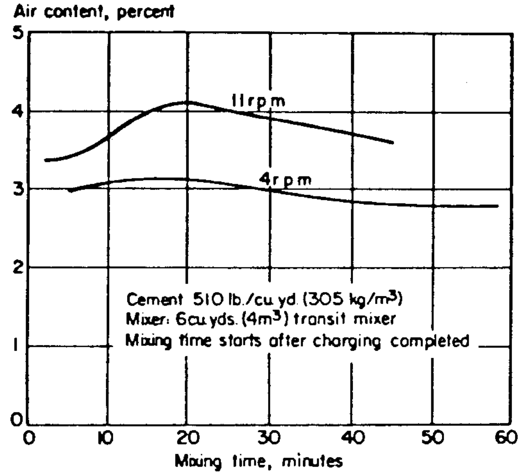

Figure 4. Relationship between mixing time and air content of concrete.

Vibration. Vibration reduces the air content of concrete; indeed, that is what it is supposed to do, since consolidation is the process of removing the large air pockets and bubbles from the concrete. Typical behavior is shown in Fig. 1. The larger bubbles are lost most easily and rapidly, although the thickness of the lift from which the air is being expelled has a lot to do with the rapidity of loss,[5] so the quality of the air system, which resides mostly in the smaller bubbles, may not be impaired. Stark[31] did find a degradation of the system, especially with relatively high vibration frequency and concrete of high water content.

5.3 Proportioning of Air-Entrained Concrete

Two fundamental facts determine the proportioning of air-entrained concrete compared with that of non-air-entrained concrete: the air bubbles increase the slump and workability of the concrete and, at the same time, they decrease its strength.

Because of the change in consistency, less water is needed for the air-entrained mixture, if the slump is maintained constant. It amounts to roughly ten percent less for ordinary mixes, according to the ACI recommended practice.[3] The increase in the volume of air in the mixture is at least partly offset by the decrease in the volume of water and by a decrease in the volume of fine aggregate.

For comparatively rich and therefore strong concretes, the increase in strength due to the lowered water-cement ratio is more than offset by the decrease in strength due to the entrained air. Therefore, additional cement must be added to maintain constant strength. On the other hand, for a leaner concrete with a lower strength and higher water-cement ratio, the same water content decrease will bring about a greater reduction in water-cement ratio and a larger relative strength increase, so that the weakening effect of the entrained air will be just about offset, and no additional cement will be required. Such generalizations must, however, be viewed with caution, since, for any concrete, trial mixes are necessary to determine final design.

5.4 Influence of Air Entrainment on Properties of Plastic Concrete

Slump and Workability. An air-entrained concrete will have a higher slump at the same water content than one that is not air entrained, but the important change is one of an improvement in workability, rather than merely of slump. Workability refers to the ease with which concrete can be transported, placed, compacted, and finished.[5] It is, therefore, a quality that has inescapable elements of subjectivity and cannot be measured objectively. Augmentation in workability is desirable in all concretes, but those that are inherently harsh and unworkable, such as lean lightweight-aggregate concretes, are especially benefited by the use of air entrainment.

The increase in workability brought about by air entrainment is usually ascribed to some sort of "ball bearing" action of the air bubbles. They are very numerous, roughly several million per cubic inch of concrete, and they are compressible under the forces that the concrete experiences during placing and finishing, unlike the other constituents, so the bubbles allow for easier deformation when the concrete is worked, resulting in an increase of workability.

The rheological properties of concrete have been measured, and standard parameters, the yield point and plastic viscosity, have been described and investigated. Tattersall and Banfill[32] show that air entrainment reduces both these parameters of concrete, with the effect being relatively greater on the viscosity.

Bleeding and Segregation. Air-entrained concrete is less subject to bleeding and segregation than is non-air-entrained concrete. *Bleeding* is the term used to describe the emergence of mix water on the surface of the concrete during and after placement. In addition, bleeding sometimes results in the formation of internal channels, usually more or less vertical, and voids under pieces of coarse aggregate. Bleeding is usually bad for the concrete, and its virtual elimination by proper air entrainment is a major benefit.

Segregation refers to settlement of the solids that is sufficiently great to destroy the homogeneity of the concrete and become technically troublesome. Segregation can occur either in the forms during consolidation or when the concrete is being transported, chuted, pumped, and otherwise handled. Details are discussed by Popovics.[33] Although entrained air decreases segregation, it cannot be expected to cure excessive ills, such as those caused by poor grading of the aggregate, excessively lean or wet mixes, and improper handling of the concrete.

The precise mechanism by which air entrainment reduces bleeding and segregation is not well understood. The air bubbles make the concrete more cohesive and homogenous by creating a quasi structure with the solids to which they become attached through adsorbed surfactant molecules. They also, thereby, help to buoy up the solids and reduce the tendency to settle. Finally, the bubbles serve to reduce the cross section through which differential movement of water can take place, because they occupy a volume roughly equal to a fourth or fifth of the paste. On the other hand, so do the sand particles that the air bubbles have replaced, so it may be that the air-water interface is more capable of hindering the flow of water past it than is the sand-water interface, and analogies are drawn between these processes and the way in which adsorbed films inhibit the drainage of foams. Details are found in Refs. 5 and 16.

Finishability. Finishers sometimes feel that air-entrained concrete is more difficult to finish, owing largely to its lack of bleed water. There are complaints that air-entrained concrete is "sticky" and that it hangs up on the finishing tools. But if proper tools are used (generally magnesium or aluminum floats) and a suitable delay is observed before starting the finishing operations, air-entrained concrete presents no difficulty.[34] Indeed, because of the lack of problems that can be caused by bleed water, air entrainment is more likely to ensure a properly-finished and durable surface.

Set Time. Air entrainment does not affect the setting time of concrete.

5.5 Determination of the Air Content of Plastic Concrete

The three ASTM standard test methods for the air content of fresh concrete are the gravimetric, C 138, the pressure, C 231, and the volumetric, C 173 methods.[9]

The *gravimetric method* involves measuring the unit weight of the concrete by weighing a tared container full of the sample. A knowledge of the mix proportions and of the specific gravity of each component permits the calculation of the air content. This is not a method normally used in the field because of uncertainties in the values of these parameters.

The *pressure method* is probably the most widely used. It is based on Boyle's law. A sample of the concrete is consolidated into a container that is then sealed closed. This container is then connected to another in which the pressure has been increased to a known value. The pressure in the now combined system will fall to a degree determined by the air content of the concrete, since the higher pressure will be transmitted hydraulically to the air bubbles. In commercial instruments the manometer is calibrated in terms of the air content of the concrete.

The only problem with this method is that air in aggregate voids is also recorded and results in a positive error that necessitates an aggregate correction factor, which is determined by running the test on the same amount of aggregate in water. This correction factor is so large for lightweight aggregates that the method is inaccurate and not recommended for lightweight concrete.

In the volumetric method, the sample is placed and compacted in a container that is the bottom half of the apparatus. The top half is a semi-conical lid. It is clamped to the bottom portion, and water is layered on top of the sample until it fills the upper portion to an index mark in a sight glass. The whole container is then stoppered and shaken or rolled to mix the concrete sample and the supernatant water. This mixing releases the air bubbles, owing to the greatly increased fluidity of the mixture, and they collect at the top. The decline in the level in the sight glass is then a direct determination of the air content of the concrete. This method is suitable for concrete containing lightweight aggregates, since the air in the aggregate pores is supposed to stay there during the course of the test and not be collected with the entrained air.

A small version of the volumetric method, called the Chace meter, operates on the same principle but uses a small portion of mortar from the concrete. This sample is only a few cubic centimeters in volume. The operation is the same as with the large apparatus, and the air content of the concrete is read off the calibrated glass stem. This calibration assumes a standard mortar fraction for the concrete, and if the sample is much different, an individual calibration using one of the other methods must be made. The advantages of this method are that it is rapid and the equipment is inexpensive. Compared with the pressure meter,[35] the Chace meter gave somewhat higher results. Even so, it provides a rapid check of the air content, although perhaps not one accurate enough for field control.

Nasser[36] developed a volumetric meter that is small compared with the conventional one, but larger than the Chace, and that uses a sample of concrete. He found excellent correlation of the values so obtained with those from the larger meter.

With any volumetric method a small amount of alcohol needs to be incorporated in the added water to kill the foam and permit an accurate reading in the sight glass. Pure alcohol exhibits a volumetric contraction with water that would result in a positive error in the measured air content if it were mistakenly used for all of the added liquid, as is sometimes the case with the Chace meter.

As discussed in Sec. 6.5, the total air content is not the most important parameter of the entrained air system. Other geometric factors are more important, and there is no method to determine these factors on the plastic concrete. If this were possible, the plastic concrete could be rejected and replaced if defective. But the only way to determine these deficiencies at present is by examination of the hardened concrete.

6.0 EFFECTS OF AIR ENTRAINMENT ON HARDENED CONCRETE

6.1 Unit Weight

Air entrainment affects the unit weight of concrete in the obvious way; the unit weight is inversely related to the air content. The ratio of the unit weight of the air-entrained concrete to that of the air-free concrete is one minus the fractional air content.

6.2 Frost Action in Concrete

The main reason for air entrainment in concrete is the great improvement it imparts to the durability in freezing and thawing. Lack of durability to frost action can arise in either the hardened cement paste or the coarse aggregate. Air entrainment greatly improves the performance of the paste; indeed it virtually solves the problem, but it has no important effect on problems arising from the use of poor aggregate. Figure 5 shows the effects of entrained air on the frost durability of concrete.[4] The figure shows that air-entrained concrete is more durable than non-air-entrained concrete, and the durability increases as the air content increases. However, excessive amount of air is not desirable because of the strength reduction it causes.

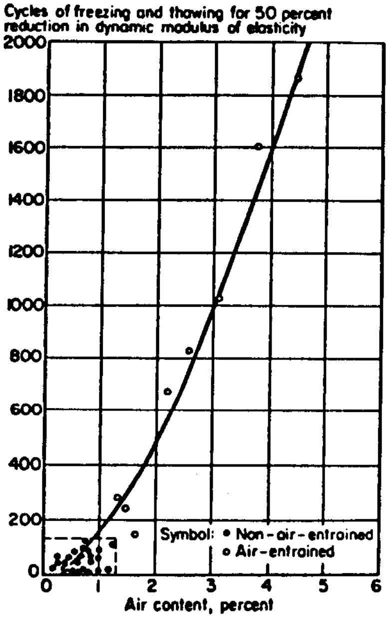

Figure 5. Influence of air entrainment on freeze-thaw durability of concrete.

6.3 Mechanisms

Hydraulic Pressure. Early attempts to understand the destruction of concrete by freezing centered on the volume increase that water experiences when it freezes. This increase amounts to approximately nine percent. The pressure needed to prevent freezing can be calculated from the Clausius-Clapeyron equation, and is about 1800 psi (12 MPa) per degree C. Therefore, a substance such as concrete, with a tensile strength of around a thousand psi (7 MPa), will fail within a fraction of a degree of subcooling if it is required to restrain the pressure of the water to ice conversion.

An important consequence is the concept of a critical degree of saturation. That is, if a given pore is not more than about ninety percent saturated with water, freezing should do no harm, because there will be enough free space to accommodate the volume increase that occurs without the generation of increased pressure. A number of studies have established the validity of this concept, for example.[37][38]

Powers recognized that almost always there is, in concrete, enough empty pore space in the form of entrapped air, honeycombing, or water voids to accommodate the volume change caused by the freezing of the water in other, critically saturated, portions of the pore system. Or, lacking such internal space, the excess water should merely move out of the concrete, since the freezing is hardly ever omnidirectional, and usually there is a route of escape through an unfrozen exterior.

Such considerations led Powers to the hydraulic-pressure hypothesis.[39] This idea contemplates that the water in a critically saturated pore freezes and forces some unfrozen water out into and through the as yet unfrozen pore system of the cement paste. Any such flow is associated with a hydraulic pressure between its source and its end point. This pressure will be directly proportional to the flow rate and the flow path length, and inversely to the permeability of the medium being traversed. If the flow path is longer than some critical value, the tensile stress generated by this pressure will exceed the strength of the material, and it will fail. For cement paste, both calculation and experiment have shown this critical length to be of the order of 0.008 in (200 μm). The smallness of this distance is because of the extremely low permeability of the paste.[40]

Accordingly, the central function of entrained air is to provide very many small, closely-spaced, empty escape places for the excess water when freezing occurs. If no spot in the paste is farther than the critical distance from such an escape place, disruptive pressures cannot be generated, and the paste will be durable to freezing.

Gel Water Diffusion (Osmosis). Powers and Helmuth[41] later advanced another theory. It was based on observations of expansion of cement pastes with time, as the temperature was held at some subfreezing level. Saturated, non-air-entrained pastes continued to expand, while air-entrained pastes not only did not expand but even contracted.

The freezing point of water in a pore is depressed below that of bulk water, and the smaller the pore the greater the depression. Calorimetric measurements have shown that water in cement pastes exhibits this phenomenon, and all of the water does not freeze until a temperature of about -40°C is reached,[42] so at any higher temperature, the water in larger pores is frozen and the rest is not. The free energy of the unfrozen water is higher than that of the adjacent ice, so a potential exists to cause the water to migrate to the ice body and generate pressure and expansive stresses, hence the name *gel water diffusion* for this process. Since the thermodynamic description is similar to that of osmosis, that name has also been applied.[43]

This mechanism is analogous in many ways to the macroscopic phenomenon of the growth of ice lenses in soils and the resulting frost heave that can be so destructive to pavements.

A strong confirmation of this mechanism is the observation that "frost" damage can occur with liquids (e.g., benzene) that do not expand on freezing,[44] and for which no hydraulic-pressure stress is possible.

A second part of this hypothesis is truly osmotic in nature. The liquid in the pores of cement paste is, for practical purposes, a solution of sodium and potassium hydroxides. When this solution freezes, the solid formed is pure ice, and the remaining unfrozen solution increases in concentration. Therefore an osmotic potential exists between the more concentrated solution in the partially frozen pore and the less concentrated solution in the unfrozen adjacent pores. The result is an additional component of expansive stress. This osmotic component is thought to be the main reason for the *salt scaling* of concrete, the additional distress to the surface that is caused by the application of de-icing salts, which increase the solute concentration in the surface pores. The fact that the distress is independent of the chemical nature of the de-icing salt[45] confirms this essentially physical description of the process.

According to the gel-water-diffusion mechanism, entrained air bubbles protect against freezing distress by presenting an alternate path to the unfrozen water. If there is a nearby air bubble, it will contain only a small amount of ice, from water forced out of the paste by hydraulic pressure. This ice will not be under pressure nor can it become so, since the bubble is never filled; so the unfrozen water can either travel to the ice-filled pore or to the ice in the air bubble. If it goes to the pore, the pressure will increase, thus raising the free energy. If it goes to the small amount of ice in the air void, the pressure will not increase. So the thermodynamic impulse is for the water to migrate to the air bubble without the generation of expansive stress. Therefore, the air protects the paste against disruption from either the gel-water-diffusion mechanism or from the hydraulic-pressure mechanism.

Other hypotheses of frost action in cement pastes have been advanced. Perhaps the most detailed of these is that of Litvan,[91] who envisions a flux of water due to vapor pressure differences between water in pores and ice in larger voids or on external surfaces. These ideas seem to involve aspects of both the two previously-mentioned hypotheses.

Frost Resistance of High-Strength Concrete. The increasing use of high-strength concrete, that with a compressive strength greater than about 8000 psi (55 Mpa), has given rise to special concerns with respect to its freeze-thaw durability. Such concrete must be made with a low water-cement ratio, which is routinely obtained in workable concrete by the use of high-range-water-reducing admixtures, originally and more usefully called superplasticizers. This concrete also frequently contains a pozzolan, usually silica fume.

If the water-cement ratio of a mature, well-cured concrete is smaller than about 0.38, its paste will have pores so small that the water they contain will not be freezable at any field temperature. Such a concrete should not require entrained air to protect it from freezing distress. The prospect of a high-performance concrete that will be durable without the strength-reducing air entrainment is obviously attractive.

The question has been reviewed in detail by Philleo.[46] The evidence, including that since his review, is conflicting. Some results show that durable, high-strength, non-air-entrained concrete can indeed be produced. But other work affirms the same need for air entrainment that is unquestioned in concrete of higher water-cement ratio, although perhaps the parameters of the bubble system need not be the same.

The problem is further complicated by several details. The ASTM standard test for freeze-thaw resistance, C 666, has been criticized as unrealistically severe. The single-freeze method, originally advanced by Powers,[47] now ASTM C 671, has been advocated as an alternative.[46]

It is also possible that test results are confused by the curing time of fourteen days suggested in C 666. Perhaps silica-fume concrete requires more curing in order to develop its changed pore structure and decreased permeability, both of which probably augment its frost resistance. The matter was studied by Cohen,[48] who found that an intermediate time of curing was worse than either shorter or longer ones.

Finally, there are important questions of whether freeze-thaw failure at the surface, i.e., scaling, involves different critical air parameters than does failure at depth.

Effects of Aggregate on Durability. Failure of concrete in freezing and thawing can also occur because of the use of nondurable coarse aggregate. The effects are reasonably well understood.[49]-[51] Air entrainment cannot improve the frost resistance of concrete containing nondurable aggregates.

6.4 Determination of Air Parameters of Hardened Concrete

Investigation of the air system in hardened concrete is done microscopically. The ASTM standard is C 457.[9] Two procedures are set forth. They differ as to method, but the information gained is the same. Unfortunately, these methods are not as precise as would be desirable. An error analysis was published by Langan and Ward.[52]

Sample Preparation. For either method of investigation the sample is prepared in the same way. A sawed surface is cut. The orientation of the cut depends on the purpose of the investigation. The sawed surface is then ground successively with finer grades of grinding powder until a surface is obtained that is highly polished and plane. Various types of commercial lapping equipment are available, although the job can be done satisfactorily by hand on a lap wheel, or even on a glass plate.

Linear Traverse Method. The linear traverse method is based on the equality of the fractional length of a random line that passes through a given phase and the volume fraction of that phase. That is, if L_a is the length of the random line that passes through the air voids, and L_t is the total length of that line, the air content $V_a/V_t = L_a/L_t$. The development of these concepts is given by Hilliard.[53]

The line is delineated by placing the polished sample on a traversing platform that is advanced by the rotation of a lead screw. The surface is observed through a binocular microscope as successive passes are made across the surface. Traverse through air is accomplished by one lead screw, and traverse through all other phases of the concrete by another. Traverse distances are totalled by rotational counters on the lead screws or by some other appropriate means.

Microscope magnification can vary from about 50X to 125X. The total length of line that must be traversed for a statistically satisfactory result depends on the maximum size of the coarse aggregate, because the mortar fraction is related to this value, but it is of the order of 100 inches (2.5 m).

If parameters of the air void system other than the total air content are to be determined, an additional piece of information must be obtained by pressing a counter each time the line intersects a bubble, and so obtaining the total number of bubbles intersected, N.

Point Count Method. This method is based on the equality of the fractional number of random points that fall in a given phase and the volume fraction of that phase. If S_a is the number points that fall in the air voids and S_t is the total number of points, then the air content $V_a/V_t = S_a/S_t$.

The set of points is generated by the intersections of an orthogonal grid traced on the polished surface by moving it successively, one point at a time, under the cross hairs of the microscope. A typical translation in either grid direction is 0.1 in (2.54 mm). At each stop, the surface is observed through the microscope, and a tally counter is pushed depending on which phase the cross hairs lie upon. The counter totals the points counted in each phase, and their ratios are the required volume fractions.

In order to determine one important parameter of the air void system, the amount of the paste phase must be determined. The point count method has a big advantage over the linear traverse, because additional phases can easily be determined by using more counters. In the linear traverse method, additional phase determination required building additional lead screws into the equipment or repeating the whole determination.

The total number of points required for statistical validity is again a function of the aggregate maximum size and is about 1500 for ordinary concrete. The polished area examined is the same for either method.

The total number of bubbles intersected, N, is an important quantity in determining the parameters of the bubble system. The most difficult aspect of the determination, by either method, is to decide whether or not the line intersects a bubble at a point of apparent tangency, or indeed whether a small bubble is really there or not. This is the reason why an extremely smooth surface is required.

Image Analysis. In pursuit of the trend toward instrumental analysis, and in order to obviate the subjective errors of the microscopical methods, recent work has applied the techniques of image analysis to the determination of the air bubble parameters of concrete.[54] These methods have the large advantage of being able to provide information on the size distribution of the air bubbles. Their disadvantages include the cost of equipment. Whether they will replace the microscopical techniques remains to be seen.

6.5 Air Bubble Parameters

The most important parameters of the bubble system are the air content, the bubble frequency, the specific surface, and the spacing factor.

Air Content. The air content A is the fractional volume of air in the concrete:

$$A = V_a / V_c = L_a / L_t = S_a / S_t = n\bar{l}$$

where:

V_a = volume of air
V_c = volume of concrete
L_a = length of traverse line through air
L_t = total length of traverse line
S_a = counts that fall in air
S_t = total number of counts
$\bar{l}$ = average chord intercept = L_a/N where N is the total number of bubbles intersected
n = bubble frequency = N/L_t

Frequently the air content is expressed as a percentage.

In doing the microscopical analysis, a distinction is sometimes made between entrained and entrapped bubbles, on the basis of size and shape; entrapped bubbles are considered to be those larger than 1 mm and of a non-circular section (i.e., a non-spherical shape). And the entrained bubbles are considered the only ones important to the durability of the concrete. Such a distinction is fundamentally improper, because any air-filled void will protect a region of paste around it. The only difference is one of efficiency in this task; the small bubbles are much more efficient.

Properly air-entrained concrete will usually have an air content of 4–8 percent, depending on the maximum aggregate size. These values correspond to about ten percent air in the mortar fraction. The air content of hardened concrete is generally a few tenths of a percent smaller than that determined on the same concrete when still plastic. The differences depend on the agent used and on the method of determining the plastic air content.[55][56]

Bubble Frequency. The bubble frequency $n = N/L_t$. It is the number of bubbles intercepted per unit length of total traverse, whether the linear traverse or the point count method is used. The larger the value the better, at least up to a point, because smaller bubbles are more numerous for a given air content. The Portland Cement Association[4] recommends that the number per inch be one and one half to two times the percentage air content. So properly air-entrained concrete will have a bubble frequency of about 8 to 16 per inch (300–600 per meter).

Specific Surface. The specific surface α is the surface area of the air bubbles per unit volume of air. Important relationships of α are as follows:

$$\alpha = A_a/V_a = 4/1 = 4n/A$$

where: A_a = surface area of air bubbles
V_a = volume of air bubbles

and the other symbols are as previously defined. Since the average chord intercept is not determined by point count, the last relationships, $\alpha = 4n/A$, is the one used to determine the specific surface when using that method. A properly air-entrained concrete will have values of a of about 600–1200 in^{-1} (24–48 mm^{-1}). It is obvious that the values of A, n, and α are related. If the concrete has proper values for two of them, the third must be proper also.

Spacing Factor. Powers[57] developed the idea of the spacing factor as a test parameter for the adequacy of the bubble system in air-entrained concrete. The idea is based on the postulate that no point in the paste should be farther than the critical distance from an air bubble. In ASTM C 457 the spacing factor is defined in two ways. If the paste to air ratio p/A is less than 4.342, i.e., when the air content is relatively high, the spacing factor should be calculated from

Eq. (1) $$\bar{L} = p/4n = p/Aa$$

where p = paste content, the volume fraction of the concrete that is paste. The paste content is determined in a manner entirely analogous to the air content, by either the linear traverse or the point count technique.

An analysis of the above relationship shows that the spacing factor, so defined, is the thickness of the paste layer on the surface of the air bubbles, if the volume of the paste were spread uniformly over all the bubble surfaces. So by this model, if the spacing factor is smaller than the critical distance, the paste should be protected from frost damage.

If the paste-air ratio is larger than 4.342, which is more often the case, (p/A will range from about 3.7 to 6, for ordinary concrete), the calculation of is by the equation

Eq. (2) $$\bar{L} = 3/\alpha\,[1.4\,(p/A + 1)^{1/3} - 1]$$

The model on which this equation is based is a cubic lattice with equal-sized bubbles. The spacing factor is then half the distance between bubbles on the cube diagonal.[5]

For properly air-entrained concrete, the Powers spacing factor will probably be between about 0.004 in and 0.008 in (100–200 µm), The frost durability improves greatly when the spacing factor falls to about 0.01 in (250 µm). Figure 6 is based on the results of Backstrom.[58]

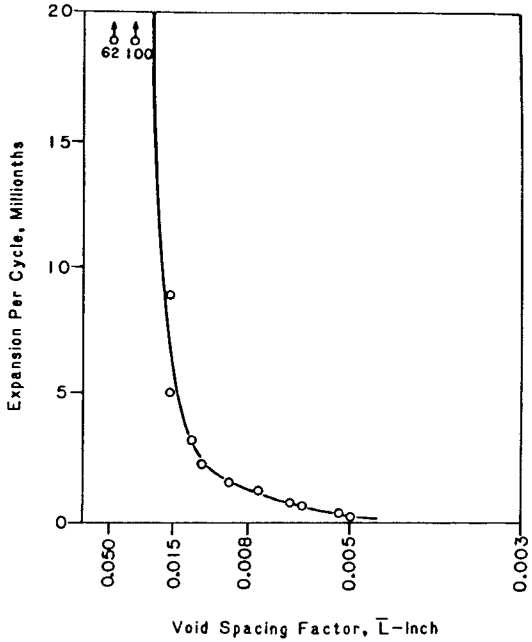

Figure 6. Influence of spacing factor on freeze thaw durability of concrete.

The spacing factor depends on the paste content, which can be determined by either microscopical method. It can also be calculated from the concrete's proportions, if known, and for some purposes, an assumed value, say 0.25, can be used with sufficient accuracy to decide if is $\bar{L}$ is adequate or not.

The bubbles in air-entrained concrete are not all the same size. There is a distribution of sizes, and therefore of chord intercept lengths. Many different size distributions could have the same specific surface. The Powers spacing factor does not take these differences into account. Some time ago it was shown[59] that the distribution of bubble sizes could be obtained from the distribution of chord intercept lengths. The only problem is that obtaining the requisite data is a most tedious task. There is hope that image analyzers can make the whole process virtually automatic.

Philleo considered the consequences of the distribution of bubble sizes and developed the so-called "protected paste volume" concept.[60] In this development, the air content and the bubble concentration, i.e., the number per unit volume of paste, are related quantitatively to the fraction of the paste that is within a certain distance from a bubble. If this distance is equal to the critical distance, then that fraction of paste will be protected from frost damage.

The distance from air bubbles within which ninety percent of the paste lies is called the *Philleo (spacing) factor,* and has been advocated as a better indicator of the adequacy of air entrainment than the Powers spacing factor.[61] The Philleo factor is about two thirds of the Powers spacing factor, for the same concrete. There has been only a little application of this concept. At present, most workers seem satisfied that the Powers spacing factor is a reasonable determinator of whether the concrete is protected or not.

6.6 Spacing Factor for Durable Concrete

The general consensus is that the Powers spacing factor must be less than 0.008 in (200 μm) if concrete is to be durable in freezing-and-thawing exposure. This value was developed and confirmed for ordinary concrete, that with a comparatively high water-cement ratio and, therefore, a paste porosity capable of containing readily freezable water.

If the nature of the concrete or its exposure is not usual, the required spacing factor may be different. If the freezing rate is low, as is typical of mild exposure, larger spacing factors have been shown to be adequate,[62] a confirmation of the hydraulic-pressure theory. The converse seems also to be true.[63] Critical spacing factors were found to be lower for protection during the salt-scaling test than for the standard freeze-thaw test.[64]

If the spacing factor is sufficiently small, the concrete will be completely immune to frost damage, including the effects of salting. The only exception seems to be those instances in which the concrete is under a head of water for a long time, such as in some locks for instance. The air bubbles can then become full of water and unable to fulfill their mission as escape places. If such a concrete freezes, the damage would probably be extensive.

In recent years there has sometimes been the feeling that the air-entrainment process is not as effective as it once was. Deteriorated concrete has been observed that did not have the air content or spacing factor that it "should" have had. These feelings led to an ACI discussion symposium entitled "Where Have All the Bubbles Gone?"[65] Many possibilities were considered, e.g., the increasing alkali contents of cements, but no firm conclusions were reached, so the problem, if there really is one, is not yet solved.

The need for properly entrained air to protect concrete from frost damage is sometimes questioned by those who point to the undeniable fact that some concrete, made before the advent of air entrainment, is still in service and has been durable for a long time. Surely, such concrete was proportioned properly, with a low water content and a sufficient cement factor. It was placed and finished properly, and it was cured well. Such a concrete will be dense and impermeable, and it may well be remarkably resistant to frost damage, but it is always potentially nondurable. What is forgotten by the detractors of air entrainment is that an enormous amount of poorer quality non-air-entrained concrete has long ago been replaced or covered up.

6.7 Influence of Type of Agent on Bubble System

The chemical nature of the air-entraining agent, its molecular structure, influences the bubble system that is obtained in the concrete. The details of this influence are not known, and there is no way to predict the air bubble parameters in concrete from chain length of the nonpolar tail, nature of the polar head, molecular geometry, solubility of the calcium salt, etc. Some work with pastes[18] has shown the anionic surfactants to be superior to the cationic or nonionic types. Dodson[66] shows similar results for concrete. Backstrom[58] shows bubble size distribution curves for concrete that indicate the nonionic agent used gave a comparatively poor bubble system. Many commercial agents, owing to their molecular complexity, can probably never be understood from this point of view.

Superplasticizers constitute a special case. By themselves, superplasticizers are not good air-entraining agents. When, however, they are used along with ordinary air-entraining agents, they influence the bubble system in the concrete in ways that are not yet clear and that depend on the chemical nature of all substances involved—the superplasticizer, the air-entraining agent, and the cement.

Most work has shown that the result of using superplasticizers in air-entrained concrete is to increase the spacing factor of the bubble system. Pigeon and his co-workers did exhaustive studies.[67]-[69] Others found similar results.[70][71] The change was also found in flowing concrete.[72]

Eriksen and Andersen[73] used a foam stability test to show that combinations of superplasticizers and air-entraining agents which produced a foam that decayed quickly gave poor bubble systems with large spacing factors, and vice versa.

Even though the use of superplasticizers seems frequently to cause a higher spacing factor, many workers[71][74]-[76] have found the concrete so produced to be durable to freezing and thawing. Others, however, have found such concrete to be nondurable.[77]

High durability of concrete with a comparatively large spacing factor may be explained by the increase in critical spacing factor found when the water-cement ratio is decreased.[78][79] This finding is in some contradiction to the hydraulic pressure hypothesis, since the critical distance is proportional to both the permeability and the strength of the paste, and a change in the water-cement ratio causes a greater change in the permeability than it does in the strength.

6.8 Other Approaches to Frost Durability

Means other than air entrainment have been advocated to increase the frost durability of concrete. The use of very low water-cement ratios in the production of high-strength concrete has already been discussed.

Another procedure is the inclusion in the concrete of a portion of finely-divided porous solid.[80] Commercial bricks, diatomaceous earth, and sintered fly ash, all ground to smaller than 1 mm in size, were used to increase the durability of pastes and concretes, without the corresponding strength reduction that results from air entrainment. Presumably, the pores in the added particles acted in much the same way as entrained air bubbles.

6.9 Effects on Mechanical Properties

Strength. The reduction in strength of concrete that is a consequence of air entrainment is its most serious drawback. The usual "rule of thumb" is that each percent of air will reduce the strength by about five percent. This is only an approximation, useful at the usual air contents. Popovics[81] has analyzed a large group of data and given equations that show the combined effect of both the air content and water-cement ratio on concrete strength. The flexural strength seems to be reduced to about the same degree as the compressive strength.

Modulus of Elasticity. The Young's modulus of air-entrained concrete is reduced to about the same degree as the compressive strength. That is, the usual relationship between strength and modulus is not altered by the presence of entrained air.

Shrinkage and Creep. Air entrainment seems not to influence either creep or shrinkage to a large extent. Some studies have shown larger creep with air-entrained concrete, but the reasons are confused with the changes in mix design brought about by air entrainment. Neville[82] concluded that air entrainment is not important to the creep of concrete.

6.10 Effects on Permeability

The term *permeability* refers to the resistance of a porous body to the flow of a fluid that saturates its pores, but sometimes the term is incorrectly used to refer to the amount of liquid taken up by capillary suction, which is the *absorption,* or the rate at which this capillary absorption occurs, which is the *sorptivity.*[83]

The effects of air entrainment on these properties of concrete are due to the inclusion of the comparatively large air voids in the pore structure of the material and to the changes in mix proportions that result from air entrainment.

The flow of a fluid through a porous solid is proportional to the volume of pores and to the square of the pore size. Therefore, with no other changes considered, the inclusion of comparatively large spaces into the matrix should increase the permeability of the material. The absorption would be relatively unchanged, because the air bubbles would not cause more water to be absorbed, since they do not fill by capillarity owing to their large size and the consequent small capillary potential.

Air entrainment results in proportioning changes, as discussed in Sec. 5.3. The decrease in mix water results in a smaller volume of paste, but more importantly, it results in a decrease in the water to cement ratio. Since the permeability of paste is greatly decreased with the lower the w/c ratio,[40] this is the determining factor. Therefore, both the permeability and the rate of capillary absorption are smaller for air-entrained concrete than for non-air-entrained concrete.

6.11 Effects on Chemical Durability

Air entrainment improves the resistance of concrete to deterioration by sulfate attack.[84][85] The effect seems to be directly related to the decrease in water-cement ratio that is obtained and, thereby, to the decreased permeability and ingress of attacking solutions.

The effects of air entrainment on the susceptibility of concrete to alkali silica reaction have not specifically been tested. Vivian[86] showed that even though extensive reaction occurs, mortars with a comparatively large amount of void space do not expand. McCoy and Caldwell[87] found air-entraining agents to be among the additives that reduce the expansion of mortar bars. The void space seems to limit expansive stresses in some way, perhaps by providing space for the accumulation of reaction products, since in affected concretes they are sometimes found there.

7.0 CODES AND PRACTICES

7.1 American Society for Testing and Materials

The ASTM specification for air-entraining admixtures is C 260.[9] The standard specifies uniformity from sample to sample and performance in terms of the behavior of the admixture under test compared with that of a reference admixture, neutralized vinsol resin. The properties compared are bleeding, set time, compressive and flexural strengths, resistance to freezing and thawing, and shrinkage. Uniformity from sample to sample is specified in terms of pH, specific gravity, and air-entraining ability with a standard mortar. ASTM Standard C 233 is the description of the foregoing test methods. The specification for air-entraining portland cements is C 150 and that for air-entraining blended cements is C 595.

7.2 British Standards Institution

The British specification for air-entraining admixtures is BS 5075: Part 2. This specification requires uniformity from sample to sample in terms of solids content, ash content, specific gravity, and chloride content.

The properties imparted to a concrete by the admixture are compared with those of a reference concrete, without admixture. The tests are for air content of the plastic concrete, density of the hardened concrete, and compressive strength. The resistance to freezing and thawing is in terms of a maximum expansion of 0.050 percent after 50 cycles.

7.3 National Standard of Canada

The Canadian specification for air-entraining admixtures is CAN3-A266.1-M78. In addition to uniformity requirements similar to those discussed above and performance requirements for initial set, compressive strength, and relative durability factor, there is an optional requirement of a maximum spacing factor of 200 µm that the purchaser can specify instead of the durability factor.

8.0 ADMIXTURE ESTIMATION AND ANALYSIS

8.1 Analysis of Admixtures

The determinations usually performed on the admixture as supplied are specific gravity, pH, solids content, and sometimes chloride and ash contents. These tests are performed in the usual way by standard methods.

Other types of examinations mentioned in C 260 are ultraviolet and infrared spectroscopy, when it is desired to investigate uniformity or molecular composition more thoroughly.

If it is desired to determine the nature of the surfactants present, procedures are available.[88] Most air-entraining admixtures, however, are mixtures of complex substances, and the problems of separation and identification of components are formidable. It should be remembered also that proprietary formulations are changed on occasion, and sometimes without a change of brand name.

8.2 Detection and Determination of Admixtures in Hardened Concrete

The determination of the amount of an air-entraining admixture in hardened concrete is a difficult and seldom-performed task. It is called for when a microscopical determination shows the air system to be deficient (or absent) and it is questioned if the agent really was added to the concrete, or when low strength is traced to high air content and the question of overdosage is raised.

Air-entraining agents are used in extremely small quantities, in the neighborhood of 30 ppm, based on the concrete, and they are complex substances, therefore their accurate determination is a difficult analytical problem. In general, the methods that have been used are instrumental. Exceptions are components that can be uniquely identified with the admixture. Examples are chloride, which can be determined accurately by argentimetric methods, and nitrogen by means of the Nessler procedure.

Instrumental methods are based on the extraction of the admixture from the concrete, followed by some procedure, frequently spectrophotometric, for its identification or quantitative determination. Procedures for admixtures in general are given by Rixom and Mailvaganam,[6] Hime,[89] and Figg and Bowden.[90]

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Abbreviations

ACI = American Concrete Institute

ASTM = American Society for Testing and Materials

HRB = Highway Research Board

PCA = Portland Cement Association

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9

Polymer-Modified Mortars and Concretes

Yoshihiko Ohama and V. S. Ramachandran

1.0 INTRODUCTION

In spite of their extensive use, cement mortar and concrete possess some disadvantages such as delayed hardening, low tensile strength, large drying shrinkage, low bonding strength in repair applications, and low chemical resistance.

Some of these disadvantages can be overcome by the use of polymer modified cement, mortar or concrete. The polymers used include latexes, redispersible polymer powders, water soluble polymers, liquid resins, and monomers. The polymer-modified mortar and concrete have a monolithic co-matrix in which the organic polymer matrix and the cement gel matrix are homogenized. In the systems modified with the latexes, redispersible polymer powders and water-soluble polymers, film or membrane formation occurs. In the systems modified with the liquid resins and monomers, water induces the hydration of the cement and the polymerization of the liquid resins or monomers.

The concept of a polymer-hydraulic cement system is not new, and in 1923 a patent of the system was filed by Cresson.[1] This patent refers to natural rubber latexes, containing cement. The patent on the polymer latex-modified systems was filed by Lefebure[2] in 1924. Throughout the 1920s and 1930s, the polymer-modified mortar and concrete using natural rubber latexes were developed.

In the 1940s, some patents on the polymer-modified systems with the synthetic latexes such as chloroprene rubber (Neoprene) latexes[3] and polyacrylic ester latexes[4] were published. Also, polyvinyl acetate-modified mortar and concrete were actively developed for practical applications. Since the late 1940s, the polymer-modified mortar and concrete have been used in various applications. In 1953, Geist et al.[5] reported a detailed study on the polyvinyl acetate-modified mortar.

In the 1960s, styrene-butadiene rubber-[6], polyacrylic ester-[7] and poly(vinylidene chloride-vinyl chloride)-[8] modified mortars and concretes became increasingly used in practical applications. Since the 1960s, the development of polymer-modified mortar and concrete have advanced significantly in various countries, particularly USA, Russia, West Germany, Japan and U.K. Important references on polymer concrete are as follows:

1. Patents by E I. du Pont de Nemours and Co.,[9] The Master Mechanics Co.,[10] American Cyanamide Co.,[11] Dow Chemical Co.[12] and Onoda Cement Co.[13]
2. Books written by Yu. S. Cherkinskii,[14] Namiki and Ohama,[15] Solomatov,[16] Satalkin, et al.,[17] Paturoev,[18] Wilson and Crisp,[19] ACI Committee 548,[20] Ohama,[21] Schron[22] and Ramakrishnan.[23]
3. Papers by Wagner,[24]-[27] Petri,[28] Mori, Kawano, Ohama, et al.,[29] and Ohama.[30]-[33]
4. Papers presented at main congresses and conferences on polymers in concrete listed in Table 1.

Nutt[34][35] developed a system modified with an unsaturated polyester resin, in the late 1960s. The system, called "Estercrete," is available commercially. In 1971, Dikeou, Steinberg, et al.,[36] also studied other systems. Donnelly[37] and Duff[38] patented systems based on epoxy resins in 1965 and 1973 respectively. In 1959, a system modified with urethane prepolymer was patented.[39] Chapter 17 deals with patents pertaining to polymer modified systems.

Methyl cellulose is very popular as a water-soluble polymer and used as a cement modifier, and has been widely used in the field of adhesive polymer-modified mortars for ceramic tiles (polymer content < 1%) since the early 1960s.[40] Shibazaki[41] showed that other polymers, such as hydroxyethyl cellulose and polyvinyl alcohol (poval) are effective for the water-soluble polymer-modified mortars. In 1974, a review of the polymer-modified systems was written by Riley and Razl.[42]

Considerable research and development of polymer-modified mortar and concrete were conducted in the world in the last 25 years and modified mortar or concrete has become the dominant material in the construction industry. Table 1 gives the list of major International Conferences held on polymer concretes in the years 1984–1993.

Table 1. Major International Congresses and Symposia on Polymers in Concrete

Year	Venue	Congress or Symposium
1984	Liege, Belgium	International Symposium, Future for Plastics in Building and in Civil Engineering
1984	Darmstadt, West Germany	Fourth International Congress on Polymers in Concrete
1986	Prague, Czechoslovakia	International Symposium, Mechanics of Polymer Composites
1986	Aix-en-Provence, France	RILEM International Symposium, Adhesion between Polymers and Concrete
1987	Brighton, U.K	Fifth International Congress on Polymers in Concrete
1990	Shanghai, China	Sixth International Congress on Polymers in Concrete
1991	Bochum, Germany	International Symposium on Concrete-Polymer Composites
1991	San Francisco, California, U.S.A.	ACI-ICPIC North American Workshop on Polymers in Concrete
1992	Johannesburg, South Africa	Second South African Conference on Polymers in Concrete
1992	Moscow, Russia	Seventh International Congress on Polymers in Concrete
1993	Salvador, Brazil	ICPIC/IBRACON Workshop on Polymers in Concrete

2.0 APPLICATIONS

Of the polymer-modified mortar and concrete, latex-modified mortar and concrete possess superior properties, such as high tensile and flexural strengths, excellent adhesion, high waterproofness, high abrasion resistance, and good chemical resistance, to those of ordinary cement mortar and concrete. The latex-modified mortar is more widely used than the latex-modified concrete. Typical applications of the latex-modified mortar and concrete are listed in Table 2. Recently, redispersible polymer powder-modified mortar is being increasingly used.

Table 2. Typical Applications of Latex-Modified Mortar

Application	Location of Work
Floorings and Pavements	Floors for houses, warehouses, schools, hospitals, offices, shops, toilets, gymnasiums and factories, passages, stairs, garages, railway platforms, roads, airport runways, monorails, etc.
Integral Waterproofings and Liquid-Applied Membrane Waterproofings	Concrete roofdecks, mortar walls, concrete block walls, water tanks, swimming pools, septic tanks, silos, etc.
Adhesives	Tile adhesives, adhesives for floorings, walling materials and heat-insulating materials, adhesives for joining new cement concrete or mortar to old cement concrete or mortar, etc.
Decorative Coatings (including surface-preparing materials)	Wall coatings, lightweight aggregate coating materials, cement filling compounds and self-levelling cements for surface preparations, etc.
Repair Materials	Grouts for repairing cracks and delaminations of concrete structures, patching materials for damaged concrete structures, rustproof coatings for corroded reinforcing bars, etc.
Anticorrosive Linings	Effluent drains, chemical or machinery plant floors, grouts for acid-proof tiles, floors for chemical laboratories and pharmaceuticals warehouses, septic tanks, hot spring baths, rustproof coatings for steel roof decks and soils, etc.
Deck Coverings	Internal and external ship-decks, bridge decks, footbridge decks, train floors, etc.

Although more expensive than latex-modified mortar and concrete, liquid resin-modified mortar and concrete appears to be getting increased acceptance in the construction industry. They have more rapid hardening, higher thermal stability, and better water resistance characteristics over the latex-modified systems. Epoxy-modified systems are beginning to gain popularity and other liquid resin-modified mortar and concrete may need experience at the site before widespread application.

Modification of cement mortar and concrete with small amounts of water-soluble polymers such as cellulose derivatives and polyvinyl alcohol is used for improving workability. The water-soluble polymers are mixed with the mortar and concrete as powders or aqueous solutions.

In Japan, polymer-modified mortar is widely used as a construction material for finishing and repairs, but polymer-modified concrete is seldom employed because it is not economical. However, the polymer-modified concrete is widely used for bridge deck overlays and patching work in U.S. In particular, it is estimated that each year over 1.2 million m^2 of bridge decks are overlaid with the polymer-modified concrete.[43] It is estimated that about 60,300 m^3 of polymer-modified concrete is placed each year on both new and existing deteriorated concrete structures in the U.S.[44] Table 3 lists recent projects that have used SBR-modified concretes as overlays on bridge decks in U.S.[45] In U.K., about £500 millions are spent each year on the repair of the concrete structures.[46] Thus the polymer-modified mortars and concretes have become promising materials for preventing chloride-induced corrosion and repairing damaged reinforced concrete structures.

3.0 GENERAL PRINCIPLES

Polymer-modified mortar and concrete are prepared by mixing either a polymer or monomer in a dispersed, powdery or liquid form with fresh cement mortar and concrete mixtures, and subsequently cured, and if necessary, the monomer contained in the mortar or concrete is polymerized in-situ. The polymers and monomers used as cement modifiers are shown in Fig. 1.

Several types of the polymer-modified mortars and concretes, i.e., latex -redispersible polymer powder-, water-soluble polymer-, liquid resin- and monomer-modified mortars and concretes are produced by using the polymers and monomer. Of these the latex-modified mortar and concrete are by far the most widely used cement modifiers.

Table 3. Some Bridge Deck Overlay Projects Using SBR-Modified Concretes in the U.S.

Year Overlay Installed	Project	Location
1982-1988	Delaware Memorial Bridge I-295 over Delaware River	Wilmington, Del.
1984	Newburgh-Beacon Bridge I-84 over the Hudson River	New York
1985	Reedy Point Bridge over Chesapeake-Delaware Canal	Delaware
1982	Columbia River Bridge	Portland, Ore.
1983	Marquham Street Bridge	Portland, Ore.
1983	Wicasset Bridge	Wicasset, Me.
1980	Denny Creek Bridge	Snoqualmie Falls, Wash.
1980	Sandusky Bay Bridge	Sandusky, Ohio
1978	O'Hare Departure Ramp	Chicago, Ill.
1987	Chesapeake Bay Bridge	Maryland

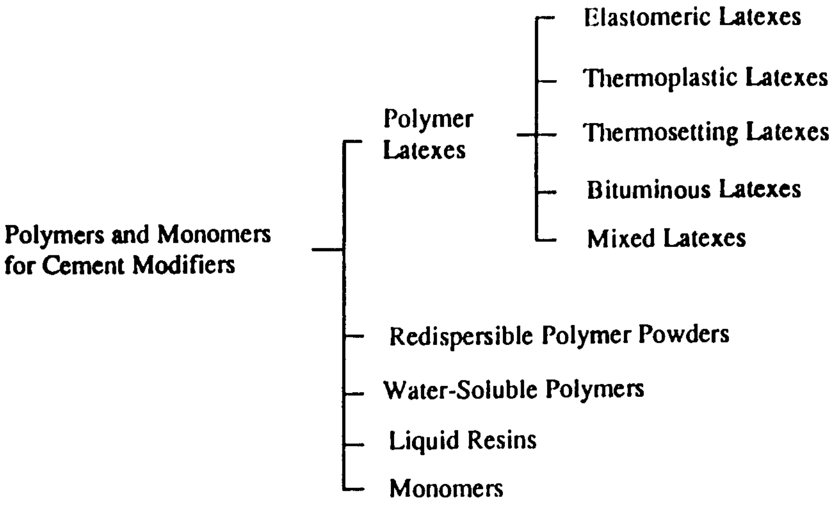


Figure 1. Polymers and monomers for cement modifiers.

Although polymers and monomers in any form such as latexes, water-soluble polymers, liquid resins, and monomers are used in mortar and concrete, it is very important that both cement hydration and polymer phase formation (coalescence of polymer particles and the polymerization of monomers) proceed well to yield a monolithic matrix phase with a network structure in which the hydrated cement phase and polymer phase interpenetrate into each other. In the polymer-modified mortar and concrete structures, aggregates are bound by such a co-matrix phase. The superior properties of the polymer-modified mortar and concrete to conventional mortar and concrete are characterized by such a distinct structure.

3.1 Latex Modification

Latex modification of cement mortar and concrete is governed by both cement hydration and polymer film formation processes in their binder phase. The cement hydration process generally precedes the polymer formation process.[24] In due course, a co-matrix phase is formed by both cement and polymer film formation processes.

Mechanism of Polymer-Cement Co-matrix Formation. It is believed that a co-matrix phase, which consists of cement gel and polymer films, is generally formed as a binder according to a three-step simplified model shown in Fig. 2.[47] Grosskurth has proposed a similar model involving the formation of the polymer-cement co-matrix.[48] Sugita et al.[49] have recently investigated the microstructures and composite mechanism of latex-modified pastes and mortars, and observed the interfacial layer of cement hydrates with a large amount of polymer particles on the aggregates and cement particles. Thus both the particle dispersion of the polymer and the formation of polymer films are necessary for the composite mechanism of the latex-modified systems.

The process of the polymer film formation on the cement hydrates is represented in Fig. 3.[47]

In the first step, when polymer latexes are mixed with fresh cement mortar or concrete, the polymer particles are uniformly dispersed in the cement paste phase.

In the second step, with drainage due to the development of the cement gel structure, the polymer particles are gradually confined in the capillary pores. Ohama presented a mechanism which involves interaction between the polymer and carboxylate group[50] (Fig. 4). The effects of the chemical bonds are apt to be offset by increasing entraining air as discussed later.

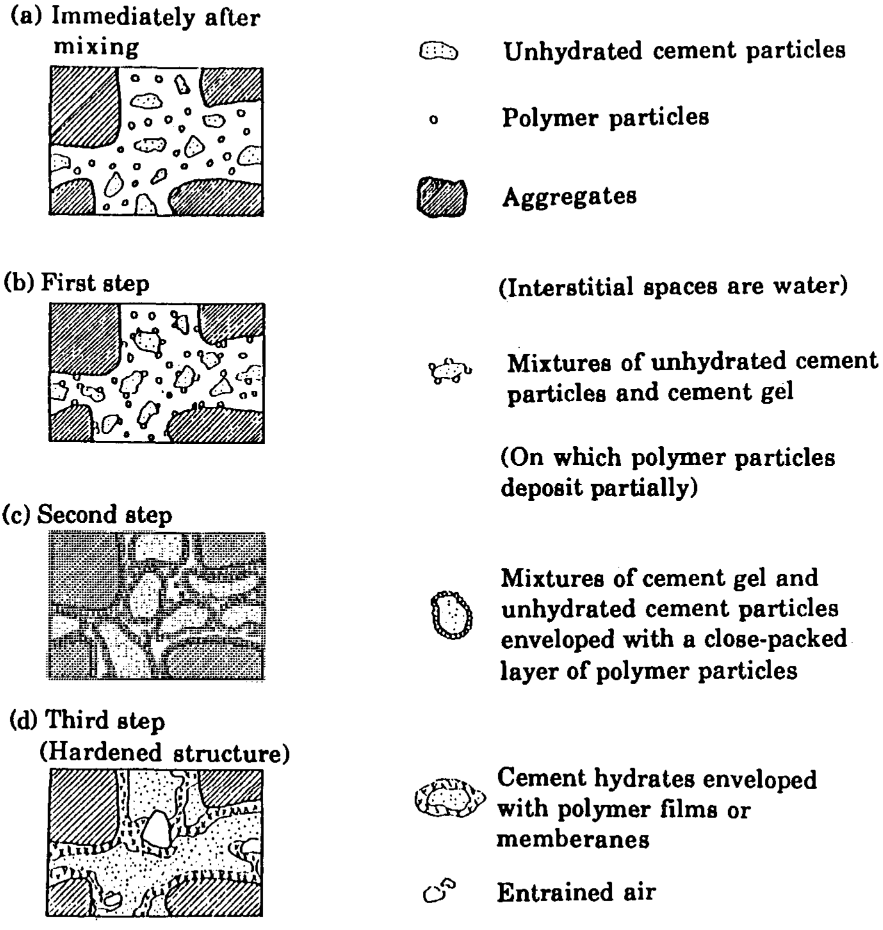


Figure 2. Simplified model of formation of polymer-cement co-matrix.

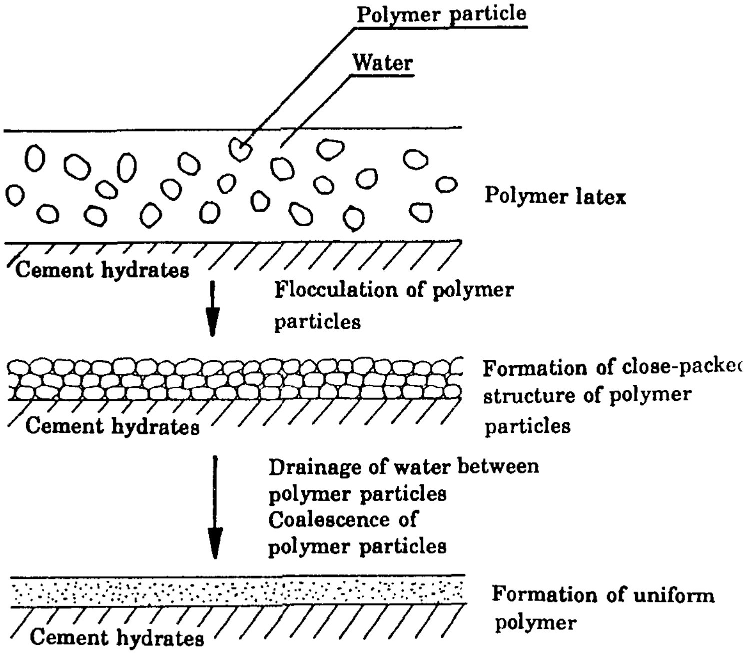


Figure 3. Simplified model of process of polymer film formation on cement hydrates.

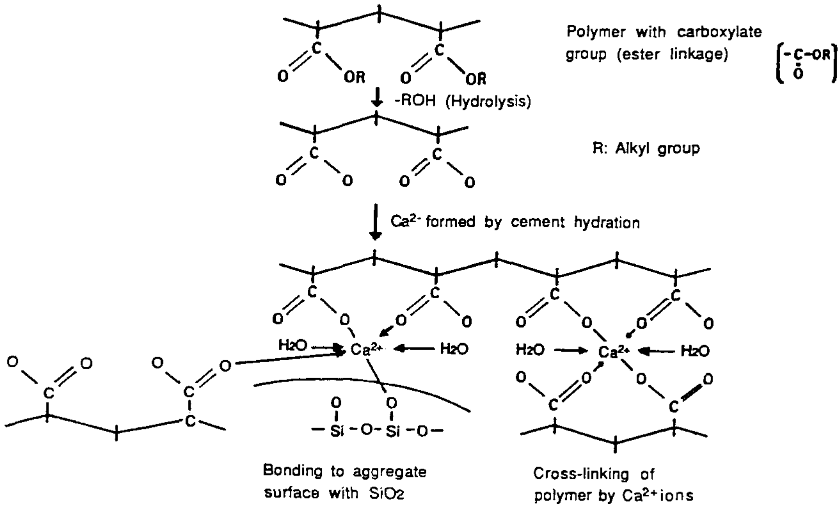


Figure 4. Schematic illustration of reaction between polymer with carboxylate group (ester linkage), ordinary portland cement and aggregate.

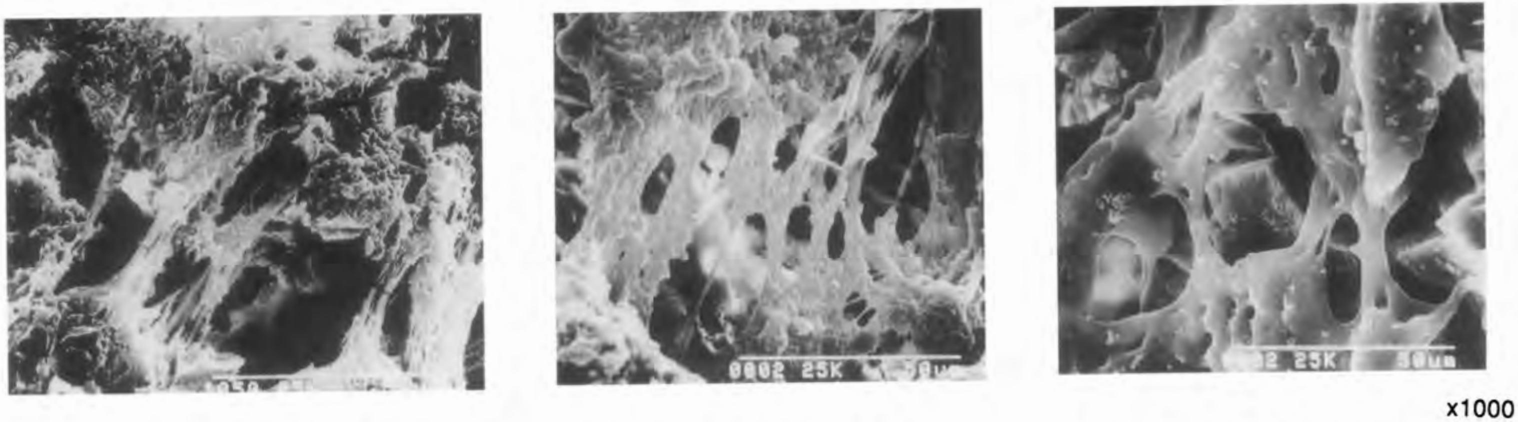
Ultimately, with water withdrawal by cement hydration, the close-packed polymer particles on the cement hydrates coalesce into continuous films or membranes, and the films or membranes bind the cement hydrates together to form a monolithic network in which the polymer phase interpenetrates throughout the cement hydrate phase. Such a structure acts as a matrix phase for latex-modified mortar and concrete, and the aggregates are bound by the matrix phase to the hardened mortar and concrete.

Physical and Mechanical Properties. The hardened cement paste is an agglomerated structure of calcium silicate hydrates and calcium hydroxide bound together by the weaker van der Waals forces, and therefore, microcracks occur easily in the paste under stress. This leads to poor tensile strength and fracture toughness of ordinary cement mortar and concrete. By contrast, in the latex-modified mortar and concrete, it appears that the microcracks are bridged by the polymer films or membranes which prevent crack propagation, and simultaneously a strong cement hydrate-aggregate bond is developed. This aspect is evident in the scanning micrographs of cross-sections of SBR-and PAE-modified mortars, as shown in Fig. 5.

Such an effect increases with an increase in the polymer content or polymer-cement ratio (defined as the weight ratio of the amount of total solids in a polymer latex to the amount of cement in a latex-modified mortar or concrete), and leads to increase tensile strength and fracture toughness. However, excess air entrainment and polymer inclusion cause discontinuities of the formed monolithic network structure, whose strength is reduced although some chemical reactions proceed effectively, as shown Fig. 4. The sealing effect and porosity due to the polymer films or membranes formed in the structure also provide a considerable increase in waterproofness or watertightness, resistance to chloride ion penetration, moisture transmission, carbonation and oxygen diffusion, chemical resistance, and freeze-thaw durability. Such an effect is promoted with increasing polymer-cement ratio.

3.2 Redispersible Polymer Powders

The principle of modification of cement mortar and concrete with redispersible polymer powders is almost the same as that of latex modification, except that it involves the addition of redispersible polymer powders. Mostly the redispersible polymer powders are used by dry mixing with the cement and aggregate premixtures, followed by wet mixing them with water. During the wet mixing, the redispersible polymer powders are re-emulsified in the modified mortar and concrete, and behave in the same manner as the latexes for cement modifiers.



Polymer Film in SBR-Modified Mortar

Polymer Film in EVA-Modified Mortar

Polymer Film in PAE-Modified Mortar

Figure 5. Electron micrographs of latex-modified mortars.

3.3 Water Soluble Polymers

In the modification with water-soluble polymers such as cellulose derivatives and polyvinyl alcohol, small amounts of the polymers are added as powders or aqueous solutions to cement mortar and concrete during mixing. Such a modification mainly improves their workability and prevents the *dry-out* phenomena. The prevention of the dry-out is interpreted in terms of an increase in the viscosity of the water phase in the modified cement mortar and concrete, and a sealing effect due to the formation of very thin and water-impervious film in them. In general, the water-soluble polymers hardly contribute to an improvement in the strength of the modified systems.

3.4 Liquid Resins

In this system, considerable amounts of polymerizable low molecular weight polymers or prepolymers are added in a liquid form to cement mortar and concrete during mixing. The polymer content of the modified binder generally is higher than that of the latex-modified systems. In this modification, polymerization is initiated in the presence of water to form a polymer phase and, simultaneously, the cement hydration occurs. As a result, a co-matrix phase is formed with a network structure of interpenetrating polymer and cement hydration phases, that binds aggregates. Consequently, the strength and other properties of the modified mortar or concrete are improved in much the same way as those of the latex-modified systems.

3.5 Monomers

The principle of cement composites with monomers is about the same as that of liquid resin modification except that it involves the addition of monomers instead of the liquid resins. In such a modification, considerable amounts of the monomers are mixed with the cement mortar and concrete, and both polymerization and cement hydration occur at the same time during or after curing to make a monolithic matrix, which binds aggregates. Generally, such a modification has not been successful because of the poor properties of the modified systems. Interference with the cement hydration, degradation of the monomers by the alkalis from the cement, and difficulty in uniformly dispersing the monomers and other components during mixing are some of the reasons for the poor performance.

4.0 LATEX-MODIFIED SYSTEMS

The process technology of the latex-modified mortar and concrete is similar to that of the conventional binding systems. Most polymers such as latexes are in a dispersed form, and are added to the cement mortar or concrete during the mixing. The polymers are used in larger amounts than when air-entraining agents or water-reducing admixtures are incorporated in these systems. The latex-modified mortar or concrete, with proper mix proportions, are mixed and placed similar to normal concreting and cured under the optimum conditions.

4.1 Materials

The materials used in latex-modified systems are the same as those employed in normal mortar and concreting operations.

Cements. Ordinary portland cement is widely used for latex-modified mortar or concrete. According to their applications, other portland cements such as high early strength portland cement, moderate heat portland cement and white portland cement, blended cement, high alumina cement and ultrarapid-hardening cement are also employed. Air-entraining cement should not be used because of the air entrainment occurring due to latex addition.

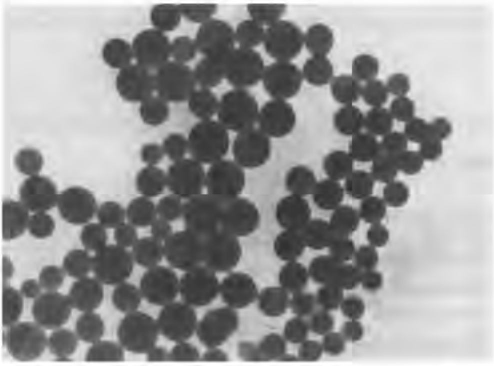
Aggregates. The usual types of aggregates used for normal concreting operations may be recommended for latex mixes. The use of aggregate with excessive water content should be avoided because the required polymer-cement ratio may not be achieved. The aggregates should be clean, sound and possess proper grading.

Polymer Latexes. Polymer latexes consisting of very small diameter particles (0.05–5 ∝cm) in water are shown in Fig 6 and they are produced by emulsion polymerization.

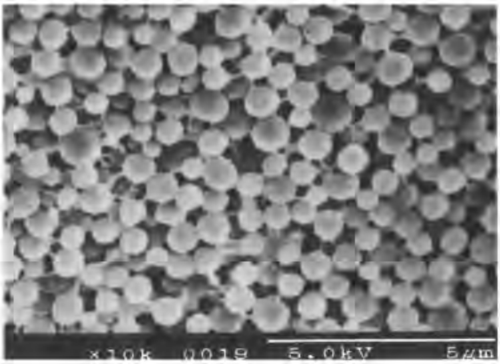
A typical formulation of the materials used for emulsion polymerization is given in Table 4.[51]

Three types of polymer latexes are distinguished: cationic, anionic and nonionic. The formulations for emulsion polymerization of typical latexes are listed in Table 5.[51]

In general, polymer latexes are copolymer systems of two or more different monomers, and their total solid content including polymers, emulsifiers, stabilizers, etc., is 40–50% by weight. Most commercially available latexes for cements are based on elastomeric and thermoplastic polymers which form continuous polymers when dried. The polymer latexes that are underlined in Fig. 7 are those that are in general use today. Table 6 gives the chemical structures of the main polymer types. Of these, polyvinyl acetate latex and poly (vinylidene chloride-vinyl chloride) latex are generally not recommended as cement modifiers because of poor resistance and chloride ion liberation. Table 7 provides typical properties of polymer latexes.



SBR Latex x30000
(Courtesy of the Japan Synthetic Rubber Co., Ltd.)



EVA Latex x10000
(Courtesy of the Hoechst Gosei Co., Ltd.)

Figure 6. SBR and EVA latexes for cement modifiers.

Table 4. Typical Recipe of Materials for Emulsion Polymerization

Material	Parts by Weight
Monomers	100.0
Surfactant	1.0-10.0
Initiator	0.1-2.0
Water	80.0-150.0
Other Ingredients	0-10.0

Table 5. Formulations for Emulsion Polymerization of Typical Polymer Latexes as Cement Modifiers

Type of Latex	Material	Parts by Weight
Vinyl Acetate, Homo- and Copolymer Latexes	Vinyl Acetate	70.0-100.0
	Comonomer (butyl acrylate, ethylene, vinyl ester of versatic acid)	0.0-30.0
	Partially Hydrolyzed Polyvinyl Alcohol	6.0
	Sodium Bicarbonate	0.3
	Hydrogen Peroxide (35%)	0.7
	Sodium Formaldehyde Sulfoxylate	0.5
	Water	80.0
Acrylic Copolymer Latex	Ethyl Acrylate	98.0
	A Vinyl Carboxylic Acid	2.0
	Nonionic Surfactant	6.0[a]
	Anionic Surfactant	0.3[b]
	Sodium Formaldehyde Sulfoxylate	0.1
	Caustic Soda	0.2
	Peroxide	0.1
	Water	100.0
Styrene-Butadiene Copolymer Latex	Styrene	64.0
	Butadiene	35.0
	A Vinyl Carboxylic Acid	1.0
	Nonionic Surfactant	7.0[a]
	Anionic Surfactant	0.1[b]
	Ammonium Persulfate	0.2
	Water	105.0

[a] The nonionic surfactants may be nonyl phenols reacted with 20-40 molecules of ethylene oxide.

[b] The low levels of anionic surfactant are used to control the rate of polymerization.

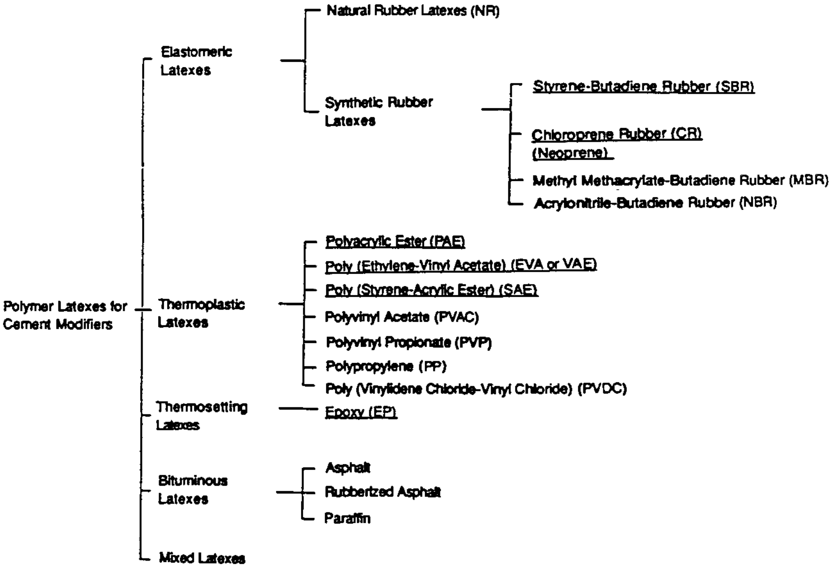


Figure 7. Commercially available polymer latexes for cement modifiers.

Table 6. Chemical Structures of Main Polymer Latexes for Cement Modifiers

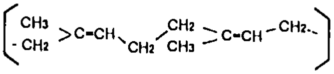
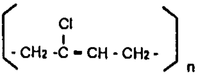
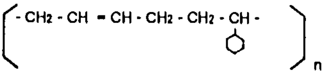
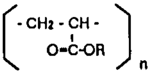
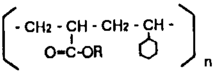
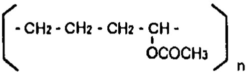
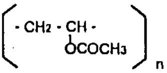
Type of Polymer Latex	Abbreviation	Chemical Structure
Natural Rubber Latex	NR	
Chloroprene Rubber Latex (Neoprene)	CR	 $\left(-CH_2-\overset{Cl}{C}=CH-CH_2-\right)_n$
Styrene-Butadiene Rubber Latex	SBR	
Polyacrylic Ester Latex	PAE	 $\left(-CH_2-\underset{O=C-OR}{CH}-\right)_n$ R : Alkyl group
Poly (Styrene -Vinyl Acrylic Ester) Latex	SAE	 R : Alkyl group
Poly (Ethylene-Vinyl Acetate) Latex	EVA or VAE	 $\left(-CH_2-CH_2-CH_2-\underset{OCOCH_3}{CH}-\right)_n$
Polyvinyl Acetate Latex	PVAC	 $\left(-CH_2-\underset{OCOCH_3}{CH}-\right)_n$

Table 7. Typical Properties of Commercially Available Polymer Latexes

Type of Polymer	Brand Name	Stabilizer Type	Appearance	Particle Size (ηm)	Total Solids (%)	Specific Gravity (20°C)	pH (20°C)	Viscosity (20°C, cP)	Surface Tension (20°C, dyn/cm)
SBR	Asahi Chemical Industry Latex DL-460	Nonion	Milky-White	200	46.5-49.5	1.010	10.0-11.0	10-12	32
	JSR Tommaku Super	Anion	Milky-White	219	44.0-46.0	1.016	7.06	53	31
PAE	Primal M-30	Nonion	Milky-White	500	44.5-45.5	1.054	8.6-10.2	29	45
	Rhoplex MC-450	Nonion	Milky-White	500	44.0-46.0	1.054	9.4-10.0	1328	45
CR	Neoprene 950	Cation	Milky-White	120	50.0	1.100	9.0	16	35
	Denka Chloroprene LK-50	Cation	Milky-White	700	50.0	1.100	6.0	10	30
EVA	NS Hiflex 1000	Nonion	Milky-White	700	52.8	1.050	6.0	1100-1600	75
	Movinyl 101E	Nonion	White	400	55.0	1.060	4.5-6.5	3000-7000	40-45
	Moviton M310	Anion	Milky-White	300	50.0	1.127	5.0-7.0	5000	40

The general requirements for polymer latexes as cement modifiers are as follows:

a. Very high chemical stability towards the active cations, such as calcium and aluminum, liberated during the hydration of cement.
b. Very high mechanical stability under high shear mixing, and in metering and transfer pumps.
c. Low air entrainment due to the addition of antifoaming agents.
d. No adverse influence on cement hydration.
e. Formation of continuous films in mortar or concrete. High adhesion of the films to cement hydrates and aggregates.
f. Very good water, alkali and weatherability resistance.
g. Thermal stability

Table 8 shows the quality requirements for the polymer latexes specified in JIS 6203.

Table 8. Quality Requirements for Latexes Specified in JIS A 6203 (Polymer Dispersions for Cement Modifiers)

Kind of Test	Test Item	Requirement
Latex Test	Appearance	Exclusive of coarse particles, foreign substances and coagula
Polymer-Modified Mortar Test	Total solids	Not less than 35.0% and within ±1.0% of the value marked by the manufacturer
	Flexural strength	Not less than 40kgf/cm^2 (3.9MPa)
	Compressive strength	Not less than 100kgf/cm^2 (9.8MPa)
	Adhesion	Not less than 10kgf/cm^2(0.98MPa)
	Water absorption	Not more than 15.0%
	Amount of water permeation	Not more than 30g
	Length change	0 to 0.150%

The most widely used latexes include styrene-butadiene (SBR), polychloroprene rubber (CR), polyacrylic ester (PAE), and poly (ethylene-vinyl acetate) (EVA) copolymers. All latex systems contain proper amounts of antifoaming agents.

Other Materials. Production of colored latex mortars needs inclusion of pigments that are alkali resistant and weatherproof. They should also not interfere with the stability of latexes and hydration of cements. Alkali-resistant glass, steel, polyamide, polypropylene, polyvinyl alcohol (poval), acramide, and carbon fibers are employed as reinforcements.

4.2 Mix Proportioning

The mix design of latex-modified mortar and concrete is usually carried out in much the same way as that of ordinary mortar and concrete, depending on the workability, strength, extensibility, adhesion, waterproofness (or watertightness) and chemical resistance requirements.

Latex-modified mortar and concrete mix design should recognize its improved properties such as tensile and flexural strengths, extensibility, adhesion, and durability over conventional mortar and concrete. These properties are controlled by the polymer-cement ratio rather than the water-cement ratio. Therefore, the polymer-cement ratio should be determined to meet desirable requirements. The polymer-cement ratio is defined as the weight ratio of the amount of total solids in a polymer latex to the amount of cement in a latex-modified mortar or concrete mixture.

The mix proportions of most latex-modified mortars are in the range of the cement-fine aggregate ratio = 1:2 to 1:3 (by weight), the polymer-cement ratio of 5 to 20%, and the water-cement ratio of 30 to 60%, depending on their required workability. The standard mix proportions for the latex-modified mortars for various applications are shown in Table 9.[52]

The mix proportions of most latex-modified concretes cannot be easily determined in the same manner as those of latex-modified mortars because of many factors considered in the mix design. Normally, the polymer-cement ratio of the latex-modified concrete ranges from 5 to 15%, and the water-cement ratio from 30 to 50%. A rational mix design system has been developed for the latex-modified concrete by Ohama. Nomographs have been developed.

Table 9. Typical Applications and Standard Mix Design of Latex-Modified Mortars

Application	Location of Work		Standard Mix Proportions			Thickness of Troweling or Coating (mm)
			Cement	Sand	Latex	
			(by weight)			
Paving Materials	Floors for general houses, warehouse, office and shops, toilet floors, etc.		1	3	0.2-0.3	5-10
Floorings	Passages, stairs, chemical plants, railway platforms, roads, garages, etc.		1	3	0.3-0.5	10-15
Waterproofing Materials	Concrete roof-decks, mortar and concrete block walls, water tank, swimming pools, septic tanks, silos, etc.		1	2-3	0.3-0.5	5-20
Adhesives	Adhesives when flooring materials, walling materials, heat insulting materials etc. are bonded to concrete floors and walls.		1	0-3	0.2-0.5	-
	Jointing new concrete to old concrete and new mortar to old mortar.		1	0-1	over 0.2	-
	Repair cracks		1	0-3	over 0.2	-
Anticorrosive Linings	Effluent drains, chemical factory floors, grouting for acid-proof tiles, septic tanks, foundations for machinery plants, floors for chemical laboratories, pharmaceutical warehouses, etc.		1	2-3	0.4-0.6	10-15
Deck Coverings	Internal and external ship decks, bridge decks,	Undercoat	1	2-3	0.9-1.0	1-2
	train or car floors,	Midcoat	1	3	0.4-0.6	5-6
	foot bridge decks, etc.	Topcoat	1	3	0.5-0.6	3-4

The water-cement ratio (W/C) and unit cement content (C) of latex-modified concrete can be generally expressed as a function of the binder-void ratio (α) with every polymer type at each polymer-cement ratio by the following equations:

Eq. (1) $W/C + - m\alpha + n$

Eq. (2) $C = q\alpha + r$

where m, n, q and r are empirical constants. The examples of nomographs for estimations of W/C and C, which are drawn using the above relationships, are illustrated in Fig. 8.[53] These figures are obtained for a type of SBR-modified concrete.

An appropriate mix design system is proposed as represented in Fig. 9[54] and this involves using equations developed by Ohama.

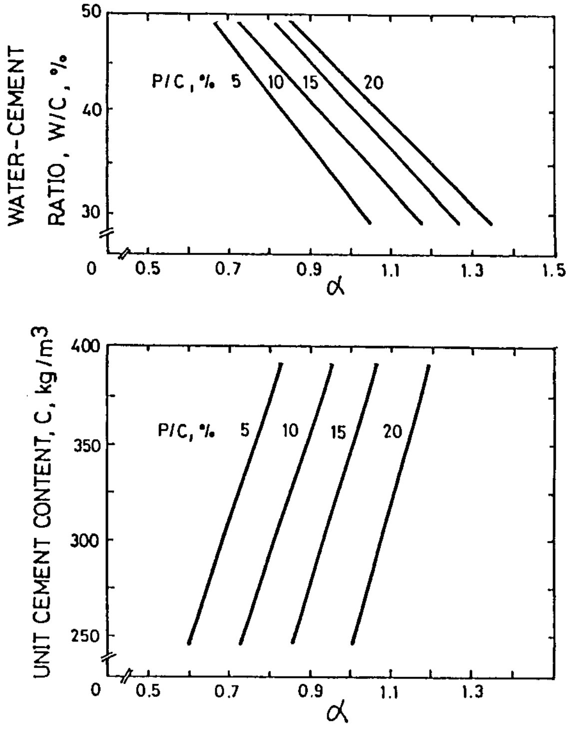


Figure 8. Nomographs for water-cement ratio and unit cement content of SBR-modified concretes.

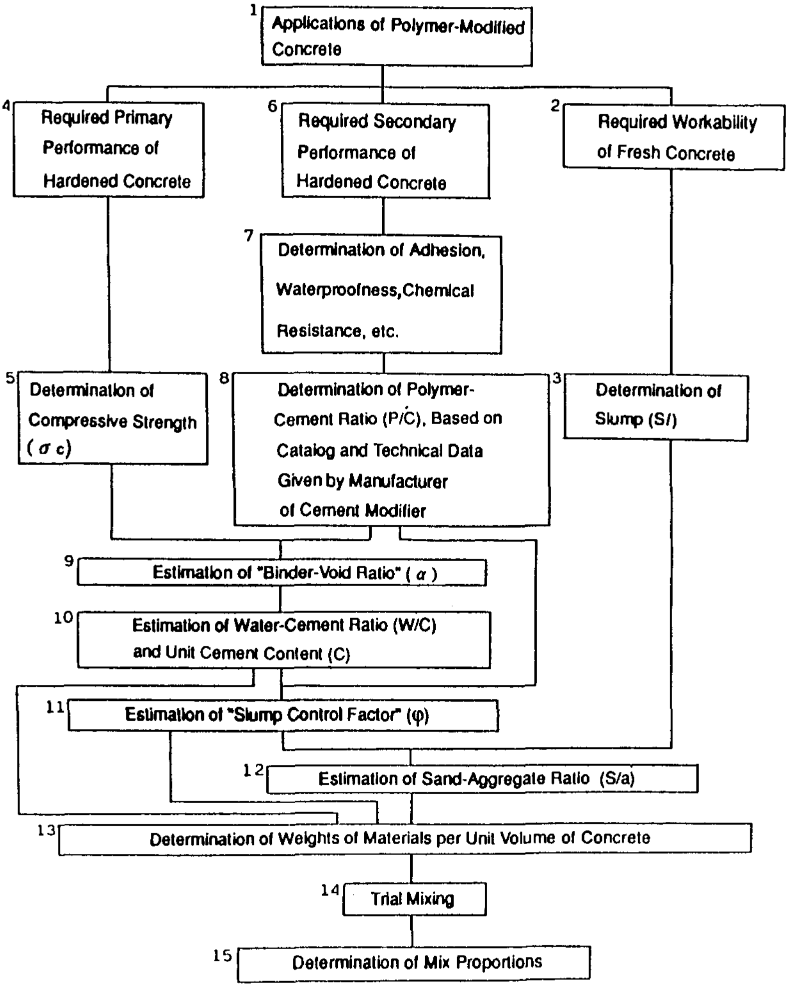


Figure 9. Chart showing mix design procedure for latex-modified concretes.

The limits of validity of these equations and nomographs are as follows:

Types of Materials Used

Types of cement: ordinary portland cement (ASTM-Type I)

Types of aggregate: river sand (size, 2.5 mm or finer) and river gravel (size, 5–20 mm); saturated, surface-dry

Type of polymer latex for cement modifier: Commercial polymer latexes irrespective of polymer types (containing antifoamers)

Range of Proportions in Practical Use

Unit cement content (C): from 250 to 400 kg/m^3

Polymer-cement ratio (P/C): from 0.05 to 0.20 (5 to 20 wt% of polymer with respect to cement)

Water-cement ratio (W/C): from 0.30 to 0.50 (30 to 50 wt% of water with respect to cement)

Sand-aggregate ratio (S/a): from 40 to 50 vol%

Slump (Sl): from 1 to 21 cm.

Compressive strength (sc): from 200 to 600 kg/cm^2

Tables 10 and 11 give the ACI (American Concrete Institute) suggested guidelines for the mix proportions of latex-modified concretes for bridge deck applications and patching work respectively.[55] Standard Specification ACI 548.4[56] provides a guideline for the mix proportions of SBR-modified concrete overlays, for new construction as well as repair and rehabilitation, of highway bridge decks as shown in Table 12.

4.3 Mixing

Latex-modified mortar and concrete are easily prepared by using all conventional mixing equipment and tools, such as mortar or concrete batch mixers and ready-mix trucks, as well by hand mixing in mortar boxes or concrete mixing vessels. Before actual mixing, trial mixing should be performed to determine the mix proportions. Polymer latexes are initially mixed with mixing water, and directly added to the cement and aggregate mixes. The speed and time of mixing should be properly selected to avoid unnecessary entrapment of air even though antifoaming agents are used. Air-entraining cannot be used because the polymer latexes entrain air.

Table 10. ACI Suggested Guidelines for Mix Proportions of Latex-Modified Concrete for Bridge Deck Applications

Bridge Deck Applications.

Unit Cement Content (kg/m^3)	700
Sand-Aggregate Ratio (%)	55:45 to 65:35
Polymer-Cement Ratio (%)	15
Water-Cement Ratio (%)	25 to 40
Air Content (%)	Less than 6

Table 11. ACI Suggested Guidelines for Mix Proportions of Latex-Modified Concrete for Patching Applications

Material		Weight (kg)
Portland Cement		94
Aggregate (blend of coarse and fine)		300
Polymer	Dry (total solids) Basis[a]	14 to 19
	Wet (liquid with 50% total solids) Basis[b]	29 to 38
Total Water (includes that in polymer and aggregate)		4 to 25

[a] For patching conventional concrete where there may not be a need for improved chemical resistane and a lower modulus, the polymer-cement ratio can be lowered to 7 to 12 %.

[b] The latex polymer should be formulated with an antifoamer prior to adding it to the mix.

Table 12. ACI Guidelines for Mix Proportions of SBR-Modified Concrete Overlays

Unit Cement Content, Minimum	390 kg/m^3
Unit SBR Latex Content, Minimum	121 kg/m^3
Unit Water Content, Maximum	94 kg/m^3
Air Content, Maximum (ASTM C 231)	6.5 %
Slump, Range	7.5 - 20.5 cm
Overlay Thickness, Minimum	2.5 cm
Coarse Aggregate Size, Maximum	No. 8
Fine Aggregate - Aggregate Ratio	55-70 wt%
Cement : Fine Aggregate : Coarse Aggregate (aggregates assumed saturated, surface dry)	1.0 : 2.8 : 1.7 (weight ratio)

4.4 Placing and Curing

After mixing, latex-modified mortar or concrete is placed and finished in almost the same manner as ordinary cement mortar and concrete. The latex-modified mortar and concrete have a shorter working time than the cement mortar and concrete. Although the working time depends on the ambient temperature, the latex-modified mortar and concrete should be placed and finished within about one hour after mixing.

Because they have an excellent adhesion to various materials, even to metals, all the equipment and tools such as mixers, trowels, and vibrators should be washed down or cleaned immediately after use. It also is advisable to use the most effective mold-release agents, e.g., silicone wax or grease.

For resurfacing, flooring and patching applications, all loose and nondurable materials, including laitance and mud on the substrates, must be removed by sandblast, wire-brushing, and blowing with compressed air. Oils, greases, and other chemicals should be removed with a detergent or solvent. The surfaces cleaned by the above operations should be thoroughly wetted immediately prior to the placement of the modified systems. After wetting, the substrates should be wiped off with rags or blown with compressed air to remove any standing water.

The choice of a latex-modified mortar or concrete depends on the thickness of the overlay or coating to be applied. Generally, the modified mortar can be recommended for thicknesses of 30 mm or less, and the modified concrete for the thickness exceeding 30 mm.

Latex-modified mortar and concrete are usually somewhat difficult to finish the surfaces by troweling compared to conventional cement mortar and concrete because of wet drag. The modified systems set, forming a surface skin which will easily tear. It is advisable to finish the surfaces by troweling two to three times. The over-troweling is not advisable for the modified systems. Because thin polymer films are formed on the trowel surfaces during troweling, the trowels should be frequently cleaned to remove such films. Retroweling after initial set is not recommended. Excessive vibration for compaction must be avoided to prevent water with polymers bleeding to the finished surfaces. In application to large areas, it is advisable to provide joints with a width of about 15 mm at intervals of 3 to 4 m.

Latex-modified mortar and concrete should never be placed at temperatures lower than 5°C and higher than 30°C. Adequate care should be taken to prevent floating the polymer solids to the finished surfaces due to wetting by water or rainfall immediately after placing. It is desirable that the surfaces are promptly covered with a wet burlap or polyethylene sheets. In their applications in cold climate areas or winter, the use of high-early-strength cement, ultrarapid-hardening cement, and high alumina cement can be recommended.

The curing under wet conditions, such as water immersion or moist curing, applicable to ordinary cement mortar and concrete, is detrimental to latex-modified mortar and concrete. Normally, the latex-modified mortar and concrete require a different curing method because of the incorporation of polymer latexes. Almost optimum properties of the modified systems are achieved by a combined wet and dry cure, i.e., moist cure for 1 to 3 days, followed by dry cure at ambient temperature. The curing of the modified systems can be accelerated by moderate heating; however, steam curing is not recommended. The effects of curing conditions on the strength of the latex-modified mortar and concrete is described in Sec. 4.

Generally, polymer latexes used as cement modifiers are not toxic, and are safe materials to handle. Consequently, they require no special precautions.

5.0 PROPERTIES OF LATEX-MODIFIED SYSTEMS (FRESH STATE)

The latex-modified mortar and concrete have improved properties compared to conventional cement mortar and concrete. The properties of the fresh and hardened mortar and concrete are affected by a multiplicity of factors such as polymer type, polymer-cement ratio, water-cement ratio, air content and curing conditions.

5.1 Workability

Generally, latex-modified mortar and concrete are more workable than conventional cement mortar and concrete. This is mainly interpreted in terms of improved consistency due to the ball bearing action of polymer particles and entrained air and the dispersing effect of surfactants in the latexes. Takeyashiki et al.[57] proved by zeta-potential determination and cryo-scanning electron microscopy that the improved consistency or fluidity is due to the ball bearing action of the polymer particles among cement particles.

The flow of the latex-modified mortars increases with increasing water-cement ratio and polymer-cement ratio. The slump of the latex-modified concretes tends to increase with increased unit water content (or water-cement ratio) and polymer-cement ratio, and at each unit water content a raise in the polymer-cement ratio causes an increase in the slump. This tendency is more significant at lower sand-aggregate ratio and at large unit cement content. Considering these factors, Ohama et al.[58] have expanded Lyse's rule of constant water content on ordinary cement concrete,[59] and defined *slump control factor* as follows:

$$\varphi = Vp + Vw$$

Where φ is the slump control factor of the latex-modified concretes, and Vp and Vw are the volumes of polymer and water per unit volume of the latex-modified concretes respectively. The slump of the latex-modified concretes may be generally expressed as a function of the slump control factor by the following equation:

$$\text{Eq. (3)} \qquad S = K\varphi - l/(s/a)$$

where S is the slump of the latex-modified concretes, φ is the slump control factor, s/a is the sand-aggregate ratio or sand percentage, and K and l are empirical constants. The predictions of the slump are possible by applying this equation.

The water-cement ratio of latex-modified concrete at a given slump is markedly reduced with an increase in the polymer-cement ratio. This water reduction effect is found to contribute to strength development and a drying shrinkage reduction effectively.

5.2 Air Entrainment

In most latex-modified mortars and concretes, a large quantity of air is entrained compared to ordinary cement mortar and concrete because of an action of the surfactants contained as emulsifiers and stabilizers in polymer latexes. Some air entrainment is useful to obtain improved workability. An excessive amount of entrained air causes a reduction in strength, and must be controlled by using proper antifoaming agents. Recent commercial latexes for cement modifiers usually contain proper antifoaming agents, and therefore the air entrainment is considerably decreased. Consequently, the air content of most latex-modified mortars is in the range of 5 to 20%, and that of most latex-modified concretes is less than 2%, much the same as ordinary cement concrete. Such decreased air content of the latex-modified concretes over the latex-modified mortars is probably explained by the fact that air is hard to entrain in concretes because of the larger size of aggregate used. A variation of the air content in the latex-modified mortars is larger than that in the latex-modified concretes with an increase in the polymer-cement ratio.

5.3 Water Retention

Latex-modified mortar and concrete have a markedly improved water retention over ordinary cement mortar and concrete. The water retention is dependent on the polymer-cement ratio. The reasons for this can probably be explained in terms of the hydrophilic colloidal properties of latexes themselves and the inhibited water evaporation due to the filling and sealing effects of impermeable polymer films formed. Accordingly, a sufficient amount of water required for cement hydration is held in the mortar and concrete, and for most latex-modified systems dry cure is preferable to wet or water cure. The water retention generally increases with rising polymer-cement ratio, and becomes nearly constant at a polymer-cement ratio of 5 to 10%. Such excellent water retention of the latex-modified mortars is most helpful or effective to inhibit *dry-out* phenomena (the lack of cement hydration due to water loss in the mortar or concrete) in thin layer linings or coatings on highly water-absorbable substrates such as dried cement mortars and ceramic tiles.

5.4 Bleeding and Segregation

The resistance of latex-modified mortar and concrete to bleeding and segregation is very good in spite of their larger flowability characteristics. This is due to the hydrophilic colloidal properties of latexes themselves and the air-entraining and water-reducing effects of the surfactants contained in the latexes. Accordingly, in the latex-modified systems, some disadvantages such as reductions in strengths and waterproofness caused by bleeding and segregation are not observed.

5.5 Setting Behavior

In general, the setting of latex-modified mortar and concrete is delayed to some extent in comparison with ordinary cement and concrete, and this trend is dependent on the polymer type and polymer-cement ratio. Figure 10[60] shows the setting behavior of the latex-modified concrete. The setting is delayed with an increase in the polymer-cement ratio. Such slower setting does not cause inconvenience in practical applications. NR-modified mortar causes the most delay in the setting. Usually, the reasons for the setting delay are that the surfactants such as alkylbenzene sulfonates and caseinates contained in latexes inhibit the hydration of cement.[61] Rheological studies on PVAC-modified concrete by Zivica[62] have revealed that the hydration of cement is inhibited by the adsorption of the surfactants on the binder surface.

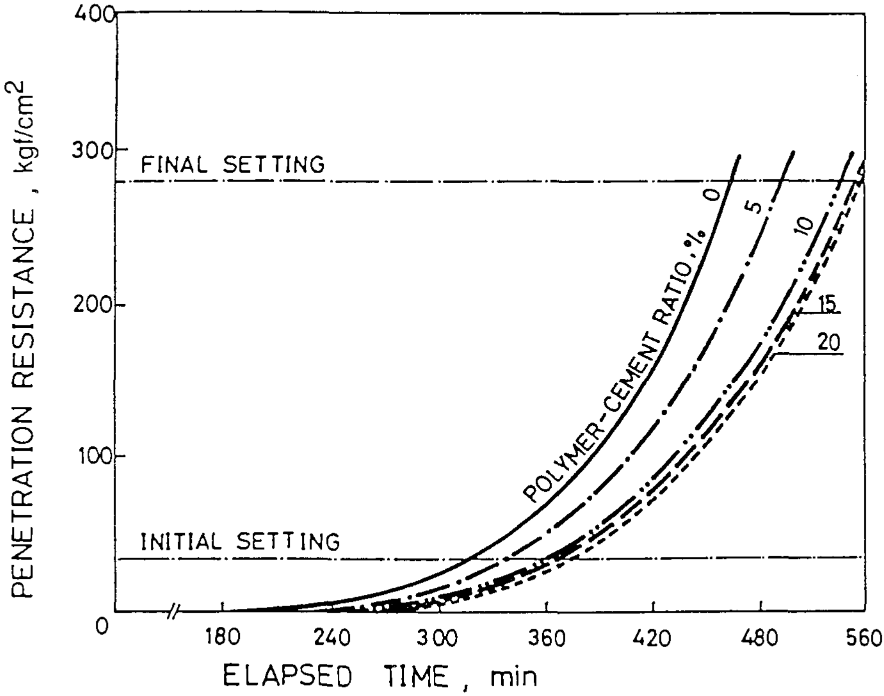


Figure 10. Elapsed time vs penetration resistance of SBR-modified concrete.

6.0 PROPERTIES OF HARDENED LATEX MORTAR AND CONCRETE

6.1 Strength

In general, latex-modified mortar and concrete show a noticeable increase in the tensile and flexural strengths but no improvement in the compressive strength when compared to normal mortar or concrete. This is due to the contribution of the polymer and cement-aggregate bond in the polymer systems. The factors that cause variation in the strength properties in polymer cementitious materials are the nature of the materials such as the type of latex, cement, aggregate and mix proportion, curing method and testing techniques.

6.2 Material Parameters

The nature of polymers in latexes depends on the monomer ratio in copolymers and the type and amount of plasticizers. The mechanical and chemical stability, bubbling, and coalescence on drying depend on the type and amount of surfactants and antifoamers and the size of dispersed polymer particles.

Ohama[63][64] studied the effect of monomer ratio in EVA, SBR and polystyrene-butyl acrylate, SAE) latexes on the strengths of latex-modified mortars. The monomer ratio affects the strengths of the latex modified mortars to the same extent as the polymer-cement ratio. The maximum strengths of EVA and poly(styrene acrylate)-modified mortars are obtained at a bound ethylene content of 13% and a bound styrene content of 55% respectively. The strengths of SBR-modified mortar increase with a raise in the bound styrene content. These results are similar to those obtained by Cherkinskii et al.,[65] The tensile strength of the dry films made from SBR latexes increases sharply when the bound styrene content is raised, and there is a positive correlation between the strength of the films and the flexural strength of SBR-modified mortars with polymer-cement ratios above 10%.[63]

The effect of plasticizer (i.e., dibutyl phthalate) content in PVAC latexes on the strengths of PVAC-modified mortars is represented in Fig 11.[66] Just as SBR-modified mortars, the strengths are governed by the nature of polyvinyl acetate (with the variation in the plasticizer content), and is reduced with the increase in the plasticizer content.

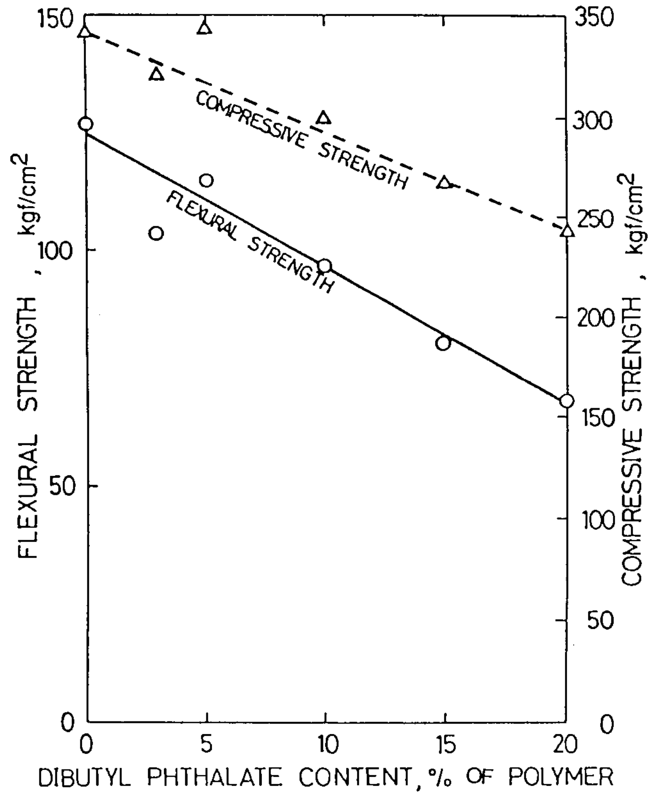


Figure 11. Effect of plasticizer content in PVAC latex on strength of PVAC-modified mortar.

The glass transition temperature (Tg) of polymers on the flexural and compressive strengths of latex-modified with a polymer-cement ratio of 15%, has been studied.[67][68] The flexural and compressive strengths of the latex-modified mortars appear to reach a maximum value at a glass transition temperature depending on a change in the minimum film-forming temperature of the latexes with rising glass transition temperature.

Generally, the mechanical and chemical stabilities of latexes are improved with an increase in the content of the surfactants selected as stabilizers, and the stabilized latexes can disperse effectively without coagulation in latex-modified mortar and concrete. On the other hand, an excess amount of surfactant may have an adverse effect on the strength of the latex-modified mortar and concrete because of the reduced latex film strength, the delayed cement hydration, and excess air entrainment. Consequently, the latexes used as cement modifiers should have an optimum surfactant content to provide the high strength of the latex-modified mortar and concrete. Such optimum surfactant contents, ranging from 5 to 30% of the weight of the total solids, can be found in Fig. 12,[69] which illustrates the relation between the surfactant content of the latexes and the flexural strength of the latex-modified mortars.

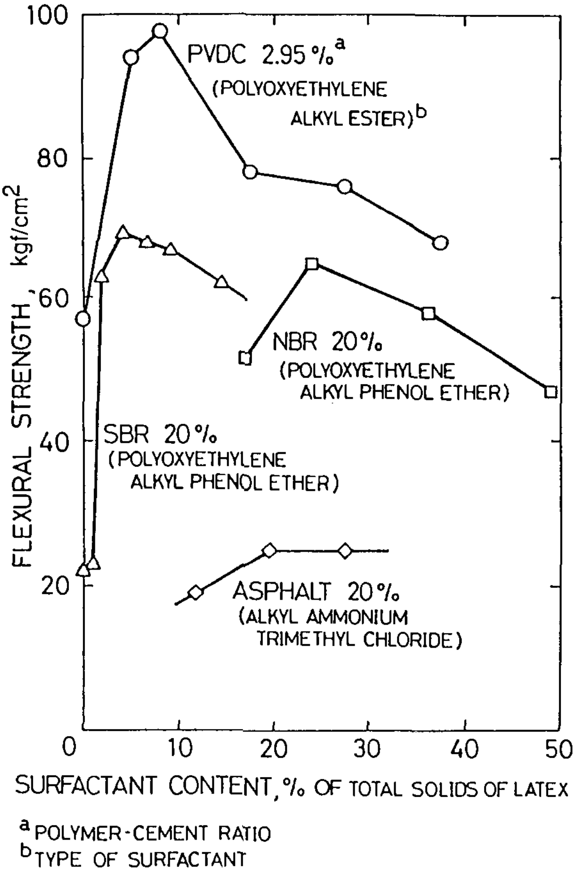


Figure 12. Relation between surfactant content of latex and flexural strength of latex-modified mortars.

Suitable antifoamers are usually added to the latexes to prevent excess air entrainment. Increased antifoamer content causes a pronounced decrease in the air content and an increase in the compressive strength.

It is important that the selected antifoamers and the surfactants as stabilizers or emulsifiers should produce no adverse effect on cement hydration. Polyoxyethylene nonyl phenol ether and silicone emulsion are a good surfactant and antifoamer respectively, but a large amount of sodium alkyl benzene sulfonate, which is a popular emulsifier, causes delayed hydration of cement, and extends the setting times.

The size of dispersed polymer particles in the latexes can affect the strength of latex-modified mortar and concrete to a certain extent. Geist et al.[70] and Brocard[71] found that PVAC-modified mortar developed a maximum strength as the particle size ranges from 1 to 5 μm or 2 to 5 μm. Wagner et al., found increases in the compressive and tensile strengths of PVDC-modified mortar with decreasing particle size. Walters investigated the effect of latex particle size on the chloride ion permeability of SBR-modified mortars with a polymer-cement ratio of 15%.[67] The chloride ion permeability was tested by ASTM C 1202 (Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration). SBR latexes with smaller particle size appear to initially provide lower chloride ion permeability to the mortars using the latexes, but a difference in the permeability between the smaller and larger particle sizes eventually becomes insignificant with additional curing period. Such an initial decrease in the permeability is attributed to the fact that the latexes with smaller particle size coalesce faster than the ones with larger particle size as indicated in the paint field.[72]

It appears that the molecular weight of the latex polymers does not have an effect on the strength of latex-modified mortar and concrete.[71]

The strength of latex-modified systems is affected to a lesser extent by the type of cement, except when high alumina cement is used as shown in Fig. 13.[73]

The latex-modified mortars using high alumina cement exhibit a strength 1.5 to 2 times higher than that of the mortars using other cements. This is found to be due to a difference in the formation at the initial stage of setting.

The effects of blended cements containing various mineral admixtures on the flexural strength of dry-cured EVA-modified mortars are illustrated in Fig. 14.[74] The flexural strength of EVA-modified mortars with the blended cements increases with an increase in the polymer-cement ratio, and is similar to that of unmodified mortar except for a few cases.

The fineness modulus of sand affects the strength of latex-modified mortars. The flexural and compressive strengths tend to increase with fineness modulus, that is, with increasing particle size of the sand-like unmodified mortar.

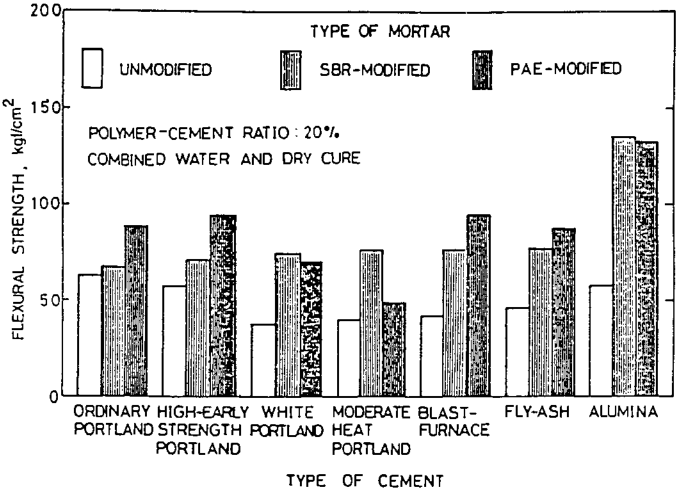


Figure 13. Type of cement vs flexural strength of SBR-modified mortars.

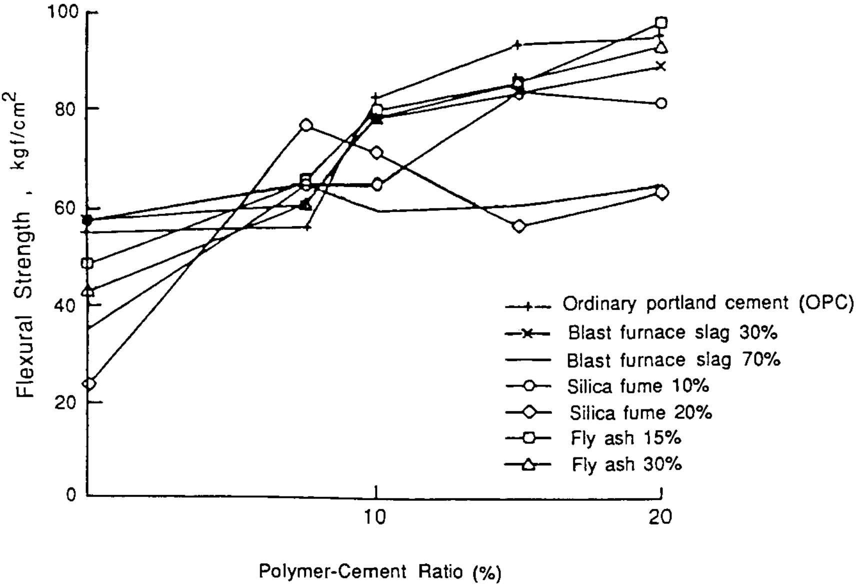


Figure 14. Effects of blended cements on flexural strength of dry-cured EVA-modified mortars.

6.3 Mix Proportions

The binder of latex-modified mortar and concrete consists of polymer latex and inorganic cement, and its strength is developed as a result of an interaction between them. The polymer-cement ratio has a more pronounced effect on the strength properties than the water-cement ratio. However, this effect depends on polymer type, air content, curing conditions, etc. The relation between the strength properties and polymer-cement ratio has been discussed in a number of publications.[75]-[78] The summarized results are presented in Fig. 15.

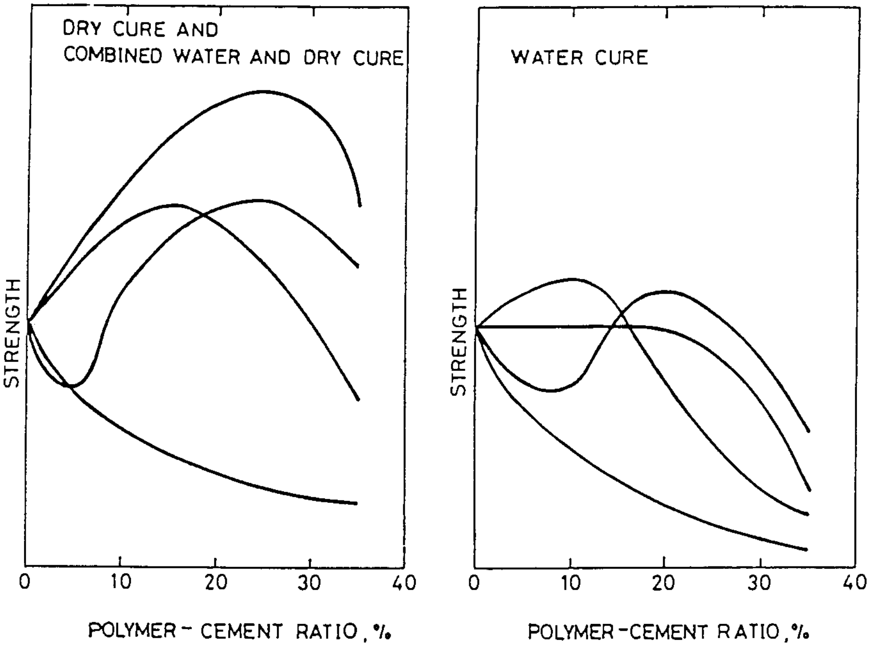


Figure 15. Relation between strength properties and polymer-cement ratio of latex-modified mortar and concrete.

Table 13[79] shows the strength properties of typical latex-modified concretes at various polymer-cement ratios and a constant slump of 18 ± 1 cm, which were exposed for 2 days at 20°C-moist cure plus 5-day-20°C-water plus 21-day–20°C–50% R.H. dry cure. The development of tensile and flexural strengths is more significant than that of the compressive and shearing strengths except for PVAC-modified concrete. Most latex-modified mortars and concretes show a maximum strength at polymer-cement ratios of 10 to 20% and 20 to 30% in the dry cure and the combined water and dry cure, and at polymer-cement ratios of 5 to 15% and 15 to 25% in the water cure. Some latex-modified systems show a minimum strength at a polymer-cement ratio of 5 to 10% irrespective of the curing conditions. A few systems provide a sharp decrease in strength with rising polymer-cement ratios regardless of the curing conditions. Most latex-modified mortars and concretes cured under favorable conditions have effective strength properties at polymer-cement ratios up to 20 to 30%, and the strength may be reduced at polymer-cement ratios exceeding 20 to 30%. Up to these ratios, the polymer acts to strengthen the mortar or concrete microstructure, but a further increase in the polymer-cement ratios leads to discontinuities in the microstructure which reduce the strength. Low polymer-cement ratios of 5% or less also are not effective because of little improvement in the strength. Consequently, the polymer-cement ratio range of 5 to 20% is used in practice.

Table 13. Modulus of Elasticity and Poisson's Ratio of Latex-Modified Concretes

Type of Concrete	Polymer-Cement Ratio (%)	Modulus of Elasticity in Compression ($\times 10^5$ kgf/cm^2)	Poisson's Ratio
Unmodified	0	2.11	0.17
PAE-Modified	5	2.27	0.16
	10	2.36	0.17
	15	2.30	0.17
	20	2.24	0.17
SBR-Modified	5	2.28	0.16
	10	2.43	0.18
	15	2.42	0.18
	20	2.02	0.18
PVAC-Modified	5	1.90	0.16
	10	1.79	0.19
	15	1.35	0.24
	20	1.00	0.29

At a given consistency, a considerable reduction in the water-cement ratio due to increased polymer-cement ratio contributes largely to an increase in the strength of most latex-modified systems.

Entrainment of air exerts a marked influence on the strength of most latex-modified systems. Decreased air content in PVDC, SBR and PAE systems increases strength, and strength increases as the antifoam content increases.

Wagner[80] expanded Powers and Brownyard's theory for ordinary cement paste,[81] and developed a general expression to predict the compressive strength of latex-modified mortars, using the water-cement ratio and the content of entrained air. This expression was obtained under a special condition of complete exclusion of water loss during curing, and the practical application of this equation is somewhat difficult. Expanding Talbat's void theory[82] on ordinary cement mortar and concrete, Ohama[83]-[85] defined *binder-void-ratio* (α) or *void-binder-ratio* (β), and empirically proposed the equations using α and β to predict the compressive strength of the latex-modified mortars and concretes as follows:

Latex-modified mortars:

$$\log\sigma c = (A/B^{\beta}) + C \text{ or } \sigma c = (A/B^{\beta}) + C$$

Latex-modified concretes:

$$\sigma c = a\alpha + \beta$$

where σc is the compressive strength of the latex-modified mortars and concretes, $\beta = 1/\alpha = (Va + Vw)/(Vc + Vp)$, Vc, Vp, Va and Vw are the volumes of cement, polymer, air and water per unit volume of the latex-modified mortars and concretes respectively, and A, B, C, a and b are empirical constants.

Sand-Cement Ratio. When the sand-cement ratio increases, the flexural and compressive strengths of latex-modified mortars are remarkably reduced, and the effect of the polymer-cement ratio on the strengths gradually becomes smaller.

As seen in Fig. 16,[86] the addition of steel fibers into latex-modified systems has a positive effect on the strength with increasing polymer-cement ratio and steel fiber content.

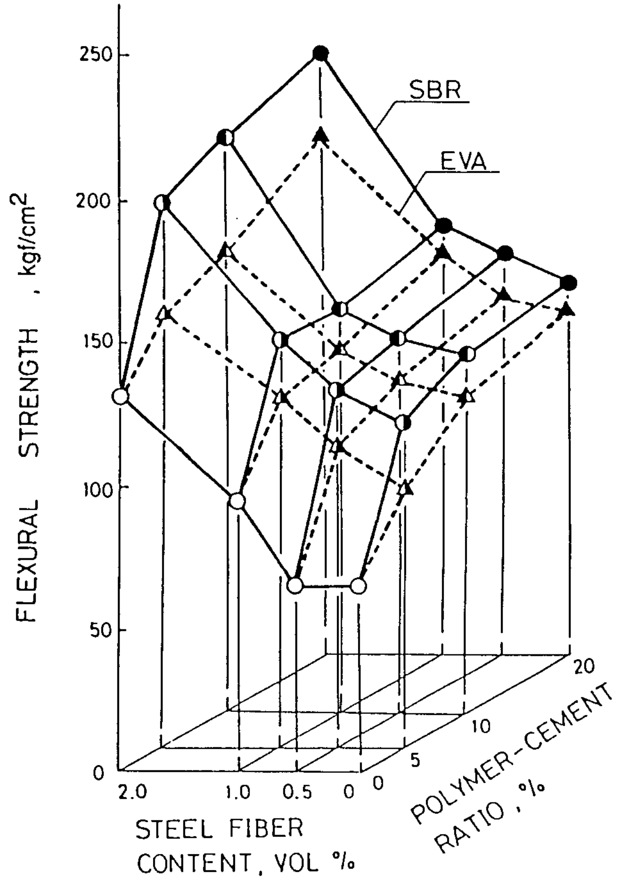
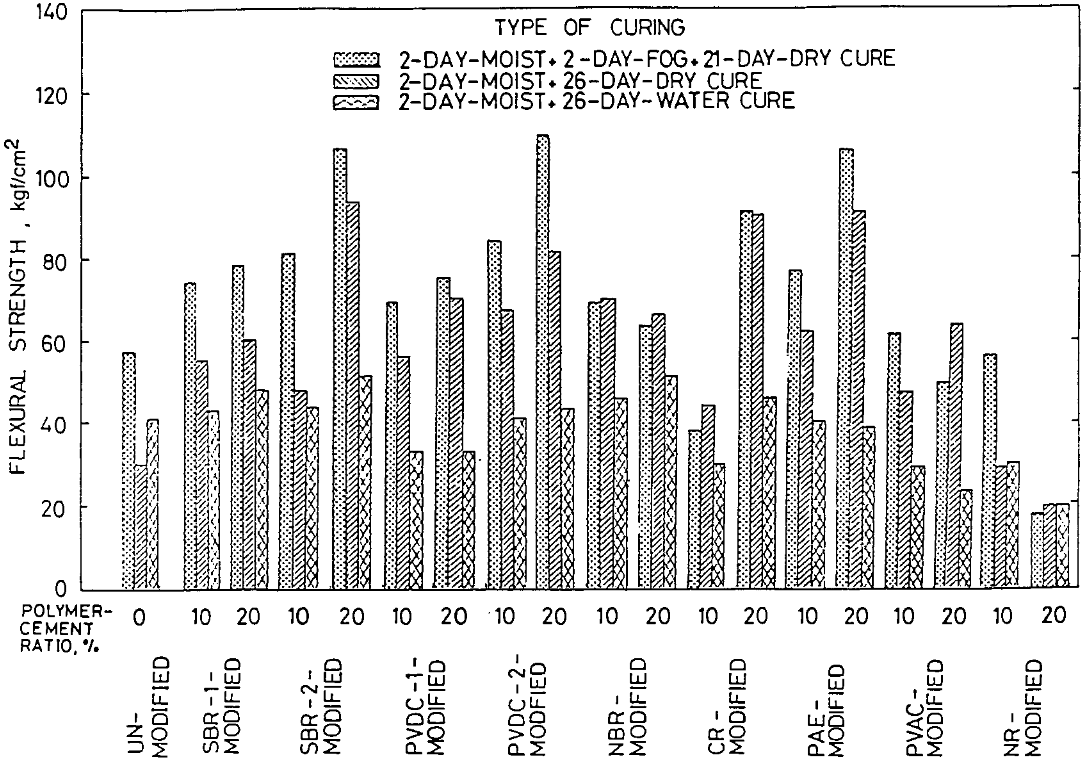


Figure 16. Steel fiber content and polymer-cement ratio vs flexural strength of latex-modified concretes.

6.4 Effects of Curing Conditions

Favorable curing condition requirements for latex-modified mortar and concrete differ from those for ordinary cement and concrete, because their binder consists of two phases of latex and hydraulic cement with different properties. Optimum strength in the cement phase is developed under wet conditions such as water immersion and high humidities, whereas strength development in the latex phase is attained under dry conditions. Figure 17[87][88] shows the effect of the curing conditions on the strength of the latex-modified mortars.

Figure 17. Effects of curing conditions on flexural strength of latex-modified mortars.



The optimum strength in most latex-modified mortars and concretes is obtained by achieving the reasonable extent of cement hydration under wet conditions at early ages, followed by dry conditions to promote a polymer film formation due to the coalescence of polymer particles in the latexes. In other words, such curing conditions are most suitable or ideal for most latex-modified mortars and concretes. This is confirmed by Wagner's study.[75] The curing conditions are more sensitive for the mortars than for the concretes because of a difference in the water retention due to their specimen sizes.

Water immersion subsequent to dry cure causes a sharp reduction in the strength of all latex-modified systems. Such an influence on strength appears reversible because of the recovery of the strength by drying storage subsequent to water immersion as ascertained by Ohama[89] and Frondistou-Yannas and Shah.[90]

The dry curing period after a 2-day–moist and 5-day–water cure vs compressive strength, as well as the surface area-volume ratio, polymer-cement ratio vs compressive strength of latex-modified concretes has been studied.[91] In general, the compressive strength of SBR-modified concretes does not change markedly with additional dry curing period, and becomes nearly constant at 182 days regardless of specimen size. The compressive strength at this age increases sharply with a raise in the polymer-cement ratio, and reaches 2 to 3 times the value before dry cure, i.e., after 7-day wet cure. The main reason for this is the hydration of cement in the latex-modified concretes progresses through a considerably long dry curing period because of their excellent water retention capacity due to polymer film formation. Such a large strength development is found to be one of the advantages of the latex-modified concretes over ordinary cement concrete. The compressive strength tends to increase with increasing surface area-volume ratio, i.e., with decreasing specimen size irrespective of the polymer-cement ratio. The trend is almost the same as for unmodified concrete.[92][93]

The probability of formation of cracks and flaws in a specimen will increase with an increase in its volume, i.e., with an increase in its size.[94]

A method of developing high strength by the heat treatment of latex-modified systems using thermoplastic copolymers with special thermal properties has been devised.[95] The copolymers were made from two monomers which form homopolymer with different second-order transition points above and below ambient temperatures. Superior flexural and compressive strengths are obtained by this method. Optimum strength properties by this special curing are attained in the temperature range of 70 to 120°C. The mechanism of such high strength development seems to be explained in terms of the promotion of continuous polymer film formation and pore filling effect.

6.5 Surface Hardness

The surface hardness of latex-modified systems is generally improved to some extent over ordinary cement system, depending on the polymer type and the polymer-cement ratio. A definite correlation between the surface hardness and compressive strength of most latex-modified systems is recognized.[96]

6.6 Modulus of Elasticity and Ductility

Latex-modified mortar and concrete contain polymers (modulus of elasticity, 0.001–10 x 10^4 kgf/cm^2) with considerably lower modulus of elasticity compared to cement hydrates (modulus of elasticity, 10–30 x 10^4 kgf/cm^2). Consequently, their deformation behavior and ductility (or extensibility) can differ to a great extent from those of ordinary cement mortar and concrete. Most latex-modified mortar and concrete provide a higher deformation, ductility (or extensibility), and elasticity than ordinary cement mortar and concrete, their magnitude depending on polymer type and polymer-cement ratio.

Figure 18[97] shows the compressive stress-strain curves for latex-modified mortars. Generally, the maximum compressive strain at failure increases with rising polymer-cement ratio, even though there is no pronounced change in the modulus of elasticity in compression. The maximum compressive strain at a polymer-cement ratio of 20% increases to 2 to 3 times that of unmodified mortar.

Figure 19[98] represents the tensile stress-strain curves of SBR-modified concretes, where as the polymer-cement ratio is raised, the modulus of elasticity in tension decreases. The elongation increases and is 2 to 3 times greater than that of unmodified concrete. This is explained by considering that the polymer films formed in the concrete may effectively halt propagating microcracks through their high tensile strength and elongation.

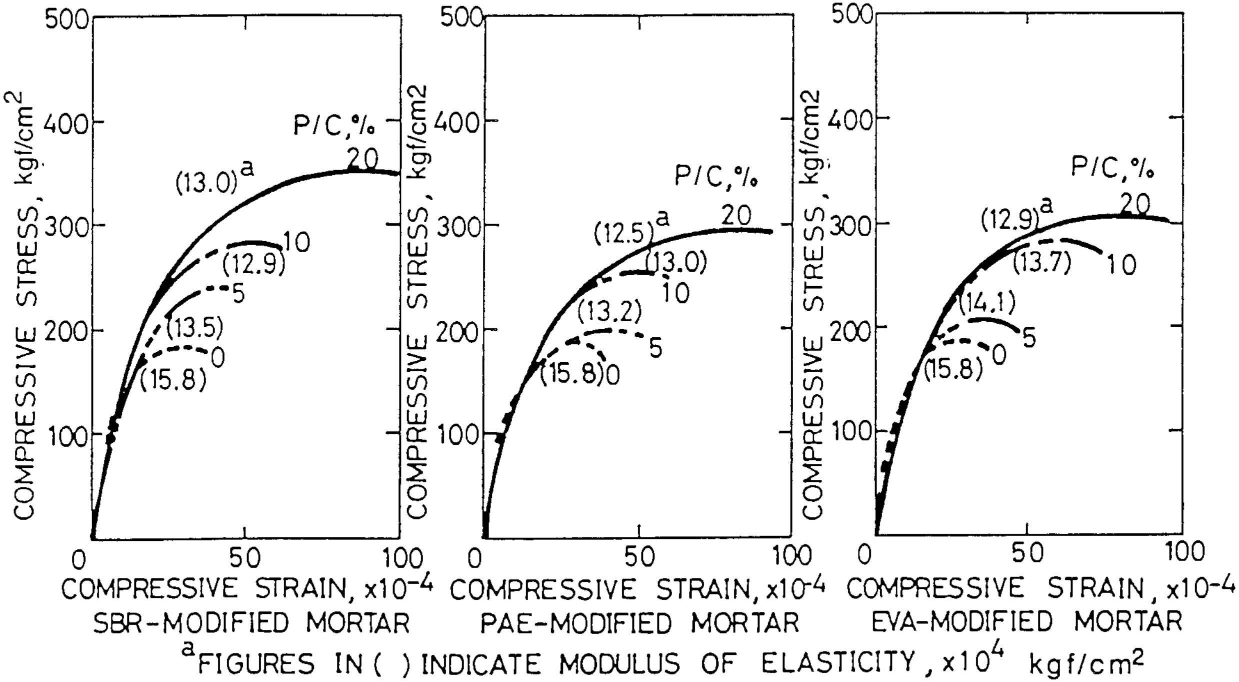


Figure 18. Compressive stress-strain curves for latex-modified mortars.

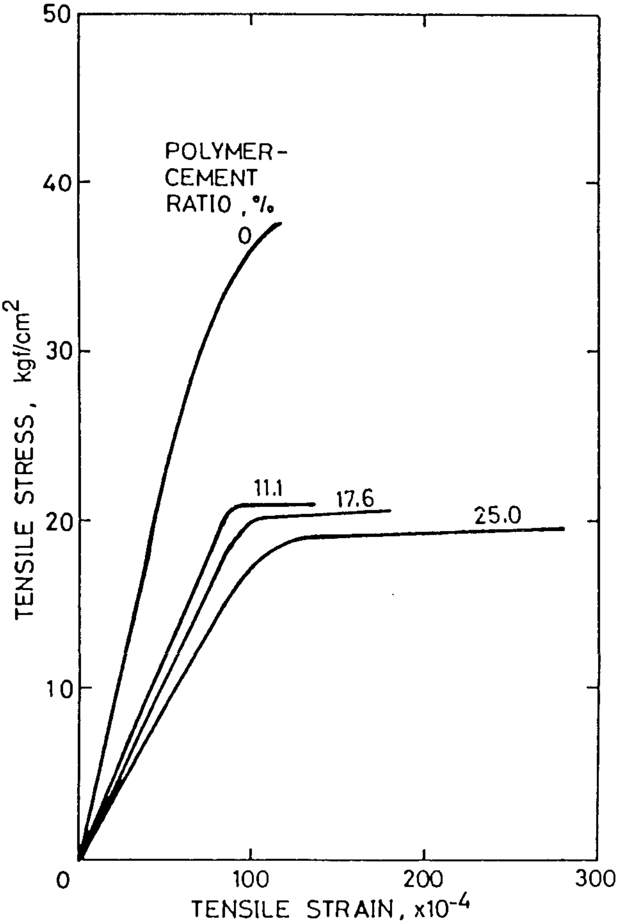


Figure 19. Tensile stress-strain curves for SBR-modified concrete.

The modulus of elasticity in compression and Poisson's ratio of latex-modified concretes are listed in Table 14.[99] The modulus of elasticity generally decreases with a raise in the polymer-cement ratio. The Poisson's ratio of PAE-and SBR-modified concretes is nearly equal to that of unmodified concrete regardless of the polymer-cement ratio, but that of PVAC-modified concretes increases with rising polymer-cement ratio.

The flexural load-deflection curves for steel fiber reinforced SBR- and EVA- modified mortars has been determined. It seems that after reaching the maximum flexural load, steel fibers in the mortars can resist the rupture due to work needed to pull them out of the matrix. Accordingly, the toughness is remarkably improved with increasing steel fiber content and polymer-cement ratio. The effect of the steel fiber content on the toughness is much more significant than that of the polymer-cement ratio. Soroushian[100] showed the improved flexural toughness due to SBR latex modification of pitch-based carbon fiber reinforced mortars.

Table 14. Modulus of Elasticity and Poisson's Ratio of Latex-Modified Concrete

Type of Concrete	Polymer-Cement Ratio (%)	Modulus of Elasticity in Compression ($\times 10^5$ kgf/cm^2)	Poisson's Ratio
Unmodified	0	2.11	0.17
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	10	2.36	0.17
	15	2.30	0.17
	20	2.24	0.17
SBR-Modified	5	2.28	0.16
	10	2.43	0.18
	15	2.42	0.18
	20	2.02	0.18
PVAC-Modified	5	1.90	0.16
	10	1.79	0.19
	15	1.35	0.24
	20	1.00	0.29

6.7 Shrinkage, Creep, and Thermal Expansion

The drying shrinkage of latex-modified mortar and concrete may be either larger or smaller than that of unmodified mortar and concrete, and is dependent on polymer type and polymer-cement ratio. Data on the shrinkage measurement are somewhat variable for different testing methods or investigations. The drying shrinkage increases with additional dry curing period, and becomes nearly constant at a dry curing period of 28 days regardless of polymer type and polymer-cement ratio.[101] Generally, the 28-day drying shrinkage tends to decrease with increasing polymer-cement ratio. PVAC-, NR- and CR-modified mortars have a larger shrinkage compared to that of unmodified mortar. The largest shrinkage of PVAC-modified mortars is probably caused by the evaporation of a larger amount of water absorbed in the polymer phase due to the low water resistance of the polyvinyl acetate itself. Ohama[102] found that such an excessive shrinkage could be reduced by as much as 50% of that of unmodified mortar by the introduction of ethylene into the polymer formulations (Fig. 20). In this study, the optimum effect was obtained at bound ethylene contents of 17 to 40% and at polymer-cement ratios of 15 to 20%. NBR-modified mortars have the smallest shrinkage of all the mortars tested. This may be because the surfactant content of the NBR latex is several times higher than that of other latexes, and hence causes noticeable improvements in water retention and water reduction effects.

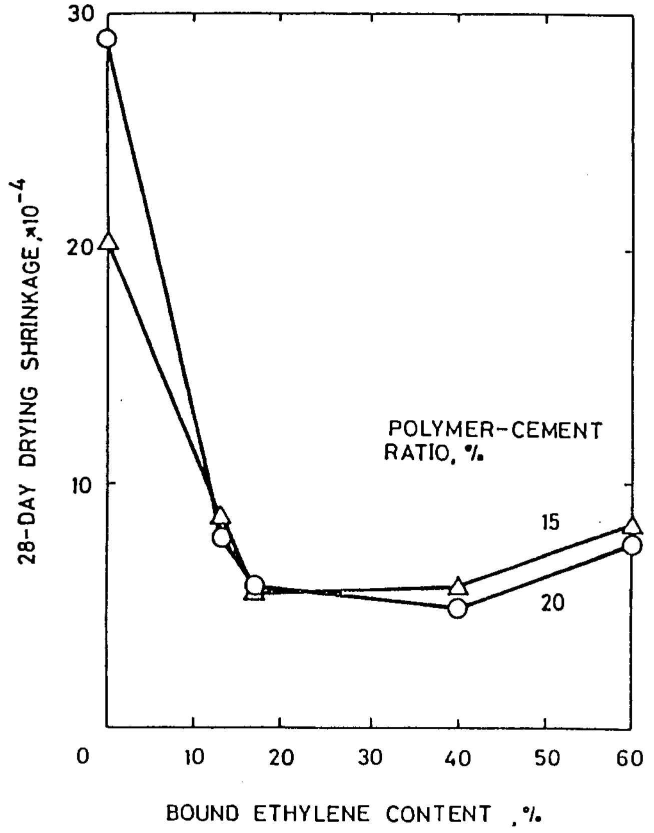


Figure 20. Effect of bonded ethylene content on 28-day drying shrinkage of EVA-modified mortar.

The relationship amongst the volume-surface area ratio (specimen size change), polymer-cement ratio and drying shrinkage of EVA-modified concretes has been determined.[91] The drying shrinkage is reduced with increasing specimen size and polymer-cement ratio because of improved water retention.

Kawano[103] found that, compared to ordinary cement mortar, a reduction in the drying shrinkage of latex-modified mortars is mainly due to the effects of the surfactants and antifoamers contained in the latexes.

The use of expansive additives such as calcium sulfoaluminate (CSA)- and calcium oxide (lime)-based compositions causes an effective reduction in the drying shrinkage of latex-modified mortars. In general, the drying shrinkage of the latex-modified mortars with the expansive additives is reduced with an increase in the expansive additive content, and transformed into expansion at higher expansive additive content.[104] Such shrinkage reduction effects of the expansive additives tend to be marked at higher polymer-cement ratio. Adequate consideration of the type of polymer and expansive additive, expansive additive content, polymer-cement ratio, and curing conditions is required in the mix design of the latex-modified mortars with the expansive additives.

The reinforcement of the latex-modified mortars with steel fibers provides a marked decrease in the drying shrinkage with increasing polymer-cement ratio and steel fiber content, and at a polymer-cement ratio of 2% and a steel fiber content of 2.0 vol% can cause a reduction of about 35% in the drying shrinkage.

Conflicting data exist on the creep behavior of latex-modified mortar and concrete. The creep characteristics of SBR- and PAE- modified concretes reported by Ohama[105] show that like ordinary cement concrete, the relationships between loading time (t) and creep strain (εc) or creep coefficient (ϕ) (i.e., creep strain-elastic strain ratio) of the latex-modified concretes fit approximately the expression:

$$\varepsilon c \text{ or } \phi = t/(A+Bt)$$

where A and B are constants. Both creep strain and creep coefficient of SBR- and PAE- modified concretes are considerably lower than those of unmodified concrete. This tendency is similar to the creep data[106] on the latex-modified mortars. The latex-modified mortars and concretes generally exhibit small creep in spite of the inclusion of flexible polymers with low glass transition temperatures. This may be related to the lower polymer content of about 3 vol%, the strengthening of binder with polymers, and the long-term strength development with improved water retention. By contrast, Solomatov[107] found that the creep deformation in flexure of poly(vinyl) acetate-dibutyl maleate)-modified mortar was several times larger than that of unmodified concrete at 20°C, and its catastrophic deformation occurred at 50°C since the polymer developed a high plasticity above its glass transition temperature.

In general, the coefficient of thermal expansion of latex-modified mortar and concrete is directly influenced by that of the aggregates used as in ordinary cement mortar and concrete. The latex-modified mortar and concrete usually have a coefficient of thermal expansion equal to or slightly larger than that of the ordinary mortar and concrete.

6.8 Adhesion or Bond Strength

The most important property of latex-modified mortar or concrete is its improved adhesion or bond strength to various substrates. The development of adhesion is attributed to the high adhesion of polymers. The adhesion is usually affected by polymer-cement ratio and the properties of substrates used. The data on adhesion often show considerable scatter, and may vary depending on the testing methods, service conditions or porosity of substrates.

The adhesion in flexure of latex-modified mortars to ordinary cement mortar as a substrate, has been studied.[102] The adhesion of most latex-modified mortars tends to increase with rising polymer-cement ratio, although for a few types there are optimum polymer-cement ratios (Fig. 21). The adhesion is also influenced by the mix proportions, namely, the strength of mortar substrate. In 1:2 mix substrate, failure in flexure occurs mostly through the interface but in 1:3 mix substrate, it occurs through the substrate rather than through the interface. However, it appears that the adhesion is lower than the flexural strength. Similar improvements in adhesion are also achieved in shear compression.[108]

The adhesion of latex-modified mortars to ordinary cement mortar as a substrate has been measured by four types of test methods.[104] Generally, the adhesion in tension, flexure, and direct compressive shear of the latex-modified mortars to ordinary cement mortar increases with an increase in the polymer-cement ratio regardless of the type of polymer and test method. The adhesion in slant (indirect) compressive shear of the latex-modified mortars attains a maximum at a polymer-cement ratio of 5 or 10%, and is extremely large compared to the adhesion values determined by other test methods irrespective of the polymer type and polymer-cement ratio. It is important to select the best test method to successfully reproduce service conditions in the applications of the latex-modified mortars.

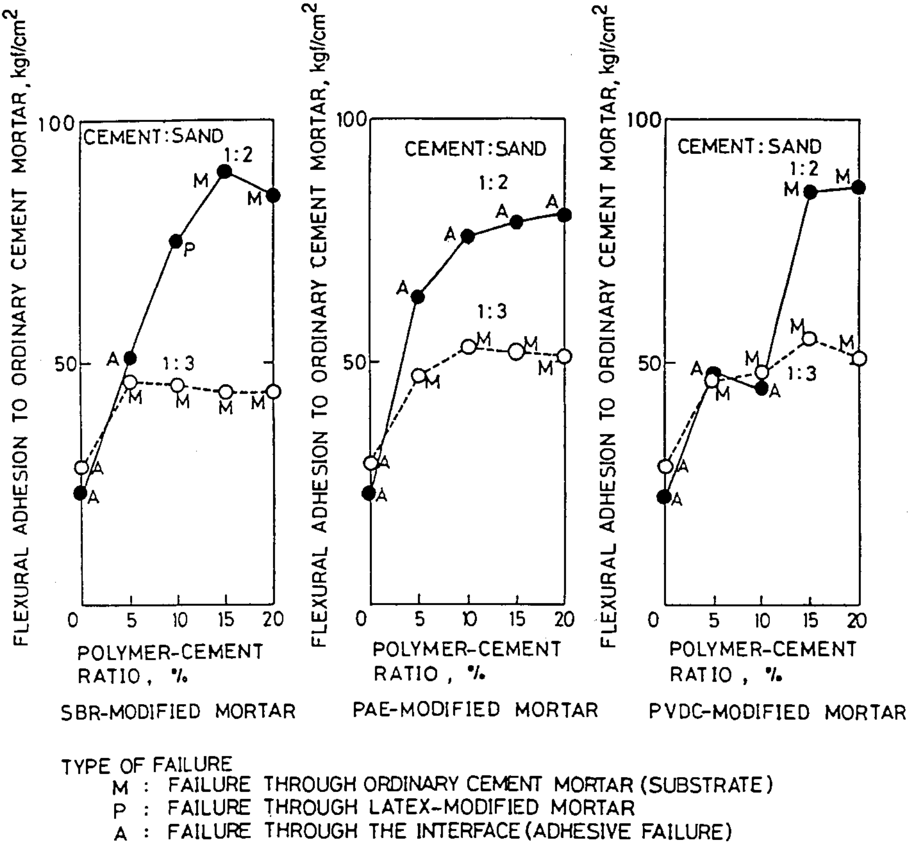


Figure 21. Polymer-cement ratio vs flexural adhesion of latex-modified mortars to ordinary cement mortar.

Kuhlmann[105] developed a test method that accurately measures the bond strength of latex-modified mortar or concrete to conventional concrete under direct tension, using the specimens prepared by casting the latex-modified mortar or concrete on the concrete substrates in 76-mm (diameter) steel pipe nipples as molds. The bond test by this method demonstrated a coefficient of variation of less that 10%.

The use of latex-modified pastes as bonding agents for ordinary cement mortar to mortar or concrete substrates is a widespread practice for troweling work. The adhesion in tension of the bonded mortar to the latex-modified paste-coated mortar substrates increases with increasing polymer-cement ratio of the latex-modified pastes, and reaches a maximum at polymer-cement ratios of about 5 to 10%. The failure modes in the adhesion tests are almost cohesive in the bonded mortar. Figure 22[106] shows the microstructures of the interfaces between the bonded mortar and latex-modified paste coated mortar substrates. The presence of the latex-modified paste layers in the diffused edges facing the bonded mortar is distinctly seen. The diffusion of the latex-modified pastes in the bonded mortar signifies the formation of a monolithic bond between the bonded mortar and latex-modified pastes. Moreover, the very workable latex-modified pastes fill the nonuniform mortar substrates, and develop a good bond by micromechanical interlocking mechanisms.

Ohama[63] found a nearly ten-fold increase in adhesion to ordinary cement mortar of SBR- modified mortar with a polymer-cement ratio of 20%, compared to unmodified mortar. In this case, the monomer ratio of the copolymer was important, and the high adhesion was attained at a bound styrene content of 70%.

One disadvantage of latex-modified mortar and concrete is that under wet service conditions, adhesion is reduced as seen in Fig. 23.[107] The adhesion strength of most latex-modified mortars after water immersion is, however, larger than that of unmodified mortar. Accordingly, this does not deter the practical use of most latex-modified mortars.

The adhesion between ceramic tiles, and that between the tiles and ordinary cement mortar, tend to increase with rising polymer-cement ratio. Most latex-modified mortars have an excellent ability to bond to steel, wood, brick and stone.

The adhesion of bond of latex-modified mortars to reinforcing bars is found to be very important for their use in repair work for damaged reinforced concrete structures. Figure 24[108] illustrates the bond strength of the latex-modified mortars to the reinforcing bars, determined under direct tension by pull-modified mortars to the reinforcing bars, determining under direct tension by pullout method.

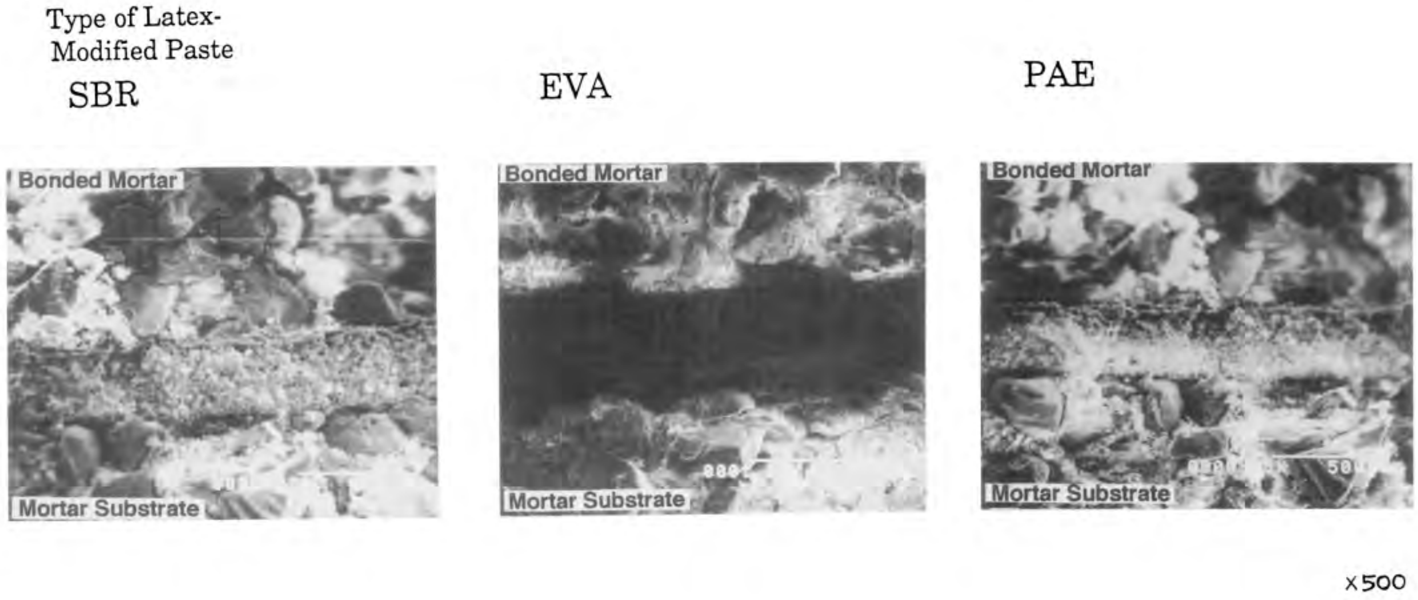


Figure 22. Microstructures of the interfaces between bonded ordinary cement mortar and latex-modified paste coated mortar substrates.

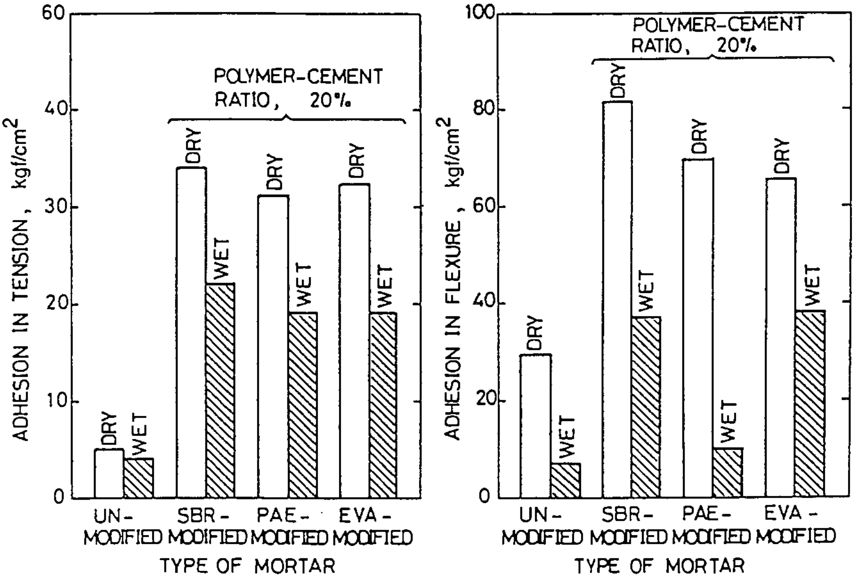


Figure 23. Effect of water absorption on adhesion in tension and flexure of latex-modified mortars.

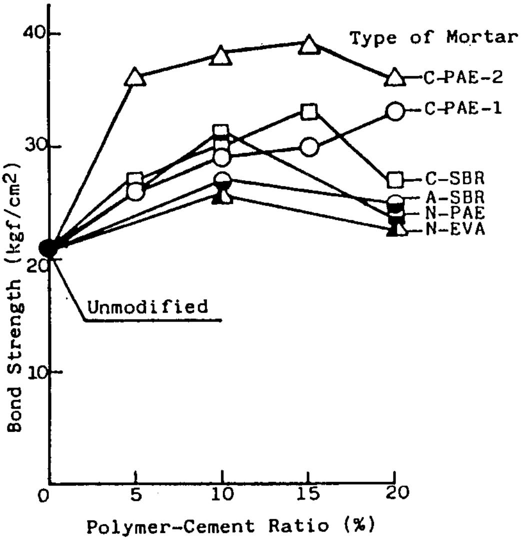


Figure 24. Polymer-cement ratio vs bond strength of latex-modified mortars to reinforcing bars.

In general, the bond strength of the latex-modified mortars to the reinforcing bars increases with an increase in the polymer-cement ratio, and reaches a maximum at polymer-cement ratios of about 10 to 15%. Cationic latex-modified mortars develop a much higher bond strength than unmodified, anionic, and nonionic latex-modified mortars. Such good adhesion or bonding between the latex-modified mortars and reinforcing bars is found to be the result of the presence of electrochemically active polymer-cement co-matrixes at the interfaces which help to relax stresses during loading and retard the friction-controlled slip of the reinforcing bars. Nakayama et al.[109] investigated the bond strength development between latex-modified pastes and steel at early ages by use of an overhanging beam method, and found that the bond strength depends on nonevaporable water content, heat of hydration, and calcium hydroxide content.

6.9 Impact Resistance

Latex-modified systems have a much higher impact resistance than those made from the conventional materials. One of the reasons is the polymers themselves have a high impact resistance. The values increase with the polymer-cement ratio. Figure 25[100] shows the impact resistance of the latex mortars. Those made with elastomers are superior to those made from thermoplastic resins. The impact resistance of NR and SBR modified mortars with a polymer-cement ratio of 20% is about 10 times greater than that of the unmodified mortar. Ohama[111] obtained excellent impact resistance for latex mortar. Another reference to SBR modified mortar[63] indicated that its impact resistance was lowered significantly by increasing the styrene content. The reinforcement of latex-modified concretes with steel fibers causes a pronounced improvement in impact strength at increased polymer-cement ratio and steel content.

6.10 Abrasion Resistance

The abrasion resistance of latex-modified mortar and concrete depends on the polymer type, polymer-cement ratio and abrasion and wear conditions. In general, the abrasion resistance is considerably improved with an increase in the polymer-cement ratio. The abrasion resistance at a polymer-cement ratio of 0.2 increases up to 20–50 times that of the unmodified mortar.[112] Techman[113] found that PAE modified mortar with a polymer-cement ratio of 0.2 had an abrasion resistance 200 times that of the conventional mortar. Gierloff[114] developed a traffic simulator for abrasion test, and showed that various PAE modified mortars with a high polymer-cement ratio and low water-cement ratio resisted traffic abrasion very well. Ohama's study[63] on SBR modified mortar showed that its abrasion resistance is increased by increased bound styrene content.

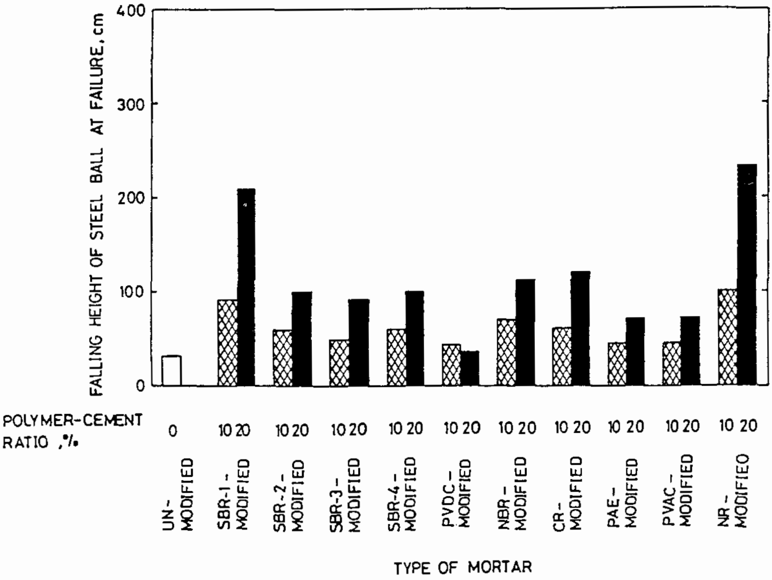


Figure 25. Impact resistance of latex-modified mortars.

6.11 Resistance to Water

Latex-modified mortar and concrete have a structure in which the larger pores can be filled with polymers or sealed with continuous polymer films. As a result, the latex-modified mortar and concrete have improved waterproofness over ordinary mortar and concrete. However, they have a poor resistance to water so that their strength is decreased when exposed to water or high humidities. Figure 26[115] shows the 48 hr water absorption and water permeation of the latex-modified mortar. Generally the water absorption and the amount of water permeation are considerably reduced with an increase in the polymer-cement ratio. In PVAC modified mortar, as the water absorption increases, the resistance to water permeation also increases. The waterproofness of PVAC-modified mortar is low. Polyvinyl acetate swells due to water absorption and is partially hydrolyzed under alkaline conditions.[116]-[118] At the initial stage of water permeation through PVAC modified mortar, the swelling can give a self-sealing effect on the pores and the mortar may show a smaller amount of water permeation. The resistance to water permeation of NBR modified mortar is markedly improved with increase in the polymer-cement ratio.[119] The water permeability of dry-cured EVA modified mortars with blended cements has been studied.[120] In this investigation the time taken for a standard amount of water to be permeated into the specimen through a 10 mm diameter x 40 mm deep hole is measured. An increase in the measured parameter of EVA modified mortars with the blended cements indicates a decrease in water permeability and increasing polymer-cement ratio decreases the water permeability by a factor of 10 or more.

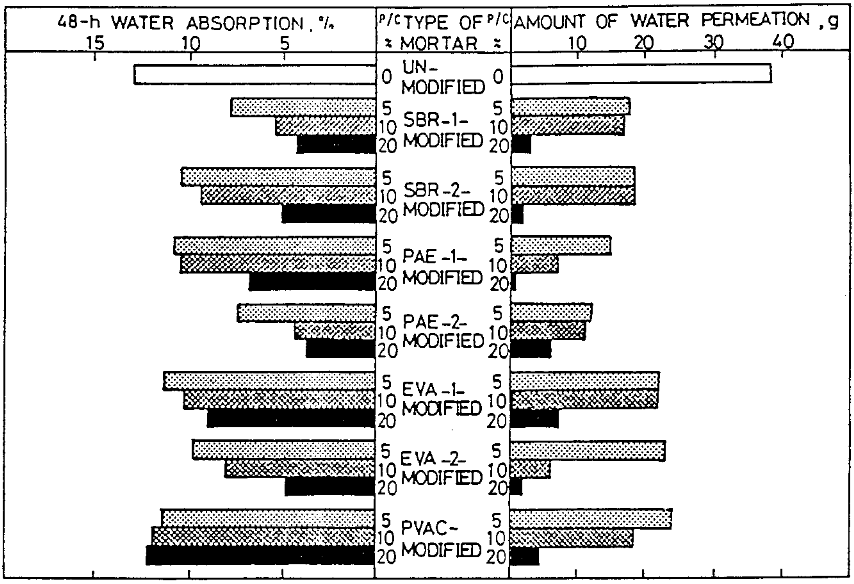


Figure 26. Water absorption and amount of water permeation of latex-modified mortars.

Figure 27[121] represents the water vapor transmission of latex modified mortars. The value decreases with increasing polymer-cement ratio.

Figures 28 and 29[122] show the effect of water absorption on the flexural and compressive strengths of latex modified mortars with a polymer-cement ratio of 0.2. In these figures, *dry* means 14-day cure and *wet* means water immersion after the dry cure. Most latex-modified mortars lose strength after immersion, especially with respect to the flexural strength.

Most latex-modified mortars however, regain strength after immersion in water and pose no problem in practice. Re-drying will usually allow the strengths to be recovered if irreversible chemical change in the polymer phase has not occurred. PVAC-modified mortars provide the poorest water resistance. This problem has been overcome by the use of copolymer modifiers.[116][118][123] In particular the EVA latex has been widely used for this purpose. The relation between the bound ethylene content and flexural and compressive strengths of EVA-modified mortars is demonstrated in Fig. 30.[124] The water resistance of EVA-modified mortars is improved at an optimum bound ethylene content of about 20%.

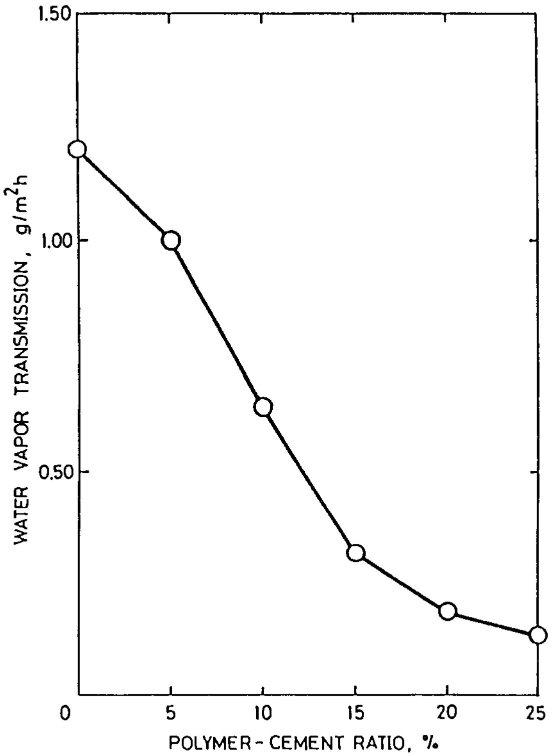


Figure 27. Effect of polymer-cement ratio on water vapor transmission of SBR-modified mortar.

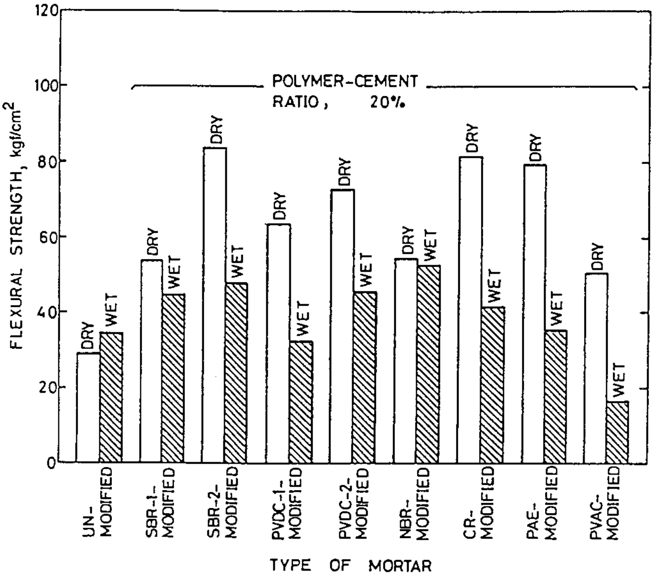


Figure 28. Effect of water absorption on flexural strength of latex-modified mortars.

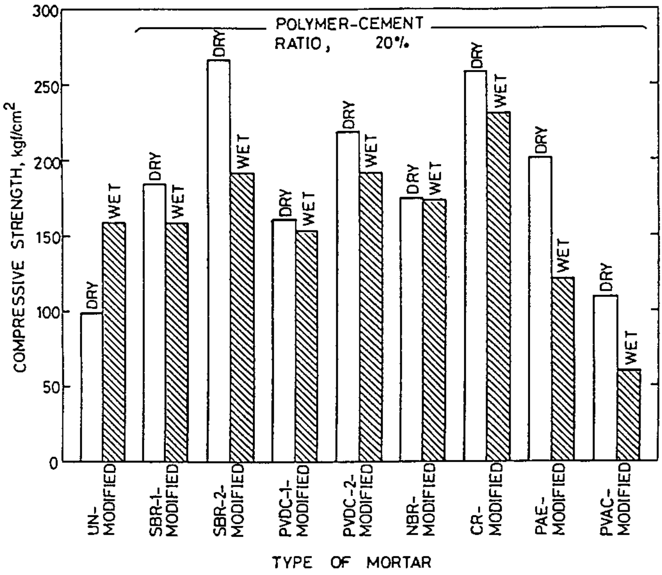


Figure 29. Effect of water absorption on compressive strength of latex-modified mortars.

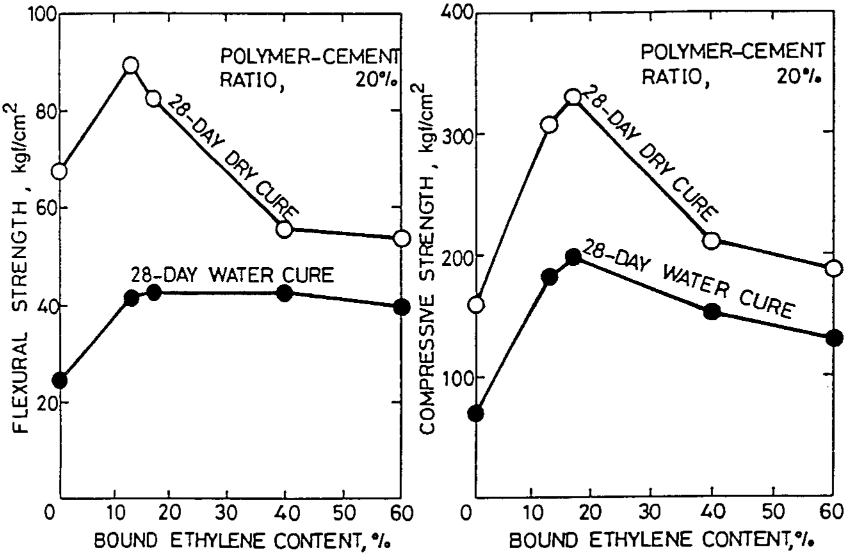


Figure 30. Relation between bound ethylene content and flexural strength and compressive strength of EVA-modified mortar.

6.12 Chemical Resistance

The chemical resistance of latex modified mortar and concrete depends on the nature of the polymer, polymer-cement ratio and the nature of the chemicals. Most latex modified mortar and concretes are attacked by inorganic or organic acids and sulfates because of the cement hydrates in them. They resist alkalis and salts except sulfates. Their chemical resistance is rated as good to fats and oils but poor to organic solvents.

Tables 15[125] and 16[126] give the resistance data of mortars using elastomeric and thermoplastic latexes respectively at a polymer-cement ratio of 0.2. In particular NBR modified mortar shows excellent resistance to organic solvents and oils, but NR based mortar does not resist these agents. Ordinary mortar fails on contact with rapeseed oil but most elastomeric and thermoplastic latex-modified mortars are resistant to it. The PVAC-modified mortar has low resistance to acids and alkalis but is stable to a great extent in organic solvents.[127]

Table 15. Chemical Resistance of Thermoplastic Latex-Modified Mortars with Polymer-Cement Ratio of 20%

Type of Chemicals	Concentration (%)	Weight Change (%)					Volume Change (%)				
		Type of Mortar					Type of Mortar				
		Un-Modified	SBR-Modified	EVA-Modified	PAE-Modified	PVDC-Modified	Un-Modified	SBR-Modified	EVA-Modified	PAE-Modified	PVDC-Modified
Sulfuric Acid	1	-8.8	-6.1	-2.2	-19.1	3.5	-17.0	-9.9	-6.6	-23.8	-2.1
Hydrochloric Acid	1	-50.0	-50.9	-48.4	-46.4	-47.9	-54.2	-52.5	-48.0	-48.2	-50.9
Nitric Acid	1	-38.6	-37.6	-34.0	-38.2	-38.6	-43.6	-40.0	-37.0	-41.1	-41.8
Acetic Acid	1	-21.1	-20.4	-21.6	-20.3	-22.7	-28.4	-23.5	-24.7	-24.1	-27.4
Lactic Acid	1	-9.3	-13.7	-13.6	-11.5	-10.1	-18.2	-17.5	-17.0	-16.4	-16.2
Sodium Hydroxide	45	6.2	-5.0	-4.7	-10.7	-1.1	-6.3	-5.5	-6.7	-9.4	-5.0
Sodium Sulfate	Sat.	12.1	4.5	3.7	4.6	7.7	-0.2	0.7	0.4	-0.3	0.1
Sodium Chloride	Sat.	10.2	-0.4	2.4	3.4	6.1	-0.5	-4.1	-1.2	-0.9	-0.9
Calcium Chloride	10	11.4	3.6	5.8	5.0	8.5	-0.4	-0.7	1.2	0.4	1.9
Ammonium Nitrate	10	1.5	-6.4	-6.7	-4.9	-8.3	-5.6	-6.7	-8.6	-8.1	-11.5
Sodium Carbonate	10	6.7	3.6	4.4	3.6	7.9	-3.1	-1.6	-0.9	-1.4	0.0
Methyl Ethyl Ketone	100	5.7	5.0	7.4	7.7	8.2	-5.8	-0.6	0.1	0.2	2.5
Xylene	100	5.3	2.3	5.5	3.1	9.8	-1.7	-2.8	-1.2	-0.5	-0.2
Rapeseed Oil	-	-100.0	2.7	6.1	5.3	7.4	-100.0	-1.2	1.0	-0.1	-0.3
Gasoline	-	3.6	0.8	0.9	1.9	0.7	-2.8	-1.5	-0.9	-0.7	-0.1
Heavy Oil	-	8.3	2.5	4.9	4.5	8.4	-2.1	-2.0	-1.4	-1.0	-0.9
Cane Sugar	Sat.	5.8	0.1	1.1	0.3	2.9	-3.4	-1.8	-1.4	-2.0	-1.8
Tap Water	-	6.9	5.1	7.4	7.8	7.1	-1.6	-0.5	-0.1	-0.3	0.1

Table 16. Chemical Resistance of Elastomeric Latex-Modified Mortars at a Polymer-Cement Ratio of 20%

Type of Chemicals	Concentration (%)	Weight Change (%)					Volume Change (%)				
		Type of Mortar					Type of Mortar				
		Un-Modified	SBR-Modified	CR-Modified	NBR-Modified	NR-Modified	Un-Modified	SBR-Modified	CR-Modified	NBR-Modified	NR-Modified
Sulfuric Acid	5	-38.8	-44.4	-80.9	-62.6	-86.1	-43.8	-46.9	-70.3	-64.1	-87.3
Hydrochloric Acid	5	-87.7	-77.8	-87.9	-76.7	-82.9	-89.1	-78.1	-89.1	-76.6	-84.4
Chromic Acid	5	-59.5	-52.8	-46.4	-48.4	-55.8	-75.0	-53.1	-48.4	-39.1	-57.8
Hydrofluoric Acid	5	-33.3	-27.6	-37.9	-27.0	-57.0	-37.5	-28.1	-40.6	-31.3	-57.8
Sulfurous Acid	6	-61.0	-25.4	-58.9	-60.5	-59.4	-60.9	-26.6	-57.8	-60.9	-59.4
Acetic Acid	5	-66.7	-42.1	-56.1	-	-44.3	-56.6	-43.8	-54.7	-	-43.8
Butyric Acid	5	-	-4.8	-	-	-	-	-6.3	-	-	-
	10	-52.5	-	-46.7	-42.5	-55.2	-68.8	-	-18.4	-57.8	-62.5
Lactic Acid	5	-	-23.8	-	-	-	-	-25.0	-	-	-
	20	-77.6	-	-63.7	-59.2	-72.7	-79.7	-	-65.6	-60.3	-73.4
Sodium Hydroxide	45	-13.0	-	0.0	0.0	-32.0	-21.8	-	0.0	0.0	-34.4
Sodium Sulfate	10	10.9	-	2.4	1.6	6.9	0.0	-	0.0	0.0	0.0
Magnesium Sulfate	Sat.	7.5	-	3.3	1.6	2.8	0.0	-	0.0	0.0	0.0
Ammonium Nitrate	50	2.4	0.0	-1.6	-1.6	4.5	0.0	0.0	0.0	0.0	0.0
Sodium Hydrogencarbonate	10	11.0	-	5.6	3.1	8.9	0.0	-	0.0	0.0	0.0
Sodium Chloride	Sat.	11.9	1.6	3.2	0.8	5.0	0.0	0.0	0.0	0.0	0.0
Benzene	100	7.4	-	0.8	2.4	48.5	0.0	-	0.0	0.0	68.8
Trichloroethylene	100	11.5	-	-100.0	3.9	101.8	0.0	-	-100.0	0.0	95.3
Rapeseed Oil	-	-100.0	0.0	0.0	0.8	3.9	-100.0	1.6	0.0	0.0	0.0
Gasoline	-	8.3	2.4	2.5	1.6	24.3	0.0	1.6	0.0	0.0	28.3
Kerosene	-	7.5	0.8	1.6	1.6	16.5	0.0	-3.1	0.0	0.0	15.6
Heavy Oil	-	7.3	-	0.8	1.6	1.9	0.0	-	0.0	0.0	0.0
Cane Sugar	50	8.1	-	1.6	0.8	0.9	0.0	-	0.0	0.0	0.0

6.13 Thermal Properties

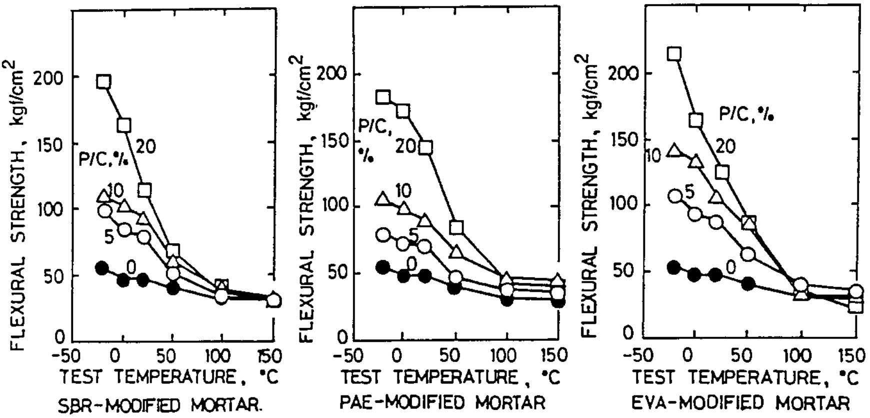
The latex modified mortars show rapid strength reduction on exposure to increased temperatures, especially at higher polymer-cement ratios.[94] The effect of temperature on flexural strength of SBR-, RAE- and EVA-modified mortars is plotted in Fig 31.[120] At 100–150°C, a difference in their strength at different polymer-cement ratios becomes smaller and the strength of the modified mortars is equal to or greater than that of the unmodified mortar. Most latex based mortars lose 50% or more of their strength at temperatures exceeding 50°C. On the other hand, their strength at less than 0°C is higher than that at 20°C.[129]

The thermal resistance of SBR-, RAE- and EVA modified mortars at 100–200°C has been studied by Ohama.[130] The flexural strength reaches a maximum at about 100°C even for a period of about 7 days. However, at 150–200°C it decreases sharply within a short period of heating and remains constant thereafter. Even after heating at 200°C, most latex-modified mortars with different polymer-cement ratios have strengths higher than those of unmodified mortar.

The incombustibility of latex mortar and concrete depends on the chemical composition of the polymers and polymer-cement ratio or polymer content. In Japan, the incombustibility of materials is evaluated as Grade 1 (incombustible), Grade 2 (semi-incombustible), Grade 3 (quasi-incombustible), and below this grade the material is not acceptable by JIS 1321. Most latex mortars have a Grade 1–3 rating except CR-modified mortars.[131] The mortars modified with chlorine-containing polymers, i.e., CR and PVDC, and PVAC give excellent incombustibility values. The incombustibility of the PVAC mortars is due to the action of a large amount of acetic acid which forms as a combustion product.[132] All the mortars with a polymer-cement ratio of 5% or lower exhibit Grade 1 rating.

6.14 Resistance to Chloride, Carbonation, and Oxygen Ingress

The pore structures of latex-modified mortar and concrete are influenced by the type of polymers in the latexes used and the polymer-cement ratio. Generally, latex in mortar and concrete reduces the large radii of 0.2 µm or more, and increases greatly the smaller radii of 75 nm or lower. The decreased porosity at higher polymer-cement ratio contributes to the improvements in impermeability and durability.



SBR-MODIFIED MORTAR. PAE-MODIFIED MORTAR EVA-MODIFIED MORTAR

Figure 31. Effect of temperature on flexural strength of latex-modified mortars.

Latex-modified mortar and concrete have a good water impermeability and thus provide the high resistance of the latex-modified mortar and concrete to chloride ion (Cl^-) penetration. Table 17[133] gives the apparent chloride ion diffusion coefficient of latex-modified mortars and concretes, in artificial sea water (NaCl content, 2.4%). The resistance to the chloride ion penetration of the latex-modified mortars and concretes is improved at an increasing polymer-cement ratio. A rapid test method developed by Whiting,[134] has widely been used in the United States and Canada. According to this test method, the chloride ion permeability of latex-modified concretes is determined by the total charge passed through the specimens, and evaluated by the required chloride ion permeability ratings. The test method has recently been published as ASTM C 1202 (Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration). Figure 32[132] represents the chloride ion permeability of five types of latex-modified mortars with a polymer-cement ratio of 15%, evaluated by the same method. Except for PVAC-modified mortar, the other four types of latex-modified mortars provide chloride ion permeability values in the moderate to low ranges. PVAC-modified mortar gives a high chloride ion permeability because of the hydrolysis of polyvinyl acetate. The chloride ion permeability of SBR-modified field concretes is very low regardless of the sampling locations, and significantly decreases with age.[136]

Table 17. Apparent Chloride Ion Diffusion Coefficient of Latex-Modified Mortars and Concretes

Type of Mortar	Polymer-Cement Ratio (%)	Apparent Chloride Ion Diffusion Coefficient (cm²/s)	Type of Concrete	Polymer-Cement Ratio (%)	Apparent Chloride Ion Diffusion Coefficient (cm²/s)
Un-Modified	0	6.4×10^{-8}	Un-Modified	0	2.2×10^{-8}
SBR-Modified	10 20	6.4×10^{-8} 3.9×10^{-8}	SBR-Modified	10 20	1.9×10^{-8} 9.3×10^{-9}
EVA-Modified	10 20	4.4×10^{-8} 2.4×10^{-8}	EVA-Modified	10 20	7.9×10^{-9} 1.0×10^{-8}
PAE-Modified	10 20	3.8×10^{-8} 4.4×10^{-8}	PAE-Modified	10 20	6.2×10^{-9} 5.8×10^{-9}

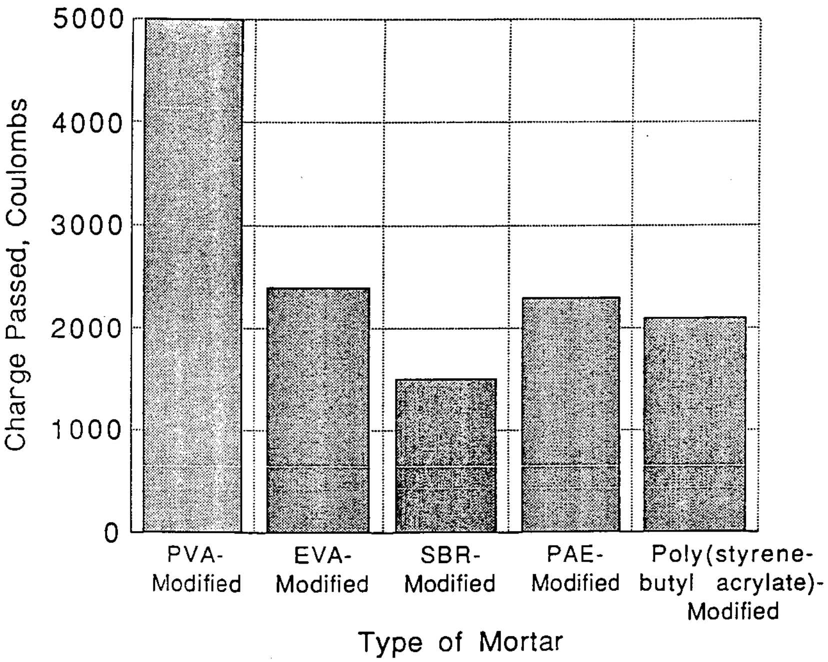


Figure 32. Chloride ion permeability of latex-modified mortars with polymer-cement ratio of 15%.

Marusin[137] determined the penetrated chloride ion content of acrylic and SBR-modified concretes by the potentiometric titration of chloride ions in the drilled powder from their specimens, and showed that both latex-modified concretes have similar performance in minimizing the penetration of chloride ions into them.

The effects of filling and sealing with polymers in latex-modified mortar and concrete are reflected in the reduced transmission of such gases as air, carbon dioxide (CO_2), oxygen (O_2) and water vapor, as well as increased water impermeability. The carbonation resistance of the latex-modified mortar and concrete is remarkably improved with an increase in polymer-cement ratio, depending on the type of polymers and carbon dioxide exposure conditions. The carbonation resistance is also the most important factor for the corrosion of reinforcing bars as well as the resistance to chloride ion penetration. Ohama and Demura[138] found that the carbonation depth of the latex-modified mortars through outdoor exposure can be predicted by the following equation as for ordinary cement mortar and concrete.

$$C = a(t + b)^{1/2}$$

where C is the carbonation depth of the latex-modified mortars, t is outdoor exposure period, a is carbonation rate coefficient, and b is an empirical constant.

Latex-modified mortar and concrete also have an excellent oxygen diffusion resistance, since they have an impermeable structure as stated above. Excellent oxygen diffusion resistance is found to contribute to the prevention of the rust formation in the corrosion of reinforcing bars in reinforced concrete structures.

In recent years, various latex-modified mortars or pastes have widely been used as repair materials for reinforced concrete structures because of their superior resistance to chloride ion penetration, carbonation and oxygen diffusion as mentioned above. Rust-inhibitors such as calcium nitrite [$Ca(NO_2)_2$] and lithium nitrite ($LiNO_2$) are often added to the latex-modified mortars or pastes to improve their corrosion-inhibiting property. Figure 33[139] represents the effects of polymer-cement ratio and calcium nitrite content on the corrosion rate of reinforcing bars embedded in the latex-modified repair mortars. The corrosion-inhibiting property of the latex-modified mortars as repair mortars for reinforced structures is considerably improved with rising polymer-cement ratio and calcium nitrite content. The corrosion-inhibiting property at low polymer-cement ratio is remarkably improved by the addition of calcium nitrite without increasing polymer-cement ratio.

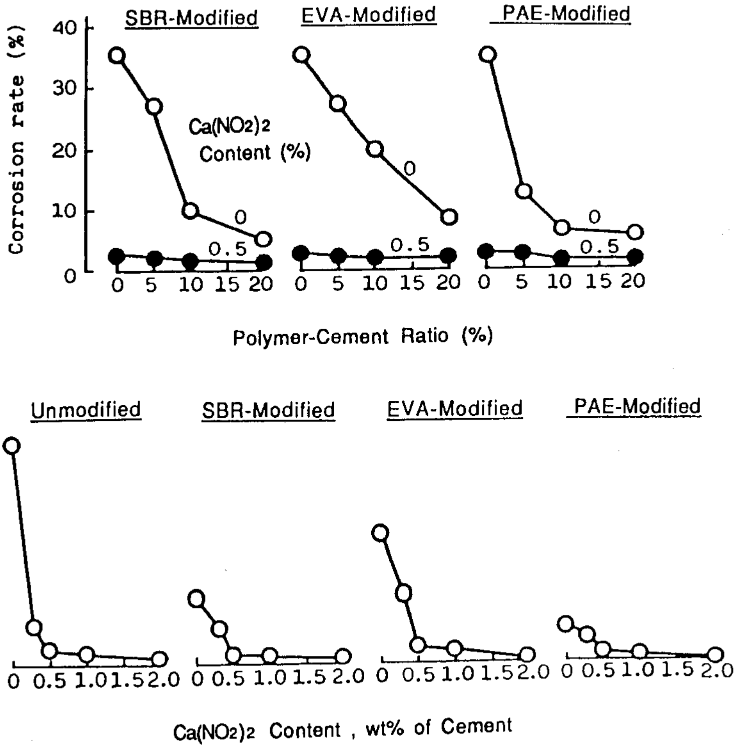
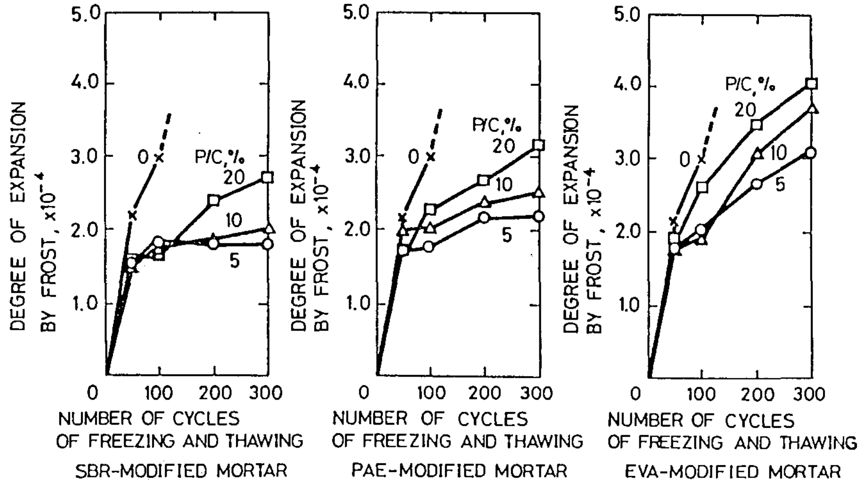


Figure 33. Effects of polymer-cement ratio and calcium nitrite content on corrosion rate of reinforcing bars embedded in latex-modified mortars with calcium nitrite.

6.15 Frost Resistance

Latex-modified mortar and concrete have improved resistance to freezing and thawing, compared to conventional mortar and concrete. This is due to the reduction of porosity as a result of decreased water-cement ratio and filling of pores by polymers, and the air entrainment introduced by polymer and surfactants. Figure 34 represents the freeze-thaw durability in water (-18 to 4°C) of combined water and dry-cured SBR- PAE- and

EVA-modified mortars.[140] The frost resistance of SBR-, EVA-modified mortars is improved significantly at polymer-cement ratios of 5% or more. As the degree of expansion by frost (calculated from the residual expansion of specimens after thawing) is increased, the relative dynamic modulus of elasticity of SBR-, PAE- and EVA-modified mortars is reduced. Increasing polymer-cement ratio of the latex-modified mortars does not necessarily cause an improvement in the frost resistance. Accordingly, such a good frost resistance should be caused by the composite effects of polymer modification and air entrainment. Field tests also confirm the increased resistance of latex-modified mortars to frost attack.



SBR-MODIFIED MORTAR PAE-MODIFIED MORTAR EVA-MODIFIED MORTAR

Figure 34. Number of cycles of freezing and thawing vs degree of expansion due to frost of latex-modified mortars.

According to the data of Solomatov[141] on latex-modified concrete using a copolymer of vinyl acetate and dibutyl maleate, the wet-cured concrete is more liable to be attacked than the dry-cured concrete.

A few studies on the frost resistance of latex-modified mortar and concrete have been conducted in chloride[142] and sulfate[141] solutions.

Figure 35[135] illustrates the weatherability of five types of latex-modified mortars with a polymer-cement ratio of 15%, assessed by measuring a flexural strength retention after 336 accelerated weathering (4-hour–

60°C–ultraviolet light plus 4-hour–50°C–100%-R.H. exposure) cycles. Generally, the latex-modified mortars provide the high retention of flexural strength. SBR- and PAE-modified mortars have a higher weatherability than the other latex-modified mortars.

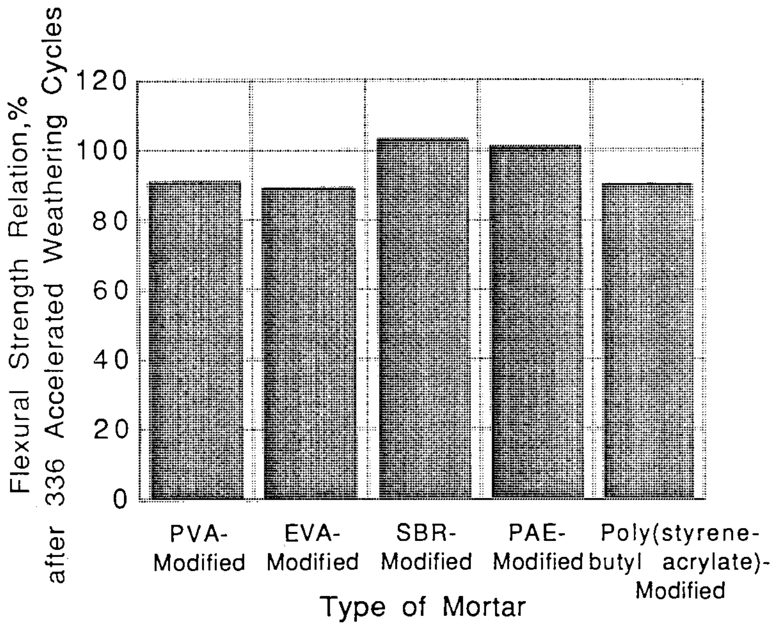


Figure 35. Weatherability of five types of latex-modified mortars with polymer-cement ratio of 15%.

In the early 1980s, the corrosion of structural steel supports due to chloride ions liberated from PVDC-modified mortar which had been used to repair an old brick building, led to a civil suit in the United States,[143] and therefore, PVDC latex is not currently used as a cement modifier in the United States and other countries. In a laboratory study, the liberation of chloride ions is observed in such a chloride-containing polymer, and a possibility of the corrosion of the reinforcing bars, induced by the chloride ions in reinforced concrete structures, is suggested.[144][145] The use of PVDC-modified mortars with polymer-cement ratios of 5% or more causes the liberation of sufficient chloride ions to exceed the tolerable corrosion limits for the reinforcing bars in reinforced concrete structures.

In the United States, SBR-modified concrete has been used as an overlay for highway bridge decks over the past 20 years, since its first application to a bridge deck in Virginia[146] in 1969. Sprinkel[147] investigated the performance of 14 bridge decks with SBR-modified concrete overlays ranging in age from 2 to 20 years, and reported that SBR-modified concrete overlays are performing satisfactorily compared to ordinary cement concrete overlays. In particular, when placed on decks, SBR-modified concrete overlays with chloride ion contents of less than 1.2 kg/m^3 at the reinforcing bars can be expected to have a service life exceeding 20 years.

7.0 REDISPERSIBLE POLYMER POWDER-MODIFIED SYSTEMS

7.1 Manufacture

The redispersible polymer powders are manufactured by two-step process. Initially, polymer latexes are made by emulsion polymerization, and then are spray dried. Before spraying, the latexes are formulated further with some ingredients such as bactericides, spray drying aids and antifoaming agents. Anti-blocking aids such as clays, silica, and calcium carbonate are added to the polymer powders during or after spray drying to prevent "caking" of the powders during storage.

7.2 Process Technology

It is similar to that used for the latex-modified mortar or concrete. At present they are classified as shown in Fig. 36. Table 18 gives the properties of typical redispersible polymer powders. These powders are usually free-flowing. When the powders are placed in water under agitation, they disperse or emulsify easily and provide the polymer latexes of particle sizes in the range of 1 to 10 μm.

Generally, these polymer powders are blended with cement and aggregate followed by wet mixing with water. During wet mixing, the redispersible polymers are redispersed or re-emulsified. If needed, powder or liquid antifoaming agents are added to the wet mix.

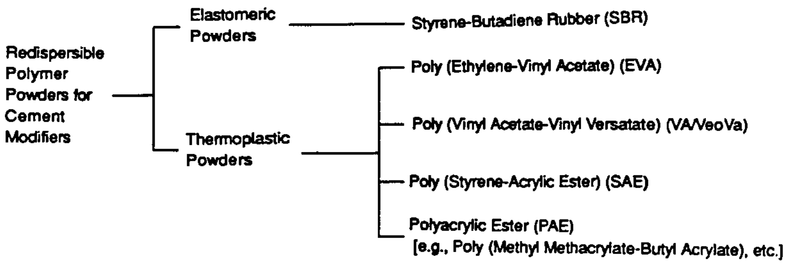


Figure 36. Commercially available redispersible polymer powders for cement modifiers.

Table 18. Properties of Typical Redispersible Polymer Powders

	Type of Redispersible Polymer Powder			
	VA/VeoVa	EVA	PAE	SBR
Appearance	White Powder	White Powder	White Powder	White Powder
Average Particle Size (μm)	10 - 250	70	45 - 75	5 - 50
Bulk Density (g/cm^3)	0.54 - 0.64	0.40	0.31 - 0.51	0.40
pH (redispersed, 50 % solids)	4	5 - 6	10 - 12	7 - 8

7.3 Properties

Similar to latex systems the redispersible polymers impart superior properties to mortar or concrete. These depend on the nature of the polymer and polymer-cement ratio. Figure 37[148] represents the strengths obtained with the powder modified mortars. The strengths are increased with the increase in the polymer-cement ratio. The redispersible polymer powder modified mortars are inferior to SBR modified mortars in some of the properties. The Va/Veo Va powder-modified mortars show better properties than EVA modified mortars. The film formation characteristics of recent powders as cement modifiers have been improved, and the continuous polymer films can be found in these systems. This results in better strength development.

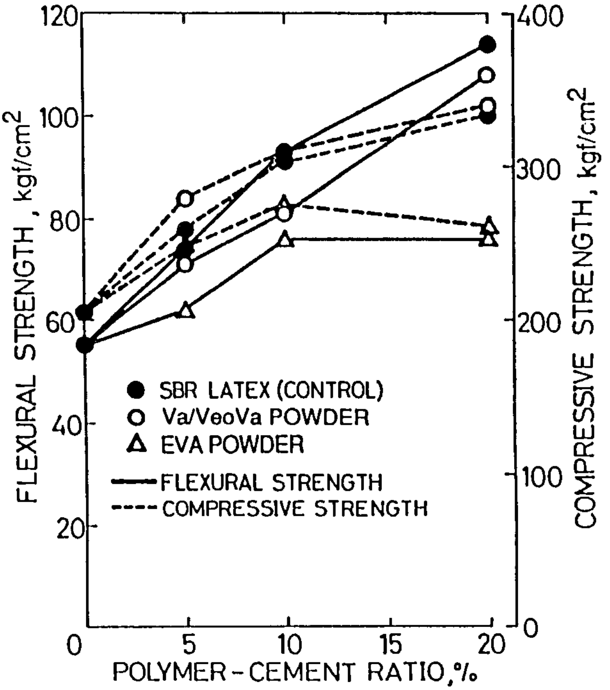


Figure 37. Polymer-cement ratio vs flexural and compressive strengths of redispersible polymer powder-modified mortars.

The physical properties of various latex-modified mortars and redispersible EVA powder-modified mortars have been compared and the results have shown that the properties of EVA systems are at least equal to those of the latex-modified mortars (Fig. 38).[149]

Lambe et al.[150]-[151] have reported that the redispersible polymer concrete shows high resistance to diffusion of chloride ions, oxygen and carbon dioxide and has also low shrinkage. According to Afridi et al.,[152] the redispersible polymer modified mortars provide a good freeze-thaw durability. Schneider[153] concluded that the EVA powder with a glass transition temperature of -10°C is more effective than the one with a glass transition temperature of 10°C with respect to adhesion to plywood and flexibility. These powder based mixtures are used to produce prepackaged-type products such as decorative wall coatings, ceramic tile adhesives, self leveling floor overlays and patching mortars for concrete structures.

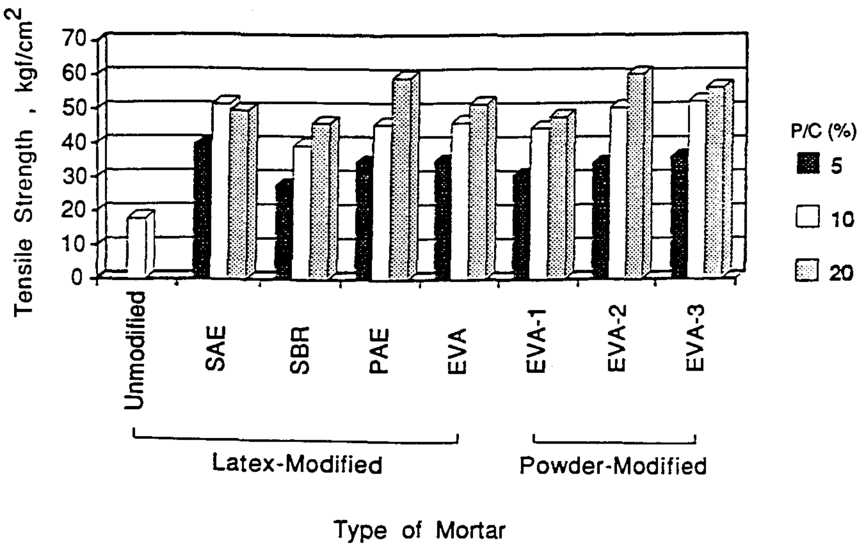


Figure 38. Comparison of tensile strength of latex- and redispersible EVA powder-modified mortars.

8.0 WATER SOLUBLE POLYMER- MODIFIED SYSTEMS

The mix proportions and other methods of fabrication of this system are similar to those adopted for normal mortar and concrete. Small amounts of polymer are added in the form of powders or aqueous solutions to cement mortar or concrete during mixing. When added in the powder form, it is advisable to dry-blend the polymers with the cement -aggregate mixtures and then to mix with water. Their main requirement is improvement of workability and normally a polymer-cement ratio of 3% is used. The water soluble polymers employed as cement modifiers are cellulose derivatives including methyl cellulose (MC), carboxymethyl cellulose (CMC) and hydroxyethyl cellulose (HEC), polyvinyl alcohol (PVA), polyethylene oxide, polyacrylamide, etc. The water-soluble polymer modified mortar and concrete are easy to handle during mixing, troweling or placing. No special curing is needed for this system.

8.1 Properties

Water soluble systems are generally used at a considerably low polymer-cement ratios for improved workability. This is due to the plasticizing effect of air entraining agents and plasticizing effects. This system shows high water retention with respect to the ordinary cement systems and the value increases with the polymer-cement ratio (Table 19).[154] Consequently superior adhesion to porous substrates such as ceramic tiles, mortars and concrete occurs. The setting time is generally increased.[155] In Table 20 the strength properties are given.[156] The tensile, flexural and compressive strengths are decreased with the addition of polymers.

The water absorption of methyl cellulose-modified system increases with the increase in the polymer-cement ratio. However, the water permeation decreases with the polymer-cement ratio. Methyl cellulose causes considerable swelling due to water absorption and seals capillary cavities in the modified systems and hence decreases permeability. The drying shrinkage is generally larger than that of the unmodified system.[156] However, methyl cellulose-modified systems exhibit lower drying shrinkage than the unmodified systems. This value decreases with the increase in the polymer-cement ratio.

Table 19. Properties of Methyl Cellulose-Modified Pastes and Mortars

		Polymer-Cement Ratio (%)	Water-Cement Ratio (%)	Water Retention (%)	Tensile Strength (kgf/cm²)	Adhesion to Tile (kgf/cm²)	Water Absorption (%)
Paste		0.0	56.0	84.2	25.4	2.5	8.2
		0.1	30.9	92.5	32.8	16.2	4.6
		0.2	31.2	96.4	32.1	20.1	4.8
		0.5	33.5	97.5	38.4	32.2	4.8
		1.0	38.0	99.1	35.1	23.1	6.1
Mortar	Cement : Sand =1 : 2	0.0	56.0	84.2	25.4	2.5	8.2
		0.2	76.2	96.3	21.2	6.5	12.1
		1.0	74.2	99.9	18.1	8.3	14.5
	Cement : Sand =1 : 3	0.0	85.0	73.2	14.3	1.6	10.9
		0.2	79.8	82.5	12.5	6.4	13.2
		0.5	80.8	93.1	11.2	6.6	12.8
		1.0	90.3	97.4	11.3	8.3	14.3

Table 20. Flexural and Compressive Strengths of Water-Soluble Polymer-Modified Mortars

Type of Mortar	Polymer-Cement Ratio (%)	Flexural Strength (kgf/cm^2)			Compressive Strength (kgf/cm^2)		
		3 Days	7 Days	28 Days	3 Days	7 Days	28 Days
Unmodified	0.00	26.9	43.8	69.6	112	223	408
Hydroxy Ethyl Cellulose-Modified	0.39	13.7	32.3	50.9	42	129	252
Poval-Modified (A)	0.39	23.0	33.4	48.5	78	128	223
Poval-Modified (B)	1.12	17.1	27.9	39.6	51	99	185
Polyacrylamide-Modified	0.46	22.3	36.8	62.3	80	170	320
Polyethylene Oxide-Modified	0.06	27.5	42.6	62.8	103	189	320

Cement : Standard Sand = 1:2 (by Weight)
Water-Cement Ratio = 65.0%
1-Day–20°C-Moist plus 27-Day–20°C-Water Cure

9.0 LIQUID RESIN-MODIFIED SYSTEMS

9.1 Epoxy-Modified Systems

Most liquid epoxy resins used as cement modifiers are synthesized by the reaction of one molecule of bisphenol with two molecules of epichlorohydrin, resulting in two functional groups, i.e., epoxide and hydroxyl. The epoxy resins react with hardeners or curing agents such as amines and polyamides, and harden to form the thermosetting polymers with network structures. In general, epoxy resin systems as cement modifiers are supplied as two-part systems which consist of epoxy resin, hardener, or curing agents with surfactants to disperse the resin in mortar or concrete. The antifoaming agents are added to prevent excessive air entrainment.

Process Technology. The first patent of an epoxy-modified system was taken by Donelly in 1965.[157] Valenta[158] carried out a detailed study on various emulsifiers. The mixing procedures were complicated at early stages of development, but now the incorporation of epoxy modifiers into mortars or concrete does not require any significant change in the process technology. The proportioning is similar to that adopted for the latex-modified systems.

The polymer-cement ratio of 15 to 20% is adequate.[159] The unit cement content of the epoxy-modified systems is generally in the range of

356 to 415 kg/m^3 and the water-cement ratio is about 30%.[159] In the epoxy-modified systems, cement, aggregates and half of the mixing water are mixed first, and then the epoxy resin-hardener premixture and the remainder of the mixing water are thoroughly mixed with the cement-aggregate-water mixture. The epoxy resin hardener premixture can be added to the ready mix concrete in the agitating trucks at the job site.

Properties. In epoxy-modified systems cement hydration and epoxy polymerization occur simultaneously. The hardened resin forms thin layers on the cement hydrate and binds the hydrates to form a network in which the epoxy phase interweaves throughout the cement hydrate phase. The aggregates are bound by the matrix. The structure is similar to that of the latex-modified system. The epoxy systems develop high strength and adhesion, and have low permeability, good water resistance, and chemical resistance. Table 21[160] compares the properties of typical epoxy-modified system with those of an unmodified concrete. A major advantage of this system is that it can be cured under moist or wet conditions.

Table 21. Properties of a Typical Epoxy-Modified Concrete in Comparison with those of an Unmodified Concrete

Property	Type of Concrete	
	Epoxy-Modified Concrete	28-Day Water-Cured Unmodified Concrete
Tensile Strength (kgf/cm^2)	57.6 (51.3)[a]	30.9 (32.3)[a]
Flexural Strength (kgf/cm^2)	115 (114)[a]	59.8 (60.5)[a]
Compressive Strength (kgf/cm^2)	527 (492)[a]	387 (429)[a]
Modulus of Elasticity (kgf/cm^2)	19.0×10^4	21.8×10^4
Shear Strength (kgf/cm^2)	45.0	7.03
Setting Shrinkage (%)	0.03	---
Coefficient of Linear Thermal Expansion (cm/cm/°C)	1.4×10^{-5}	1.1×10^{-5}
Resistance to Freezing and Thawing	No effect at 50 cycles	Pronounced scaling at 20 cycles
Wear Resistance (steel wheel passes necessary for 1cm wear)	7700	2400
Chemical Resistance (water, 5% NaOH, bleach, or detergent)	Very gradual penetration	Rapid penetration
(15% hydrochloric acid, 10% citric acid, or 25% acetic acid)	Slow effervescence	Rapid disintegration

[a] Strength after 28-day water immersion.

Popovics[161] suggested the use of accelerators in epoxy systems, and found that the strength reduction that occurs can be countered by an accelerator. The addition of fly ash, silica fume and superplasticizers to these systems improves their strength. Some developments have been reported on epoxy systems in Germany. They include a one-component epoxy resin system for the cement modifier,[162] and a dry mortar using epoxy resin. The former does not need a hardener. The latter is produced as a dry mixture of an epoxy resin with a hardener, cement and aggregates and can be applied by adding only water in the field.

Recently, Ohama et al. have determined that the hardening can be accomplished in the epoxy system by the alkalis present in cement.[163][164] According to a recent study, the epoxy-modified mortars can be made without the hardeners, with superior properties to those obtained with conventional epoxy mortars. Figure 39 shows the development of flexural strength as a function of the polymer-cement ratio in the system with and without the hardener.[165]

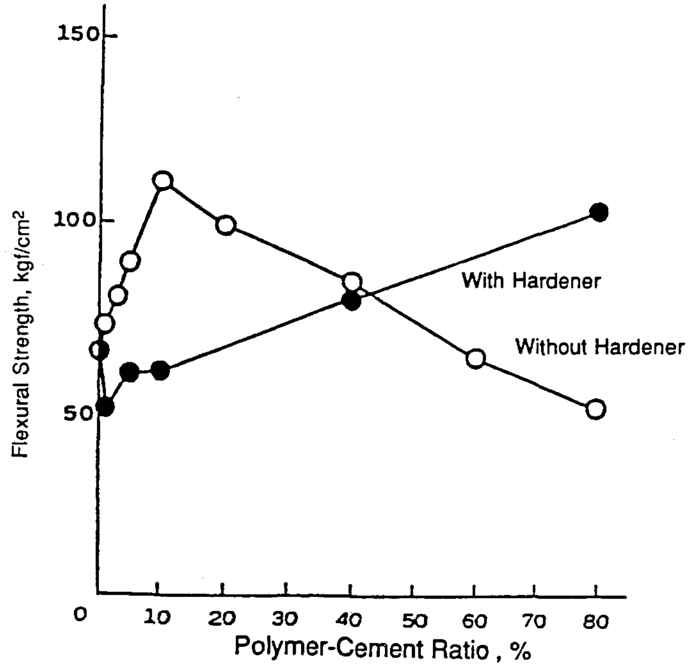


Figure 39. Polymer-cement ratio vs flexural strength of epoxy-modified mortars without and with hardener.

9.2 Polyester Modified Systems

An unsaturated polyester-modified system called "Estercrete" was developed by Nutt.[166]-[167] In this system, unsaturated polyester resin dissolved in styrene is mixed with portland cement at a polymer-cement ratio higher than 0.3, together with a water soluble redox catalyst. Table 22 gives the typical formulations for Estercrete. The resin is produced by condensation of polyhydroxy acids with polyhydrolic alcohols. The optimum water requirement is about 22%.

Estercrete sets rapidly, develops higher strength, including better bond strength to concrete and better durability including water resistance, chemical resistance, abrasion resistance, and thermal resistance in comparison with those provided by the latex-modified systems. The strengths of Estecrete using typical mix proportions are given in Table 23.[168] Similar systems have been examined by Dikeou, Stenberg et al.,[169] Samy El-Garf,[170] Birkimer and Lineman,[171] and Ye and Wu.[172]

Table 22. Typical Formulations of Estercrete for Mortar Coating

Material	Parts by Weight
Polyester Resin	50-70
Unsaturated Monomer (styrene)	25-65
Powdered Ammonium Persulfate	3-5
Powdered Sodium Bisulfite	1-3
Portland Cement (with stearic acid)	80-150

Table 23. Strength of Estercrete Mortar

Age (days)	Compressive Strength (kgf/cm^2)	Tensile Strength (kgf/cm^2)
1	175	28
7	262	38
14	280	40
28	350	44

9.3 Polyurethane- Modified Systems

The first patent of a polyurethane-modified system was taken by Szukiewicz.[173] A system modified with a polyurethane resin was patented by Shearing.[174] Ohama studied a wide range of polyurethane-modified mortar.[175] The product consists of a promoter, polyol and polyisocyanate. The preparation is as follows: cement and sand are dry blended, the promoter component is added to the cement-sand mixture, and then the polyol component is blended with the mixture. Finally the polyisocyanate is mixed with the cement-sand promoter polyol mixture until a uniform mortar is obtained.

The main advantage of this system is an improvement in strength at low temperature or under wet conditions, good adhesion to wet substrates, waterproofness and abrasion resistance. The properties of polyurethane-modified mortar are shown in Table 24.[175]

Table 24. Properties of a Typical Polyurethane-Modified Mortar in Comparison with those of an Unmodified Mortar

Property	Type of Mortar	
	Polyurethane-Modified Mortar	Unmodified Mortar
Flexural Strength (kgf/cm^2)	174 (205)[a]	44 (47)[a]
Compressive Strength (kgf/cm^2)	381 (412)[a]	157 (247)[a]
Tensile Strength (kgf/cm^2)	76	19
Modulus of Elasticity (kgf/cm^2)	5.25×10^4	32.8×10^4
91-Day Drying Shrinkage	8.92×10^{-4}	12.5×10^{-4}
Relative Water Absorption	0.03	1.00
Relative Water Permeation	0.01	1.00
Adhesion in Flexure (kgf/cm^2)	53	28

[a] Water cure.

9.4 Other Resin-Modified Systems

Systems modified with thermosetting resins such as phenol formaldehyde and urea formaldehyde (carbamide) resins have been developed by Russian workers but they have not been commercialized.[176]

9.5 Monomer-Modified Systems

These systems are directly prepared by mixing the monomers with cement, aggregate and water, followed by thermal-catalytic or radiation polymerization process. The polymerization occurs during and/or after the setting or hardening of the cement. The polymerization process converts the monomer-modified system to polymer-modified system. The compressive strength development of the polymer-modified system using monomers has been summarized in Table 25. Improvements in strength are generally low and are related to the interference effects of monomers on cement hydration. These systems are not yet commercialized. In Russia, Leirikh[181] has reported that concrete modified with furfuryl alcohol and aniline hydrochloride provides pronounced improvements in tensile and flexural strengths, bonding to reinforcement, water tightness, chemical resistance and durability. It is reported that the use of furfuryl alcohol in concrete contributes only a small extent to the strength properties.[182][183]

Table 25. Compressive Strength of Polymer-Modified Concretes Using Monomers

		Compressive Strength (kgf/cm²)						
Curing Method		R[a]	R	T[b]	R	T	R	T
Polymer-Cement Ratio (%)		25-30	20	20	5	5	10	10
Type of Monomer-Modified Concrete	Unmodified (Control)	269	550	550	372	280	496	509
	Methyl methacrylate-Modified	[c]	360	291	399	294	433	380
	Styrene-modified	300	756	707	328	311	499	401
	Acrylonitrile-modified	462	-	-	374	263	-	-
	Vinyl acetate-modified	-	-	-	287	207	-	-
	Polyester-styrene-modified	-	-	-	140	76	-	-
Reference No.		(31)	(32)	(32)	(33)	(33)	(34)	(34)

[a] Radiation.

[b] Thermal-catalytic.

[c] No test due to premature failure.

10.0 SPECIAL POLYMER-MODIFIED SYSTEMS

10.1 Hydrated-Type Flexible Waterproofing Materials

Hydrate-type flexible waterproofing materials are polymer-modified pastes or slurries with very high polymer-cement ratios of 50% or more, sometimes reaching 100% and have been used widely as liquid-applied membrane waterproofing materials, repair materials, etc.[178]-[181] These materials consist of portland cement, silica sand, polymer latexes such as SBR, PAE, EVA, SAE, epoxy and asphalt latexes, water, and various other additives. Some of the advantages that these materials provide include, safer application because of the lack of organic solvents, avoidance of precautions about moisture conditions of the substrates, excellent elongation, flexibility and crack resistance, and good waterproofing and chemical resistance characteristics.

PAE-modified waterproofing materials appear to have an excellent elongation and water resistance. The crack bridging capacity of flexible waterproofing materials, an important performance requirement, has been extensively studied in Germany.[182] These waterproofing materials are currently being used for inhibiting alkali-aggregate expansion reaction in concrete.[183] Recently, Moriyashi et al.[184] have developed a material that solidifies in water. This material has potential applications as shock absorbing, waterproof backfilling operations in dams and tunnels. The material contains asphalt emulsion, a superabsorbent polymer emulsion and cement.

10.2 Ultrarapid-Hardening Polymer-Modified Concrete

Ultra-rapid-hardening polymer-modified concrete may be classified into two types: a shotcrete system containing an ambient temperature polymerizable monomer which reacts with normal portland cement, and another system using ultra-rapid-hardening cement. The former is prepared by mixing concrete with magnesium acrylate monomer, and the setting time can be controlled within a few seconds. The shotcrete system is employed for repair and protective purposes for concrete which is leaking.[185] The latter is produced by modifying ultra-rapid-hardening cement concrete with SBR latex and it is used for repair purposes.[186] Figure 40 shows the relationship between polymer-cement ratios and the tensile and flexural strengths of the ultra-rapid-hardening SBR modified concrete.[186]

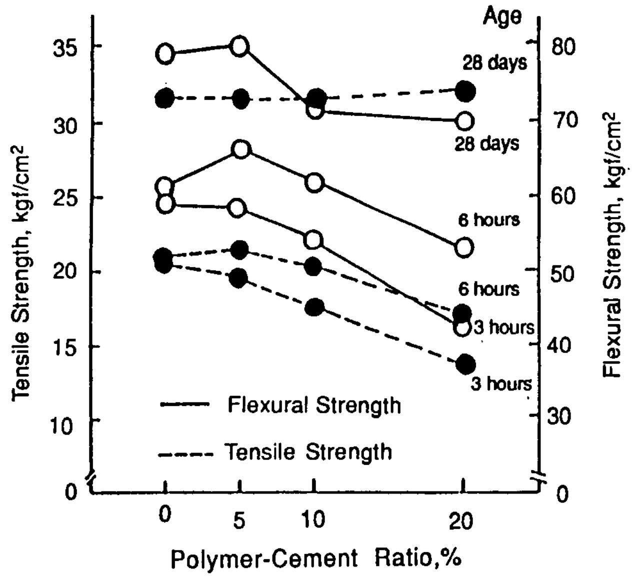


Figure 40. Relation between polymer-cement ratio and tensile and flexural strength of ultrarapid-hardening SBR-modified concretes.

10.3 Polymer-Ferrocements

Ferrocements are composite materials consisting of cement mortar and reinforcement in the form of multiple layers. The ferrocements are used for housing units, water tanks, roofing, and grain silos because of their superior toughness, crack controlling and impact resistance qualities. However, they easily form cracks under low loads because the cement mortar with low strength has conventionally been used as a matrix. Much of the improvement in mechanical properties and durability is affected by using latex-modified mortars in place of normal cement mortars. The use of SBR and EVA modified mortars is very effective in improving drying shrinkage and durability.[189]-[190] Incorporation of short steel or carbon fibers into the latex-modified mortars is also effective in enhancing their flexural behavior.

10.4 MDF Cements

One of the applications of water soluble polymers is in the fabrication of MDF (macrodefect-free) cement. MDF cements are composed of hydraulic cement, water soluble polymer (such as PVA and polyacrylamide) and admixtures. They contain large amounts of polymers and fabricated at low w/c ratios of 0.10 to 0.20. The flexural strength attains a value of 1000 kgf/cm^2, but the cement has poor water resistance. Treatments with latex, coupling agents, impregnation with polymer, cross linkage with an isocyanate and silica fume have been tried to improve water resistance, with little success.[191]-[195] Hence, MDF cement has not been used widely. The polymer modification of DSP (densified system containing homogeneously mixed ultrafine particles) material has also been used for increasing its mechanical properties.[196] The water resistance of MDF cement could be enhanced by using alumina cement and an autoclave treatment.[197]

10.5 Antiwashout Underwater Concrete

In concrete structures in harbors, bridges, and in marine environments, placement under water becomes necessary. The important requirements of concrete for such applications are antiwashout capability, segregation resistance, flowability, self leveling characteristics and lower bleeding. The antiwashout admixtures are produced by the addition of polymeric admixtures at a polymer-cement ratios of 0.2 to 2.0% for improving antiwashout properties of the concrete. These admixtures are water soluble polymers, and classified under two groups: cellulose types such as MC and HEC, and polyacrylamide-types such as polyacrylamide and polyacrylamide-sodium acrylate. Table 26 shows the properties of the antiwashout underwater concretes containing typical antiwashout admixtures.[198]

10.6 Artificial Wood

In Japan, calcium silicate-SBR latex glass fiber-based composites[199] or portland-cement–fly-ash–SBR-latex carbon fiber-based composites[200] have recently been researched for fabricating artificial wood. The artificial wood has lower strengths than the natural wood.[199] The compressive strength is only about 25% of that of the natural wood.

10.7 Composite Cement Modifiers

There have been some attempts to use polymer latexes with chemical admixtures such as superplasticizers,[201] alkyl alkoxy silane,[202] and amino alcohol derivative[203] for achieving certain benefits. Attempts have been made to inhibit alkali-aggregate expansion reaction with chemical admixtures and SBR latex.[204]

Table 26. Properties of Antiwashout Underwater Concretes Using Typical Antiwashout Admixture

Property		Type of Antiwashout Admixture	Cellulose Type (MC)	Hydroxyethyl Cellulose Type (HEC)	Polyacrylamide Type
Slump-Flow (cm)	In Air	After Mixing	48.5	51.0	50.0
		30 min after Mixing	48.0	52.0	47.5
	Underwater	After Mixing	47.5	52.0	46.5
Air Content (%)			3.0	2.6	2.1
Setting Time (h : min)		Initial Set	13:20	16:40	12:46
		Final Set	15:58	19:58	15:09
Segregation	pH		10.9	11.0	11.7
	Suspensoid Content (mg/l)		22	31	211
Compressive Strength (kgf/cm^2)	Age : 7 Days	Underwater	227	219	211
		In Air	249	252	250
		Control	254	252	268
	Age : 28 Days	Underwater	336	322	298
		In Air	368	361	374
		Control	372	360	384
Compressive Strength Ratio	Age 7 Days	Underwater / In Air	0.91	0.87	0.85
		Underwater / Control	0.90	0.87	0.79
	Age : 28 Days	Underwater / In Air	0.91	0.89	0.80
		Underwater / Control	0.91	0.90	0.78

11.0 STANDARDS AND SPECIFICATIONS

Polymer-modified mortars and concretes incorporating various polymer latexes, redispersible polymer powders, water soluble resins, epoxy resins, etc., have been used widely. Standardization work on their test methods and quality requirements has been in progress in the US, Japan, UK and Germany. Tables 27 and 28 provide JISs (Japanese Industrial Standards) and BSs (British Standards) on polymer-modified mortars. Table 29 lists the JCI (Japan Concrete Institute) Standards for Test Methods for Polymer-Modified Mortars made in Japan. In addition, Table 30 shows standard specifications and guidelines for polymer-modified mortars and concretes which are prevalent in USA, Germany and specified by RILEM.

Table 27. JISs for Polymer-Modified Mortars

JIS A 1171	Method of making test sample of polymer-modified mortar in the laboratory
JIS A 1172	Method of test for strength of polymer-modified mortar
JIS A 1173	Method of test for slump of polymer-modified mortar
JIS A 1174	Method of test for unit weight and air content (gravimetric) of fresh polymer-modified mortar
JIS A 6203	Polymer dispersions for cement modifiers
JIS A 6906	Wall coatings for thin textured finishes
JIS A 6910	Multi-layer wall coatings for glossy textured finishes
JIS A 6915	Wall coatings for thick textured finishes
JIS A 6916	Cement filling compounds for surface preparation
JIS A 6917	Lightweight aggregate coating materials

Table 28. BSs for Concrete-Polymer Composites (Including Polymer-Modified Mortars)

BS 6319	Testing of resin compositions for use in construction
BS 6319 ; Part 1 : 1983	Method for preparation of test specimens
BS 6319 ; Part 2 : 1983	Method for measurement of compressive strength
BS 6319 ; Part 3 : 1983	Method for measurement of flexural strength
BS 6319 ; Part 4 : 1984	Method for measurement of bond strength (slant shear method)
BS 6319 ; Part 5 : 1984	Method for determination of density of hardened resin compositions
BS 6319 ; Part 6 : 1984	Method for determination of modulus of elasticity in compression
BS 6319 ; Part 7 : 1985	Method for measurement of tensile strength
BS 6319 ; Part 8 : 1984	Method for the assessment of resistance to liquids

Table 29. JCI Standards for Test Methods for Polymer-Modified Mortars

(1)	Method of test for setting time of polymer-modified mortar
(2)	Method of test for tensile strength of polymer-modified mortar
(3)	Method of test for shear strength of polymer-modified mortar
(4)	Method of test for flexural strength and flexural toughness of polymer-modified mortar
(5)	Method of test for adhesion of polymer-modified mortar
(6)	Method of test for adhesion durability of polymer-modified mortar after warm-cool cycling
(7)	Method of test for impact resistance of polymer-modified mortar
(8)	Method of test for abrasion resistance of polymer-modified mortar
(9)	Method of test for resistance of polymer-modified mortar to rapid freezing and thawing
(10)	Method of test for incombustibility of polymer-modified mortar
(11)	Method of test for resistance of polymer-modified mortar to accelerated carbonation
(12)	Method of test for chloride ion penetration depth of polymer-modified mortar
(13)	Method of test for compressive strength and modulus of elasticity of polymer-modified mortar
(14)	Method of test for thermal expansion of polymer-modified mortar
(15)	Method of test for bond of polymer-modified mortar to reinforcing bar
(16)	Method of test for chemical resistance of polymer-modified mortar
(17)	Method of test for corrosion-inhibiting property of polymer-modified mortar

Table 30. Standard Specifications and Guides for Polymer-Modified Mortars and Concretes in U.S., Germany, and RILEM

Institution or Organization	Standard Specification or Guide
American Concrete Institute (ACI)	ACI 548.IR-92 Guide for the Use of Polymers in Concrete (1992) ACI 548.4 Standard Specification for Latex-Modified Concrete (LMC) Overlays(1992) ACI 546.1R Guide for Repair of Concrete Bridge Superstructures (1980) ACI 503.5R Guide for the Selection of Polymer Adhesives with Concrete (1992)
The Federal Minister for Transport, The Federal Länder Technical Committee,Bridge and Structural Engineering (West Germany)	ZTV-SIB Supplementary Technical Regulations and Guidelines for the Protection and Maintenance of Concrete Components (1987) TP BE-PCC Technical Test Regulations for Concrete Replacement Systems Using Cement Mortar/Concrete with Plastics Additive (PCC) (1987) TL BE-PCC Technical Delivery Conditions for Concrete Replacement Systems Using Cement Mortar/Concrete with Plastics Additive (PCC) (1987)
Architectural Institute of Japan (AIJ)	Guide for the Use of Concrete-Polymer Composites (1987) JASSs (Japanese Architectural Standard Specifications) Including the Polymer-Modified Mortars JASS 8 (Waterproofing and Sealing) (1993) JASS 15 (Plastering Work) (1989) JASS 18 (Paint Work) (1989) JASS 23 (Spray Finishing) (1989)
International Union of Testing and Research Laboratories for Materials and Structures (RILEM)	Recommended Tests to Measure the Adhesion Properties between Resin Based Materials and Concrete (1986)

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10

Mineral Admixtures

R. Paul Lohtia and Ramesh C. Joshi

1.0 INTRODUCTION

Mineral admixtures refer to the finely divided materials which are added to obtain specific engineering properties of cement mortar and concrete. The other, equally important, objectives for using mineral admixtures in cement concrete include economic benefits and environmentally safe recycling of industrial and other waste by-products. Unlike chemical admixtures, they are used in relatively large amounts as replacement of cement and/or of fine aggregate in concrete. Mineral admixtures are mostly pozzolanic materials. Sometimes these admixtures may also possess self cementitious properties in addition to being pozzolanic. These admixtures are available in abundance at a much lower cost compared to chemical admixtures. In the past, natural pozzolans such as volcanic earths, tuffs, trass, clays, and shales, in raw or calcined form, have been successfully used in building various types of structures such as aqueducts, monuments and water retaining structures. Natural pozzolans are still used in some parts of the world. However, in recent years, many industrial waste by-products such as fly ash, slag, silica fume, red mud, and rice husk ash are rapidly becoming the main source of mineral admixtures for use in cement and concrete.

Mineral admixtures are incorporated in portland-cement mortar and concrete, either in the form of blended cements, such as portland pozzolan or portland blast furnace slag cements, or directly added as admixtures to the concrete at the time of mixing. In Asia and Europe, large quantities of blended portland cements containing pozzolanic and cementitious additives are commercially produced for use by the concrete industry. However, in North America, industrial by-products particularly fly ash, blast furnace slag and condensed silica fume, are used directly as mineral admixtures in concrete rather than as constituents of blended cements. Industrially developed countries such as the USA, the former USSR (Commonwealth of Soviet Countries), France, Germany, Japan and U.K. are among the largest producers of fly ash, granulated blast furnace slag and condensed silica fume. In rice producing countries such as China and India, there is a promising potential of generating large quantities of rice husk or rice hull ash. Another industrial by-product which can be used as mineral admixture is calcined red mud, a waste material obtained from the aluminum extraction industry.

Vast quantities of industrial by-products, which have been found suitable for use as mineral admixtures in cement and concrete, are produced every year. These waste by-products must be effectively disposed to eliminate air, soil, and surface, as well as ground water, pollution at added cost to the industry and thus to the society. Their utilization as mineral admixtures in cement and concrete transforms a costly liability into an economical proposition. Furthermore, the costs and environmental problems associated with their disposal are minimized or eliminated. Land requirements for disposal sites are considerably reduced.

The mineral admixtures are generally used as partial replacement of portland cement, an expensive and energy intensive material. Therefore, utilization of mineral admixtures leads to considerable saving in cost and energy consumption. Utilization of increased volumes of industrial by-products as mineral admixtures in cement and concrete will lead to conservation of energy and natural resources. Bulk quantities of some industrial by-products, such as fly ash, bottom ash, and slag have been used as aggregates for concrete, and for road embankment as well as subbase construction, but such bulk uses represent low value applications. On the other hand, their use as mineral admixtures in cement and concrete due to their pozzolanic and cementitious properties represents high value applications.

Addition of mineral admixtures, particularly finely divided pozzolanic and cementitious materials, can affect the properties of cement mortar/concrete both in fresh and hardened state. In fresh or plastic state, mix proportions, water requirement for specified consistency, setting characteristics, workability including cohesiveness and bleeding, and heat of hydration are some of the properties influenced by mineral admixtures. In the hardened state, the rate of strength development and ultimate strength, permeability, durability against frost attack, sulfate attack, alkali silica reaction, carbonation, and resistance to thermal cracking are significantly affected with the incorporation of mineral admixture in cement concrete. Over the years, extensive research has been conducted all over the world to investigate the effect of mineral admixtures on properties of cement mortar/concrete. The list of references given at the end of this chapter, by no means comprehensive, manifests the research and development related to the use of industrial by-products as mineral admixtures by the cement and concrete industry. Several extensive review papers have also been published on the use of natural pozzolans in cement and concrete.[1][2][7][113][116][117]

Of the various industrial by-products fly ash, a finely divided glassy material, generated from combustion of pulverized coal in modern power plants, is the most abundant. The present rate of production of fly ash in the world is estimated to be about 500 million tons per year. Most use, and therefore, most research, has been on fly ash as a mineral admixture in concrete. ASTM standards C618 and C311, as well as other related standards, define fly ash acceptability for certain uses, primarily in concrete. Different standards are used in several countries for the use and testing of fly ash as mineral admixture in concrete to suit the local conditions.

Natural pozzolans and industrial by-products are generally available at substantially lower costs than portland cement. They are generally finer than cement and possess pozzolanic and sometimes cementitious properties. Thus their use as partial replacement for cement can lead to considerable cost savings in addition to the possible benefits such as improved workability, reduced bleeding and heat of hydration, enhanced ultimate strength, impermeability and chemical durability, and improved resistance to thermal cracking.

Granulated blast furnace slag, a waste by-product from metallurgical furnaces producing pig iron, and low calcium fly ash resulting from the burning of anthracite and bituminous coal, have long been used as portland cement additives or mineral admixtures in concrete. With the recent developments and availability of many additional by-products such as high calcium fly ash, condensed silica fume, granulated nonferrous slags, rice husk ash, and calcined red mud, the use of mineral admixtures in concrete has become more complicated and needs to be treated as a separate unified discipline rather than linked to concrete technology in a fragmented manner. This chapter is based on critical review of the recent published literature on the use of pozzolanic and cementitious by-products, with particular emphasis on fly ash as mineral admixture for cement and concrete.

2.0 CHARACTERIZATION AND CLASSIFICATION OF MINERAL ADMIXTURES

Most of the mineral admixtures are only pozzolanic. All natural pozzolans, whether raw or calcined, and some industrial by-products such as low calcium fly ash, rice husk ash, silica fume, and calcined red mud fall in this category. Mineral admixtures such as high calcium fly ash, and granulated slags containing 10% to 40% analytical CaO, are both pozzolanic and cementitious. Studies by Joshi indicate that some fly ashes containing less than 15% calcium oxide also exhibit self hardening cementitious properties besides pozzolanic activity.[57][44]

According to ASTM C618 "Standard Specification for Fly Ash and Raw or Calcined Natural Pozzolan for use as a Mineral Admixture in Portland Cement Concrete," pozzolans are defined as "Siliceous and aluminous materials which in themselves possess little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties." When pozzolans are used in combination with portland cement, calcium hydroxide liberated from the hydration of portland cement reacts with the alumino silicates present in the pozzolans to form cementitious compounds possessing cohesive and adhesive properties. These calcium alumino-silicate hydrates are also termed as pozzolanic reaction products and are very similar to the hydration products of portland cement, but pozzolanic reactions are much slower than cement hydration reactions.

Mehta[97] contends that in case of high calcium fly ashes and slags, a part or all of the calcium becomes available as free lime for the pozzolanic reaction and thus the material becomes self cementing. The authors have determined that free lime in high calcium fly ashes is no more than that in low calcium fly ashes. Nonetheless, x-ray analysis and strength tests on compacted moist ash samples suggest that anhydrite in the ash is primarily responsible for self hardening of high calcium ashes. The degree of self hardening of ashes varies significantly. The reasons for such variations are not understood as yet. Therefore, self hardening mineral admixtures can no longer be considered merely as pozzolans per the classical definition of *pozzolans.*

ASTM C618-89 categorizes the mineral admixtures into the following three classes:

- Class N: Raw or calcined natural pozzolans such as some diatomaceous earths, opaline cherts and shales, clays and shales, tuffs and volcanic ashes or pumicites. Calcined kaolin (clay) and laterite (shale), recently researched pozzolans fall in this category.
- Class F: Fly ash normally produced from burning bituminous coal. This class of fly ash has pozzolanic properties.
- Class C: Fly ash normally produced from lignite or subbituminous coal. This class of fly ash has both pozzolanic and some self cementitious properties. Some Class C fly ashes may contain lime (CaO) content higher than 10%.

Table 1 presents chemical and physical requirements for use of fly ash and raw or calcined natural pozzolans as mineral admixtures in portland cement concrete. ASTM C311 entitled "Methods of Sampling and Testing Fly Ash or Natural Pozzolans for Use as a Mineral Admixture in Portland Cement Concrete" describes the details of procedures and materials used for the requirement tests of Table 1.

In the ASTM C618 classification, the arbitrary chemical requirement for the sum of (SiO_2 + Al_2O_3 + Fe_2O_3) is not very rational and convincing, as this has no direct relationship to the properties of the material. Furthermore, several by-products such as granulated slags, condensed silica fume, and rice husk ash, which are recognized and also used as potentially important mineral admixtures, are not covered by the ASTM classification.

During the last two decades or so, various investigators have concluded that mineralogical composition, and particle morphology, as well as size and physical make up of the mineral admixtures, control the reactivity of these materials to a relatively greater extent than their chemical composition. Keeping this in view, a new classification of mineral admixture was proposed in Ref. 97 as given in Table 2. The proposed classification in

Table 2 does not include the high calcium fly ashes, possibly for the reason that such fly ashes are also self cementitious besides being pozzolanic. Therefore, a performance-based classification was introduced in Refs. 97 and 98 as given in Table 3. This classification includes high calcium fly ashes as cementitious and pozzolanic materials. But a review of data or chemical and physical properties of fly ashes from different parts of the world suggests that the classifications as suggested by Mehta in Table 3 does not represent the correct picture. There are many fly ashes which have less than 15% CaO content, as per chemical composition, yet such ashes are not only pozzolanic but self cementitious.

Table 1. Requirements for Fly Ash and Natural Pozzolans for Use as Mineral Admixtures in Portland Cement Concrete as per ASTM C618-89

	Mineral Admixture Class		
	N	F	C
Chemical Requirements			
$SiO_2 + Al_2O_3 + Fe_2O_3$, min. %	70.0	70.0	50.0
SO_3, max. %	4.0	5.0	5.0
Moisture Content, max. %	3.0	3.0	3.0
Loss on Ignition, max. %	10.0	6.0	6.0
Physical Requirements			
Amount retained when wet sieved on 45 µm sieve, max. %	34	34	34
Pozzolanic activity index, with portland cement at 28 days, min. % of control	75	75	75
Pozzolanic activity index, with lime, at 7 days min. (MPa)	5.5	5.5	--
Water requirements, max. % of control	115	105	105
Autoclave expansion or contraction max. %	0.8	0.8	0.8
Specific gravity, max. variation from average %	5	5	5
Percent retained on 45 µm sieve, max. variation, percentage points from average	5	5	5
Available alkalies as Na_2O max. %	1.5	1.5	1.5
Increase of drying shrinkage of mortar bars at 28 days, max. %	0.03	0.03	0.03
Reduction of mortar expansion at 14 days in alkali reactivity test, min. %	75	--	--
Mortar expansion at 14 days in alkali reactivity test, max. %	0.02	0.02	0.02
Air entraining required for air content of 18.0 volume %, variation max. %	20	20	20

Table 2. Classification of Mineral Admixtures[97]

Classification	Chemical and Mineralogical Composition	Particle Characteristics
II. Highly Active Pozzolans		
a. Condensed Silica Fume	Consists essentially of pure silica in noncrystalline form.	Extremely fine powder consisting of solid spheres of 0.1 μm average diameter (about 20 m^2/g surface area by nitrogen adsorption).
b. Rice Husk Ash: (Mehta-Pitt process)	Consists essentially of pure silica in noncrystalline form.	Particles are generally less than 45 μm but they are highly cellular (about 60 m^2/g surface area by nitrogen adsorption).
III. Normal Pozzolans		
a. Low-calcium Fly Ash	Mostly silicate glass containing aluminum, iron, and alkalies. The small quantity of crystalline matter present consists generally of quartz, mullite, sillimanite, heatite, magnetite.	Powder corresponding to 15-30% particles larger than 45 μm (usually 200-300 m^2/kg Blaine). Most particles are solid spheres of average 20 μm diameter. Cenospheres and plerospheres may be present.
b. Natural Materials	Besides aluminosilicate glass, natural pozzolans contain quartz, feldspar, mica.	Particles are ground to mostly under 45 μm and have rough texture.
IV. Weak Pozzolans		
Slowly-cooled blast furnace slag, bottom ash, boiler slag, field-burnt rice husk ash.	Consists essentially of crystalline silicate minerals, and only a small amount of noncrystalline matter.	The materials must be pulverized to very fine particle size in order o develop some pozzolanic activity. Ground particles are rough in texture.

Table 3. Performance Based Classification of Industrial By-products as Mineral Admixtures[97][98]

Class	Description	Example
I	Cementitious	Granulated blast furnace slag
II	Cementitious: Pozzolanic	High-Ca fly ash
III	Highly active pozzolans	Silica fume, rice husk ash (Mihta-Pitt Process)
IV	Normal pozzolans	Low-Ca fly ash
V	Weak pozzolans	Slow cooled blast furnace slag - field burnt rice husk ash

Fly ashes produced by four major power plants in Alberta, a western province of Canada, are such ashes. They contain less than 15% CaO yet are marginally self cementitious and highly pozzolanic. The degree of self hardening or the self cementitious value seems to be related to the coal source rather than the CaO content of the ash. Extensive literature review and experimental study by the authors suggests that the fly ash generated from bituminous coals with 2 to 6% loss on ignition is invariably pozzolanic, but not self cementitious. On the other hand, the fly ashes produced from subbituminous and lignite coals invariably contain less than 0.5% loss on ignition and are self cementitious to some degree besides being pozzolanic. The degree of self hardening or the self cementitious value of fly ash varies from minimal to very high. Joshi and Lam[57] and others[26] have reported that some fly ashes, when mixed with water, produce high heat of hydration and harden like cement. These ashes are generally produced from subbituminous and lignite coals. Self cementitious ashes are generally much finer than the pozzolanic and non self cementitious ashes produced from bituminous coals. The main difference between the self cementitious and non self cementitious ashes appears to be that the former have less than one-half of one percent loss on ignition as compared to 2 to 6%. Therefore the authors are of the opinion that the fly ashes should be classified not as Class F or Class C but as low and high ignition loss fly ashes as discussed in Table 3(a).

Table 3(a). Proposed Classification of Fly Ash as Pozzolanic Admixture in Cement

CLASS	DESCRIPTION	EXAMPLE
I	Pozzolanic but non-self cementitious	Bituminous ash generally exhibiting 2% or more loss on ignition
II	Pozzolanic and self cementitious	Sub-bituminous and lignite ash containing less than 1% loss on ignition

A simple test for evaluating pozzolanic activity of fly ashes and other pozzolans has so far evaded the scientific community. Detailed investigations by Joshi and Rosauer[39] on synthetic ashes produced from minerals produced from coals in laboratory scale furnace suggest that strain in glass is the main source for pozzolanic activity. The fineness and chemical composition, of course, dictate the degree of pozzolanicity in a fly ash containing strained glass. But measurement of strain in glass particles in fly ash has proven an impossible task.

The importance of strain in glass has become more evident since the introduction of NO_x burners in power plants using suspension fired furnaces. The ash produced in such power plants is not sufficiently pozzolanic and therefore is not satisfactory as a mineral admixture in cement concrete.

Fly ash is the most abundant and commonly used pozzolan in cement concrete. Because of the difficulty in evaluating the degree of pozzolanic activity, most organizations do not even identify fly ash as a pozzolanic admixture but as a mineral admixture in cement concrete. Therefore, various organizations all over the world have their own standards, codes and requirement specifications for the use of mineral admixture in cement and concrete. The object of most of the standards is to achieve specified performance and provide tests for the characterization and quality control of these materials to alleviate problems associated with the intrinsic variability of natural materials as well as industrial by-products for use in concrete.

3.0 NATURAL POZZOLANIC MATERIALS

Natural pozzolans are mostly derived from volcanic rocks and have been used in combination with lime as primary cementitious materials for the construction of ancient structures in Egypt, Greece, Rome and India. More than 2000 years ago, Romans found a reactive silica based material of volcanic origin (zeolitic tuff) in the foothills of Mount Vesuvius at Pozzvali. The term *pozzolana,* later simplified as *pozzolan,* has thus been evolved from the location Pozzvali, Italy. Besides the construction of aqueducts, pozzolan lime concrete was widely used by the Romans for the construction of cisterns, waterfront walls and brickwork lining. One of the most famous examples of Roman structures is the Pantheon in Rome which was built with lime pozzolan mortar/concrete containing pumice pozzolan. The structure has survived nearly 2000 years and has thus stood the test of time from the standpoint of durability.

In Northern Europe, Rhenish Trass, a volcanic tuff, was probably discovered during the Roman period. Trass is widely used even today in portland cement concrete. Volcanic ash from Santorin Island, in Greece, called santorian earth, was successfully used for making the concrete for the Suez Canal lining.

Early applications of pozzolan in ancient civilization and contemporary uses in Europe, Asia and some parts of North America have shown pozzolans to be useful construction materials. Deposits of natural pozzolans are located throughout the world. During the last 50 to 60 years, locally available pozzolanic materials have been used in the construction of concrete gravity dams primarily for economic reasons, but also to produce concrete with reduced heat of hydration and enhanced resistance to alkali soils and sulfates. Calcined clay in the finely ground form, locally called *surkhi,* was produced near the dam site, located in the Shivalik Hills of India, for the construction of Bhakra Dam, one of the highest concrete gravity dams in the world.

Natural pozzolans of volcanic origin are formed during explosive volcanic eruptions when the quick cooling of magma, composed mainly of alumino silicates, results in the formation of amorphous (glass) or vitreous phases with disordered structure. Due to the simultaneous evolution of dissolved gases, the solidified matter frequently acquires a porous structure with high surface area. Because of the large surface area and disordered structure, the alumino silicates present in pozzolans undergo chemical reaction with Ca^+ ions in the presence of water. This forms the basis of pozzolanic reaction with lime, and the resultant pozzolanic activity.

Clay minerals are believed to be formed as a result of the progressive transformation of the alumino silicates of volcanic glass under hydrothermal conditions. Clays in raw form are not highly pozzolanic due to the crystalline structure of the aluminosilicate minerals in the clay. Nonetheless, weathered clays in particular, and montmorillonitic clays or smectites in general, exhibit varying degree of pozzolanic activity. The weathered clay particles are reported to be covered with amorphous material which reacts with lime. In the case of smectites, lime not only causes cation exchange, but also reacts with silica in tetrahedral layer to produce pozzolanic products. However, by heat treatment, i.e., calcining around 800 to 900°C, clays can become highly pozzolanic due to conversion of their crystalline structure into an amorphous or disordered structure.

Zeolite materials, combination of alkalies with pozzolanic materials, also result from the alteration of volcanic glass under hydrothermal conditions. Zeolite minerals in a finely ground state are also reactive with lime.

Another type of natural pozzolans, diatomaceous earths, consist of opaline or amorphous hydrated silica derived from the skeletons of diatoms which are tiny water plants with cell walls made of silica shell. Diatomaceous earths are generally found contaminated with clay minerals and thus need to be calcined to improve the pozzolanic reactivity.

There are several review papers available in literature that deal with the source as well as the fundamental or engineering properties of natural pozzolans. It is difficult to classify natural pozzolans because they seldom contain only one lime reactive component. However, based upon the main lime reactive constituent present, the natural pozzolans can be classified into volcanic glasses, volcanic tuffs, calcined clays and shales, and diatomaceous earths. Deposits of natural pozzolans are found throughout the world, including industrialized countries. An account of the chemical composition (oxide content) of typical samples from some well known deposits of natural pozzolans is presented in Table 4.

Table 4. Analytical Oxides in Natural Pozzolans[85][72]

Pozzolan	SiO_2	Al_2O_3	Fe_2O_3	CaO	Mao	Na_2O	K_2O
Volcanic Glasses							
Bacoli (Italy)	53.1	18.2	4.3	9.0	1.2	3.1	7.6
Santorini Earth (Greece)	65.1	14.5	5.5	3.0	1.1	2.6	3.9
Shirasu (Japan)	69.3	14.6	1.0	2.6	0.7	3.0	2.4
Volcanic Tuffs							
Segni-Latium (Italy)	45.5	19.6	9.9	9.3	4.5	0.9	6.4
Rheinisch Trass (Germany)	52.1	18.3	5.8	4.9	1.2	1.5	5.1
Bavarian Trass (Germany)	62.4	16.5	4.4	3.4	0.9	1.9	2.1
Higashi-Matusyma (Japan)	71.8	11.5	1.1	1.1	0.5	1.5	2.6
Diatomites							
Diatomaceous Earth (California)	86.0	2.3	1.8	--	0.6	0.4	--
Calcined Clay							
Handelage (Germany)	42.2	16.1	7.0	21.8	1.9	0.30	1.0

The successful and time tested use of lime pozzolana mixtures in ancient structures, including hydraulic structures, led to the realization that natural pozzolans produced construction materials that had high durability to an aggressive marine environment. No scientific explanation about the behavior of natural material was then documented. Recent investigations related to the durability properties of concrete containing natural pozzolans have shed some light on the mechanisms responsible for enhanced durability of concrete.

Like industrial by-products with pozzolanic properties, natural pozzolans, when incorporated in concrete, cause the pore structure refinement by transforming the larger pores into smaller ones. Thus, the continued pozzolanic reactions and resultant products make the paste structure more dense and compact. Pozzolanic reactions are time dependent and continue to occur over long periods of time, much after the hydration products in cement concrete are fully formed. Consequently, both strength and impermeability increase with time in cement concrete containing pozzolans.

The incorporation of natural pozzolans not only improves the workability of mortars and concrete, but also reduces the heat of hydration during early periods of cement hydration. Thus, cracking due to heat of hydration in mass concrete structures is substantially reduced or eliminated. Resistance of concrete, containing natural pozzolans, to sulfate attack and alkali silica reaction is considerably enhanced. On the debit side, the rate of strength development of concrete containing pozzolans may be retarded. Nonetheless, ultimate strength of concrete containing pozzolan is higher, but it takes time. Because most pozzolans are available as natural or industrial by-products, their use leads to energy saving and economy compared to the use of special cements or chemical admixtures. A brief description of broad categories of natural pozzolans follows.

3.1 Volcanic Glasses

These materials derive their pozzolanic activity characteristics mainly from disordered structure of alumino silicate glass. As shown in Table 4, Santorin earth of Greece, Bacoli of Italy, and Shirasu pozzolan of Japan are the examples of volcanic glasses. These materials result due to the cooling of liquid lavas released during volcanic eruptions. Small amounts of nonreactive crystalline minerals such as quartz, feldspar, and mica are found embedded in the glassy phase. Mineralogical analysis of the Shirasu pozzolan showed 95% glass, with quartz and anorthite as main crystalline minerals. Figure 1 presents x-ray diffraction analysis of typical samples of the santorian earth. Quartz and feldspar are detected to be the principal crystalline impurities. Further, the typically pumice-like or porous structure of the santorian earth, a volcanic glassy material, is evidenced by its scanning electron micrograph shown in Fig. 2.

BET analysis by nitrogen adsorption gave 3.8 to 15.5 m^2/g values for the surface area of different samples of Santorin earth. The corresponding value of surface area for Shirasu Pozzolan of Japan was 2.95 m^2/g. The refractive index of volcanic glass lies between 1.49 and 1.507. For satisfactory pozzolanicity, the glass component of volcanic ashes should be at least 60% of the total. For alkali aggregate reaction to be effectively controlled, the glass content must be around 90%. The pozzolanic activity index of volcanic glassy pozzolans is in the range of 64% to 130% of the control at 90 days.

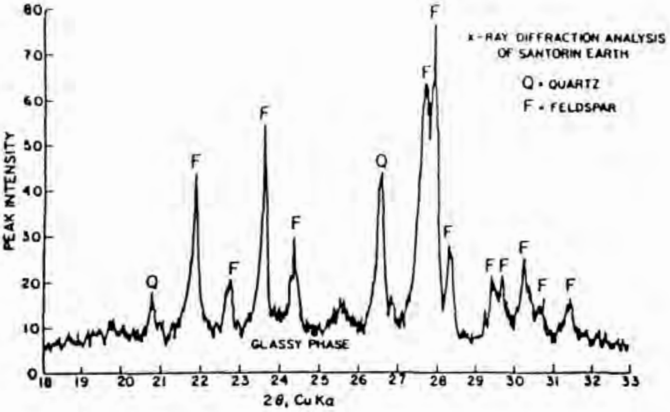

Figure 1. X-ray diffraction analysis of a typical sample of the Santorin earth.[94]

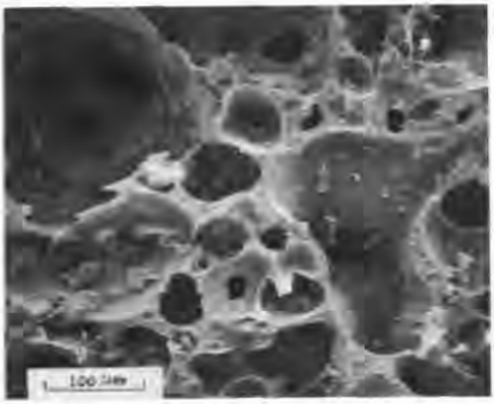

Figure 2. Scanning electron micrograph of a typical sample of the Santorin earth.[94]

3.2 Volcanic Tuffs and Trass

Rhyolite tuffs and dacite tuffs are found to be good pozzolanic materials, while andesites, basalts and basaltic tuffs are generally found to be quite unsatisfactory in quality and performance. Zeolite tuffs, formed by hydrothermal conversion of volcanic glass, have compact texture and are fairly strong, having compressive strength of the order of 10 to 30 MPa. Pozzolans of Segni-latium (Italy) and Rheinland trass (Germany) are typical examples of volcanic tuffs. Minerals present in various types of trass include augite, apatite, titanite, biotite, hauynite, nosean, sodalite, magnetite, muscovite chabazite, analcite, hematite, cristobalite, lecuite, kaolinite, illite, mica, and hornblende.[77] The principal zeolite minerals are, however, reported to be phillipsite and herschelite. In the finely ground form, the zeolitic materials show considerable reactivity with lime and develop cementitious characteristics like pozzolans containing volcanic glass.

3.3 Thermally Treated Clays and Shales

Clays and shales, unlike volcanic glasses and tuffs, require thermal treatment at temperatures greater than 540°C (range 540°C to 900°C) in order to have adequate reactivity with lime. By heat treatment, the crystal structure of the clay minerals is destroyed and an amorphous or disordered alumino silicate structure is formed. Clays are generally classified by the mineral which is present in abundance, for example, kaolinitic, montmorillonitic, illitic, etc. Glacial clays may contain large amounts of silt as well as mixed clays with altered vermiculite. Thermally treated clays must also be pulverized to a fine particle size. Surkhi, a pozzolan made in India by pulverization of burned clay bricks, is a typical example of this category. Montmorillonitic clays with Na (sodium) as the exchangeable ion are good pozzolans and are especially effective in reducing alkali-aggregate reaction. Thermally treated kaolinite clays significantly increase sulfate resistance. Clays and shales, containing large amounts of quartz and feldspar, would fail to yield good pozzolans. At present, on account of widespread and abundant availability of pozzolanic industrial by-products such as fly ashes, the production of pozzolans by calcination of clays and shales has become unpopular due to the energy requirements involved in the process.

3.4 Diatomaceous Earths and Cherts

The pozzolanic activity of these pozzolans is due to the presence of opal. Diatomite is a hydrated amorphous silica which is composed of skeletal shells from the cell walls of many varieties of microscopic aquatic algae. Large deposits are located in California (USA), Algeria, Germany, Denmark, and Canada. On account of their skeletal microstructure, these pozzolans, although quite reactive, have the disadvantage of a high water requirement which makes their use impractical in some circumstances due to reduced strength and durability of the resultant concrete. Such pozzolans may cause problems with excessive deformation (volume instability) when used in concrete exposed to wetting/drying cycles. Their surface area is usually in the range 1.7 m^2 to 45 m^2/g. Their pozzolanic activity, evaluated using ASTM tests, normally varies from 64% to 112% of control at 90 days. Diatomaceous earths and cherts also contain large amounts of clay which reduces their pozzolanic activity. For improving their effectiveness as pozzolans, they are thermally treated in the temperature range 760°C to 1000°C before use. The clay fractions thus get converted into a pozzolanic material. Opaline shales, cherts and porcellanites are examples of these types of materials. Concretes containing these pozzolans exhibit good resistance to sulfate attack and alkali-aggregate reaction if water requirements are regulated and controlled.

4.0 INDUSTRIAL BY-PRODUCTS AS MINERAL ADMIXTURES

Fly ash from combustion of pulverized coal, granulated slag from both ferrous and nonferrous metal industries, volatilized silica from silicon metal or ferrosilicon alloy industries, red mud or bauxite waste from aluminum extraction industries, and rice hull (husk) ash from the combustion of rice husk, are some of the industrial by-products which are found suitable for use as mineral admixtures in portland cement mortar/concrete. Industrially developed countries such as the USA, former USSR (Republic of Socialist Countries), Germany, France, Japan and U.K. are among the largest producers of fly ash, condensed silica fume and granulated blast furnace slag. In addition to these materials, China, India, and the USA have a potential for producing large amounts of rice husk ash. As mentioned earlier, use of industrial by-products as mineral admixtures in cement mortar/concrete, can lead to both economic and environmental benefits.

There is also considerable saving in energy consumption in addition to conservation of scarce natural resources of raw materials required for cement production.

The worldwide production of fly ash at present is estimated to be about 500 million tons per year. According to coal ash production and utilization in the world survey in 1989,[81][99] approximately 562 million tons of coal ash was produced in 1989, of which approximately 90 million tons or 16.1% was utilized. The total amount of coal ash used in concrete was about 27.9 million tons, consisting of 2.8 million tons as cement raw material, 7.6 million tons in blended cement, and 17.5 million tons for cement replacement. The former USSR was the largest producer of coal ash, with about 125 million tons in 1989. The power plants in the United States, the second largest producer of coal ash, generated 48.5 million tons of coal ash. But only 16 million tons or about 33% of the total ash produced was utilized in the USA. However the annual utilization of 6.1 million tons of fly ash in concrete in the USA was the highest in the world. Most of the fly ash in the USA has been used as a cement replacement in concrete construction and products.

Large quantities of blast furnace slag are available in many countries. However, the former USSR, France and Germany are major producers of granulated slag that possesses pozzolanic and cementitious properties.

Condensed silica fume was recognized and used as mineral admixture in concrete only about 10 to 15 years ago. About 60% of the total volatilized silica or condensed silica fume is produced in the USA, the former USSR, and Norway. Silica fume is available in loose bulk form, densified form, slurry form and in the form of blended portland SF (silica fume) cement. A few years ago, Iceland was the only country where a blended portland SF cement was manufactured.[5] Presently three major cement companies in Quebec, Canada, are producing such a blended cement. In 1990, about 170,000 tons of blended portland SF cement containing 6.5 to 8.0 SF were sold in Canada at a cost premium of 10% to 13% over that of ordinary portland cement.

The granulation and use of steel slag and nonferrous slags, as well as of calcined red mud, a by-product from aluminum industry, are still in the developmental stage. In developing countries like China and India, the production of rice husk ash could be 30% to 50% cheaper than that of conventional cement. The capital investment is also much smaller, being about $20 per ton for rice husk ash versus $120 to $200 per ton of ordinary portland cement. Among the presently available industrial by-products, fly ash is the most economic and widely used mineral admixture in concrete. The energy requirement for its production as shown in Table 5 is negligible.

Table 5. Energy Requirements for Production of Various Cementitious/ Pozzolanic Materials[19]

MATERIALS	TOTAL ENERGY REQUIRED KJ/kg OF MATERIAL
Cement	372
Lime	173
Hydrated Lime	142
Burnt Clay Pozzolan	68
Rice Husk Ash	12
Surkhi (burnt brick)	12
Fly Ash	0

More favorable properties of the resulting cement mortar/concrete are obtained with the combined use of industrial by-products as mineral admixtures. Portland fly ash cement containing ground granulated blast furnace slag is commercially used in France[114] and in Australia.[120]

High performance concrete can be produced by the combined addition of fly ash and condensed silica fume (generally also termed silica fume). Superplasticizer is, however, required to maintain the specified consistency especially when silica fume is used. The incorporation of silica fume in fly ash concrete can improve not only early strength remarkably but also the ultimate strength and durability. Carette and Malhotra[11] investigated concrete containing 70% portland cement, 30% low calcium fly ash, and 5% to 10% condensed silica fume. An appreciable increase in early age strength up to the age of 7 days was noticed. Pozzolanic activity from fly ash and silica fume was more marked between 3 and 7 days. However, pozzolanic activity from only fly ash addition became more apparent after 28 days. The combined use of blast furnace slag (60 to 70% slag) with 10% to 20% silica fume addition in portland cement concrete has been found to reduce the alkali-silica reaction significantly. A study by Sarkar et al.,[110] has indicated that with 10% silica fume and 30% slag, it is possible to produce concrete with 28 day strength of 94 MPa. Results of various studies indicate that the addition of silica fume in portland cement fly ash mixes results in pore refinement, transformation of bigger pores to smaller ones, and also a considerable decrease in overall porosity. Thus, for long-term durability also, the combined use of silica fume and other industrial by-products such as blast furnace slag and fly ash is reported to be desirable. In this section, the production, types and properties of individual pozzolanic industrial by-products are described. More emphasis is laid on fly ash because of its abundance and wide spread use in cement and concrete.

4.1 Fly Ash

This refers to finely divided, glassy material, which is separated from the flue gases during combustion of pulverized coal in suspension fired furnaces of modern thermal power plants. During the coal combustion, the volatile matter is vaporized and carbon is burned off, whereas most of the mineral matter, such as clays, quartz, and feldspar, disintegrates or slags to varying degrees. The slagged individual particles on cooling solidify as spherical glassy particles which comprise coal ash. Quartz particles are minimally affected by flame temperatures and, thus, are generally semi-rounded to angular. Fly ash constitutes 75% to 85% of the total ash and the remaining is bottom ash or boiler slag. Depending upon the collection system, electrical or mechanical precipitators or baghouses, about 85% to 99.9% of the incombustible mineral matter present in the coal is retrieved in the form of coal ash. Fly ash, because of its mineralogical composition, fine particle size and amorphous character (glassy nature) is mostly pozzolanic and in some cases also self cementitious. Figure 3 shows a schematic diagram of fly ash production and collection in a modern thermal power plant.

Types and Properties. Fly ash is generally finer than portland cement and consists mostly of spherical, glassy particles varying from less than 1 µm to over 100 µm in diameter. The chemical composition of the glass in the particles varies significantly. But the main constituents include silica, alumina and oxides of calcium and iron. The chemical composition of fly ashes generally varies with the source of coal. However, its physical and chemical properties are contingent upon several other factors such as degree of coal pulverization, flame temperature, oxidation conditions including pretreatment during or prior to combustion for SO_x removal, and system of collection and storage of fly ash. At present, ASTM specification C618 defines two broad types of fly ash, Class F and Class C, related to the type of coal burned.

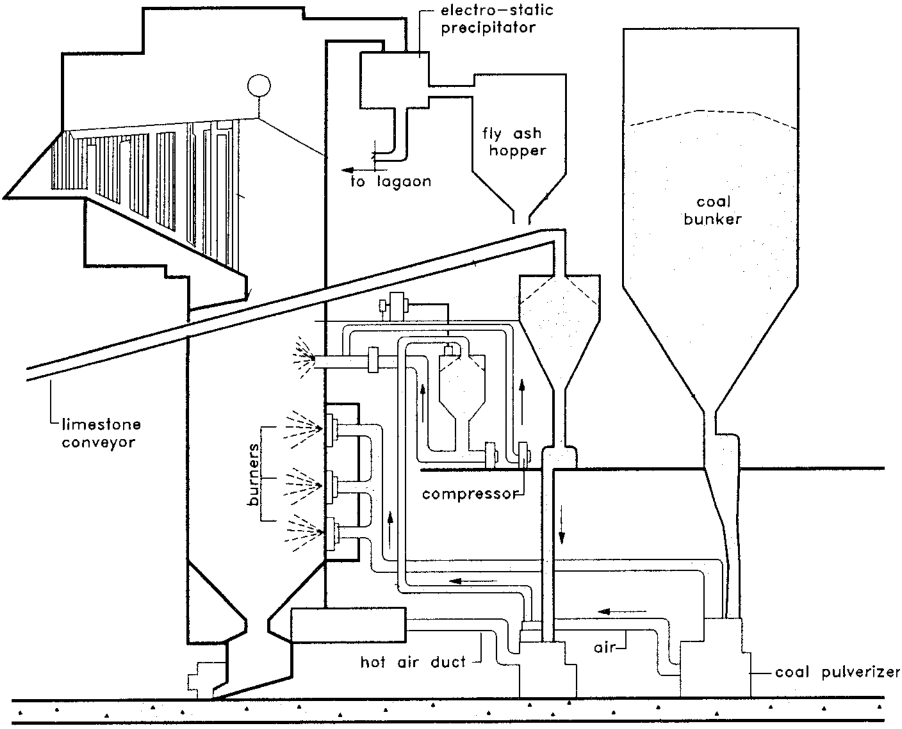

Figure 3. Schematic diagram showing fossil fuel furnace, anti-pollution additive equipment and fly ash collection systems.

The fly ash produced from burning anthracite or bituminous coal is classified as Class F as per ASTM C618, whereas Class C fly ashes normally result from the burning of subbituminous coal and lignite such as are found in some of the western parts of Canada and the USA. Presently, no appreciable amount of anthracite coal is used for power generation in North America. Therefore, all Class F fly ash now available in North America is essentially derived from the bituminous coal. Class F fly ashes with CaO less than 6%, designated as low calcium ashes, are not self hardening but generally exhibit pozzolanic properties. These ashes invariably contain more than 3% unburned carbon determined by loss on ignition (LOI) test. Quartz, mullite and hematite are the major crystalline phases identified in North American Class F fly ashes, mostly derived from eastern bituminous coal. When Class F fly ash is used for producing air entrained concrete to improve freeze-thaw durability, the demand for air entraining admixture is significantly increased. Essentially, all fly ashes and, therefore, most research concerning use of fly ash in concrete in the United States before about 1980 dealt with Class F fly ashes.

Class C fly ashes, containing usually more than 15% CaO are called high calcium fly ashes. These ashes are typically derived from Wyoming and Montana subbituminous coal or North Dakota and Texas lignite in the USA and subbituminous coal found in Alberta and lignite from Saskatchewan in Canada. Class C ashes have pozzolanic properties but may also be self cementitious. Generally, higher values of CaO denote higher degree of self hardening. This type of fly ash has become commercially available in large quantities in the United States only in the last two decades since the western coal fields have been opened. Since 1980, a number of studies concerning the characteristics and effects of Class C type fly ash on properties of concrete have been reported. In most cases, initial hardening occurs relatively fast when these fly ashes react with water just like portland cement. These ashes have very little unburned carbon and the loss on ignition (LOI) of less than 1%. The typical crystalline phases of these ashes are anhydrite, tricalcium aluminate, lime, quartz, periclase, mullite, merwinite, and ferrite.

Ashes typically derived from lignites, (Texas and Saskatchewan lignites) and from subbituminous and bituminous coal from the Western Rocky Mountain region (Alberta coals), contain CaO ranging from 7% to 15%. These ashes exhibit varying degrees of self hardening and thus seem to exhibit some of the properties of Class F and Class C fly ashes. But ashes produced in Alberta and Saskatchewan need to be studied on a case by case basis regarding their behavior in cement concrete. The main minerals present in Alberta ashes are tricalcium silicate (alite), dicalcium silicate (belite), portlandite, calcite, hematite, sodium sulfate (thenardite), and quartz.

The ASTM classification of fly ashes based on the type of coal burned does not seem to be very realistic and rational concerning the expected behavior of fly ashes when used in concrete. There are wide differences in characteristics within each class. Class F fly ash can be produced from coals that are not bituminous, for example, subbituminous Alberta coals; and bituminous coal can produce ash that is not Class F. Furthermore, Class C fly ash is not required to have any free lime. ASTM and several other organizations are considering to reclassify fly ash in a manner more closely related to the characteristics of ash itself and its influence on concrete properties. However, as yet no agreement has been reached as to the basis of such classification.

Characteristics of Fly Ash. The effective utilization of fly ash in concrete requires adequate knowledge of characteristics of fly ash defined by its physical, chemical and mineralogical properties. Coal particles are burned at high temperatures in the furnace, whereas the inorganic mineral matter in coal is transformed into ash. Ninety-five percent of mineral matter present in coal is composed of clays, pyrite and calcite. During combustion these mineral particles undergo physical and chemical changes in the presence of excess air at high temperatures. The pyrites change to iron oxide, whereas the clay particles and mica slag partially vitrify to form glass spheres of complex silicates (amorphous alumino silicates). Calcination of calcite gives rise to calcium oxide (CaO), calcium hydroxide [$Ca(OH_2)$], and carbon dioxide (CO_2). Intermixed particles of clay and calcite and gaseous matter produce calcium silicate ($CaSiO_2$) and calcium aluminate ($CaAl_2O_3$) or calcium sulfate ($CaSO_4$).[45] Other carbonates and some chlorides, if present in coal, undergo volatilization and sulfation to produce sulfates, carbon dioxide (CO_2) and hydrochloric acid (HCl). Quartz particles are rather unaffected and pass through the flame zone without much change in shape.

Coal combustion residue is quenched after it leaves the flame zone. The fine particulate, fly ash, is arrested from the flue gases by electrostatic filters or fabric filters. Due to quenching spherical to rounded fly ash particles have glassy exterior surface. Some of the gases evolved during combustion are trapped in the fly ash particles, producing low specific gravity cenospheres which float on water and are, therefore, called floaters. The glass fraction in fly ashes usually varies between 70% and 89% depending on the type and coal source, degree of coal pulverization, flame temperature in the furnace and rate of cooling of the combustion residue.

Physical Properties. These properties include size, morphology, fineness, and specific gravity. In general, fly ash particles consist of clear glass spheres and a spongy mass. Figure 4 shows scanning electron micrographs of typical fly ashes, both low calcium (Class F) and high calcium (Class C). A large fraction of ash particles has a diameter less than 3 µm. In bituminous ash, the particle sizes range from less than 1 µm to over 100 µm. The average size mostly lies in the range of 7 µm to 12 µm.[63]

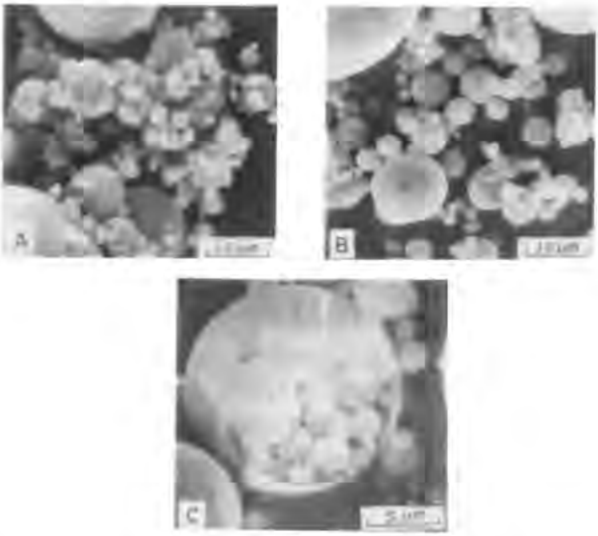

Figure 4. Scanning electron micrographs of (A) high-calcium fly ash, (B) low-calcium fly ash, and (C) broken plerosphere in a low-calcium fly ash.[97]

From the micrographs in Fig. 4, it is evident that low calcium fly ashes tend to contain smooth spherical and other particles due to a lower proportion of surface deposits consisting of lime and alkali sulfate impurities. Sometimes low calcium fly ashes may contain a small amount of hollow spheres which are either completely empty (cenospheres) or packed inside with smaller spheres (plerospheres), depending upon the burning and cooling conditions. A micrograph of a typical broken plerosphere is shown in Fig. 4C.

Joshi and Marsh[53] conducted tests for physical properties of 14 Canadian fly ashes. The test results of their study are presented in Table 6. The fineness of fly ash can be determined by measuring the percentage passing through the 45 μm (No. 325) sieve. The specific surface area can be determined by the Blaine Air Permeability method or by the B.E.T. nitrogen sorption method. For most Canadian fly ashes, surface area ranges from 1700 to 5900 cm^2/g. A higher specific surface area can be due to either large amounts of fines in the inorganic mineral matter or a significant amount of porous carbon particles.

The specific gravity of fly ash is reported to be related to shape, color and chemical composition of fly ash particles. Mineralogical composition of fly ash has also a marked influence on specific gravity. In general, specific gravity may vary from 1.3 to 4.8. However, the values of specific gravity for Canadian ashes range from 1.9 to 2.9. (Table 6). Coal particles with some mineral impurities have specific gravity between 1.3 and 1.6. Opaque spherical magnetite and hematite particles, light brown to black in color, when present in sufficient quantity in fly ash, increase the specific gravity to 3.6 to 4.8. As the amount of quartz and mullite increases, the specific gravity decreases. Grinding of fly ash particles releases some of the gases trapped during quenching inside the surface of spherical fly ash particles and increases the bulk specific gravity of the fly ash.[42][43]

Table 6. Physical Properties of Fourteen Canadian Fly Ashes[53]

Fly Ash No.	Coal Type	Source	Overall Apparent Specific Gravity	% Retained on 45 µm sieve	Specific Surface Area (m^2/g)	
					Air Permeability	B.E.T. Method
1	sub-bituminous	Alberta	2.19	32.0	0.42	1.52
2	sub-bituminous	Alberta	1.92	26.0	0.46	1.61
3	sub-bituminous	Alberta	1.91	22.0	0.43	1.61
4	sub-bituminous	Alberta	2.03	9.8	0.59	1.64
5	lignite	Saskatchewan	2.54	2.8	0.50	1.14
6	sub-bituminous	Saskatchewan	2.15	20.4	0.22	6.70
7	lignite	Saskatchewan	2.37	44.8	0.17	1.01
8	lignite	Saskatchewan	2.39	26.6	0.22	3.47
9	bituminous	Ontario	2.46	24.0	0.28	0.55
10	bituminous	Ontario	2.31	27.0	0.25	3.28
11	bituminous	New Brunswick	2.94	21.4	0.31	2.68
12	bituminous	New Brunswick	2.87	26.4	0.18	0.43
13	bituminous	Nova Scotia	2.53	28.2	0.36	0.85
14	sub-bituminous	Nova Scotia	2.44	34.4	0.38	0.67

average difference	1.10 m^2/g
standard deviation of mean of 14 readings	1.44 m^2/g

The pozzolanic reactivity of fly ash and water demand for constant workability of concrete containing fly ash as an admixture, would be controlled by particle size distribution, morphology and surface characteristics of fly ash particles. Fly ashes having a large fraction of low density particles are more reactive than those having a higher fraction of high density particles because the reactivity depends upon the amount of glass present which has a low specific gravity. High specific gravity glass is contaminated by iron and is rather non pozzolanic to slightly pozzolanic. Fly ashes comprised of clean, glassy, spherical particles in finely divided form act as good void fillers and thus should be able to reduce water requirement, particularly in lean concrete mixes or when the mixes are deficient in fine aggregate fractions. High calcium fly ashes[63] consisting of rough textured and porous, glassy, spherical particles generally possess larger surface area and thus exhibit more reactivity than smooth spheres. Hence particle size distribution alone may not control the potential reactivity of a fly ash.

Chemical Composition. Table 7 presents a summary of the test results of chemical properties of 14 Canadian fly ashes.[53] Table 8 gives the range of property parameters based upon fly ash analyses of a large number of American fly ashes collected from thermal power plants all over the United States.

Chemical constituents in fly ash reported in terms of oxides include silica (SiO_2), alumina (Al_2O_3), oxides of calcium (CaO), iron (Fe_2O_3), magnesium (MgO), titanium or rutile (TiO_2), sulfur (SO_3), sodium (Na_2O), and potassium (K_2O). Unburned carbon is another major constituent in all the ashes. Amongst these, SiO_2 and Al_2O_3 together make up about 60% to 75% of the total ash. The subbituminous and lignite coal fly ashes have a relatively higher proportion of CaO and MgO and lesser proportion of SiO_2, Al_2O_3 and Fe_2O_3 as compared to bituminous coal fly ashes. Table 9 gives ranges of CaO content for North American fly ashes derived from various classes of coal.

Bituminous coals produce fly ashes with relatively higher amounts of unburned carbon (% LOI) than subbituminous or lignite coals. The amount of unburned carbon also depends to some extent upon the degree of coal pulverization, rate of combustion, and air-fuel ratio in addition to the type and source of coal. As can be seen from Table 7 and 8, Canadian fly ashes have CaO ranging from 0.75% to 20% compared to 1.1% to 30% in American fly ashes. Subbituminous Alberta coal fly ashes have LOI less than 1% and CaO content varying from 8.4% to 13.6%.

Table 7. Summary of Test Data on Chemical Composition of Fourteen Canadian Fly Ashes[53]

Fly Ash* No.	Weight Percent ± 1σ											
	Al as Al_2O_3	Fe as Fe_2O_3	Ti as TiO_2	Ca as CaO	Mg as MgO	S as SO_3	Na as Na_2O	K as K_2O	Si as SiO_2	LOI %	Magnetic Portion+	Water Soluble Fraction Wt. %
1	22.3±0.5	4.1±0.1	1.01±0.01	13.6±0.4	1.58±0.04	0.2±0.1	0.27±0.03	1.02±0.06	54.8±0.4	0.26	≤1	4±0.5
2	23.1±0.5	3.7±0.1	0.78±0.01	13.0±0.4	1.17±0.04	0.2±0.1	2.19±0.03	1.26±0.06	57.6±0.4	0.15	≤1	2±0.5
3	21.0±0.5	3.5±0.1	0.50±0.01	11.6±0.4	0.71±0.04	≤0.1	1.68±0.03	1.51±0.06	56.4±0.4	0.61	≤1	2±0.5
4	22.7±0.5	3.7±0.1	0.60±0.01	8.4±0.4	0.75±0.04	≤0.1	2.36±0.03	1.02±0.06	57.4±0.4	0.10	≤1	4.5±0.5
5	23.7±0.5	4.4±0.1	0.94±0.01	19.2±0.4	3.96±0.04	0.6±0.1	0.54±0.03	2.41±0.06	57.9±0.4	0.13	≤1	7±0.5
6	20.4±0.5	5.4±0.1	0.60±0.01	12.2±0.4	1.38±0.04	0.1±0.1	0.84±0.3	1.93±0.06	52.6±0.4	0.12	≤1	1±0.5
7	20.8±0.5	4.1±0.1	0.97±0.01	20.0±0.4	3.13±0.04	0.2±0.1	5.66±0.07	1.14±0.06	40.7±0.4	0.83	≤1	2.5±0.5
8	20.8±0.5	3.8±0.1	0.87±0.01	18.6±0.4	2.42±0.04	≤0.1	5.80±0.07	1.45±0.06	38.1±0.4	0.34	≤1	3.5±0.5
9	22.7±0.5	16.5±0.8	1.01±0.01	4.6±0.4	0.64±0.04	0.5±0.1	0.54±0.03	2.0±0.06	44.6±0.5	5.9	85.±1.	3.5±0.5
10	21.2±0.5	7.1±0.8	0.81±0.01	6.6±0.4	0.88±0.04	0.1±0.1	0.4±0.03	1.14±0.06	51.9±0.5	5.3	69.±1.	2.5±0.5
11	13.6±0.5	38.5±0.8	0.51±0.01	1.81±0.04	0.14±0.01	0.6±0.1	0.11±0.01	1.93±0.06	34.9±0.4	0.11	96.±1.	1.5±0.5
12	13.6±0.5	42.2±0.8	0.56±0.01	1.22±0.04	0.06±0.01	0.4±0.1	0.09±0.01	1.26±0.06	31.7±0.4	2.0	87.±1.	1±0.5
13	20.8±0.5	24.4±0.8	0.76±0.01	0.94±0.04	0.12±0.01	0.6±0.1	0.34±0.03	1.63±0.06	46.7±0.4	0.53	94.±1.	1.5±0.5
14	18.0±0.5	19.2±0.2	0.74±0.01	0.76±0.04	0.75±0.04	0.99±0.05	0.39±0.03	2.93±0.06	44.7±0.4	6.25		1±0.5

*See Table 6 for fly ash source.

+This is the amount in the sample attracted to a magnet. It does not indicate the amount of magnetite fraction in ash.

Table 8. Fly Ash Analyses of American Fly Ashes and Parameter Ranges[a][26]

PARAMETER	RANGE
Silicon Dioxide %	30.92 - 62.76
Aluminum Oxide	12.30 - 26.95
Iron Oxide %	2.84 - 24.43
Calcium Oxide %	1.10 - 30.53
Magnesium Oxide %	0.69 - 6.69
Sulfur Trioxide %	0.31 - 3.85
Sodium Oxide %	0.20 - 2.04
Potassium Oxide %	0.22 - 3.03
Available Alkalies % (as eqiv. Na_2O)	0.23 - 1.54
Loss on Ignition %	<0.01 - 16.60
Carbon %	0.02 - 15.34
Specific Gravity	2.14 - 2.69
Moisture Content %	0.0 - 0.38
% Retained on 325 Sieve	3.55 - 36.90
Blaine Fineness (cm^2/g)	
as received	1579 - 5550
<325 sieve	1804 - 5350
Pozzolanic Activity Index %	
Control #1	86 - 172
Control #2	136 - 239

[a] Results of the sampling effort which included base load and upset condition fly ash samples from 16 pulverized coal-fired power plants across the United States employing electrostatic precipitators, for ash collection.

Table 9. Range of Lime (CaO) Content in North American Fly Ashes

CLASS OF COAL	CaO CONTENT (%) IN FLY ASH
Eastern bituminous	1 - 6
Colorado bituminous	4 - 8
Utah and Alberta sub-bituminous	6 - 12
Texas lignite	7 - 12
Saskatchewan lignite	10 - 15
North Dakota lignite	18 - 25
Montana and Wyoming sub-bituminous	22 - 32

Mineralogical Composition. Fly ashes in general have 15% to 45% crystalline matter. The high-calcium ashes contain larger amounts of crystalline matter ranging between 25% and 45%. Although high calcium ashes may be somewhat less glassy, they do have several crystalline phases that participate in cementitious reactions—anhydrite ($CaSO_4$), tricalcium aluminate (C_3A), calcium sulfoaluminate, and some lime—and their glassy phases are usually considered to be more reactive. Table 10 gives crystalline phases in North American fly ashes identified by XRD analysis.

Table 10. Crystalline Phases in North American Fly Ash Identified by XRD Analysis[87]

Code	Name	Nominal Composition
LOW-CALCIUM/CLASS F FLY ASH		
Hm	Hematite	Fe_2O_3
Mu	Mullite	$Al_6Si_2O_{13}$
Qz	Quartz	SiO_2
Sp	Ferrite Spinel	$(Mg,Fe)(Fe,Al)_2O_4$
HIGH-CALCIUM/CLASS C FLY ASH		
Ah	Anhydrite	$CaSO_4$
AS	Alkali Sulfate	$(Na,K)_2SO_4$
C_2S	Dicalcium Silicate	Ca_2SiO_4
C_3A	Tricalcium Alminate	$Ca_3Al_2O_6$
Hm	Hematite	Fe_2O_3
Lm	Lime	CaO
Ml	Melilite	$Ca_2(Mg,Al)(Al,Si)_2O_7$
Mu	Mullite	$Al_6Si_2O_{13}$
Mw	Merwinite	$Ca_3Mg(SiO_4)_2$
Pc	Periclase	MgO
Qz	Quartz	SiO_2
So	Sodalite Structure	$Ca_2(Ca,Na)_6(Al,Si)_{12}O_{24}(SO_4)_{1-2}$
Sp	Ferrite Spinel	$(Mg,Fe)(Fe,Al)_2O_4$

The crystalline phases can be detected using x-ray diffraction (XRD), energy dispersive x-ray analysis (EDXA), and scanning electron microscopic observations. The fly ash mineralogy presented in Table 10 was determined by a semi quantitative x-ray powder diffraction protocol. Qualitative XRD reveals that low calcium fly ash consists typically of the crystalline phases quartz, mullite, hematite, and magnetite in a matrix of alumino silicate glass. High calcium fly ashes, on the other hand, have a much more complex assemblage of crystalline phases that typically includes these four phases plus several other phases as given in Table 10. Glass compositions among the particles are more heterogeneous and range from calcium aluminate to sodium calcium alumino silicate.

In the ASTM specification C618, the pozzolanic activity of a fly ash is assumed to be related to the chemical composition, as is evident from the limitations on the sum of SiO_2 + Al_2O_3 + Fe_2O_3. Mineralogical studies indicate that a portion of the total Fe_2O_3 is present as unreactive crystalline phases. Likewise, much of SiO_2 and Al_2O_3 is present as unreactive quartz, mullite and other silicates and alumino silicates. Only the glassy phases of SiO_2 and Al_2O_3 are assumed to be pozzolanic as far as fly ash reactivity in concrete is concerned.

Anhydrite ($CaSO_4$) is a characteristic phase in high calcium fly ash. Sometimes anhydrite is also detected in low calcium ashes and in most of the intermediate calcium ashes. Anhydrite forms from reaction of CaO, SO_2 and O_2 in the furnace or flue. The amount of anhydrite increases with increasing SO_3 and CaO contents in the ash. For most ashes only about half of the SO_3 is present as anhydrite. The other crystalline phases of SO_3 are alkali sulfates and calcium sulfoaluminate. Anhydrite plays a significant role in fly ash hydration behavior because it participates, along with C_3A (tricalcium aluminate) and other soluble aluminates, in the formation of ettringite (trisulfate of calcium aluminate) immediately on adding water to fly ash. This initial hydration reaction contributes much to the self hardening characteristics of fly ash. Ettringite may also precipitate and control the solubility of potentially hazardous trace elements, thus affecting the geotechnical behavior of disposed ash in landfills.

Until recently, the ASTM C618 placed a 5.0% limit on the maximum MgO content of an acceptable fly ash for use as an admixture in portland cement concrete. Many high calcium fly ashes contain MgO exceeding 5.0%. Some intermediate calcium ashes may also contain MgO in excess of 5.0%. When MgO is present in fly ash as periclase, a crystalline phase, it may affect the soundness of the resulting concrete through its expansive hydration to brucite, $Mg(OH)_2$. However, the studies have shown that for ashes where periclase was detected, only half of the MgO was periclase and as such no adverse effects of higher MgO content in fly ash on soundness of the resulting concrete are reported. Therefore, the requirement of MgO content not exceeding 5.0% in ASTM C618 has been currently dropped.

Figure 5 shows x-ray diffractograms of typical fly ashes and granulated blast furnace slag. The diffuse bands due to glass occur at different positions in Class C (high calcium) fly ash and Class F (low calcium) fly ash. In order to obtain generic information relevant to the utilization or disposal of fly ash, it is pertinent to conduct XRD studies of the crystalline phases of the available fly ashes. There are no reference standards available yet for XRD mineralogy of fly ash. Each fly ash is unique and may, itself, vary with time due to the differences in the chemical composition and mineralogy of the coal from which it is produced. A broad data base of the fly ash mineralogy for American fly ashes based on XRD studies is under preparation by the Western Fly Ash Research and Development and Data Center housed at the University of North Dakota and North Dakota State University.[87]

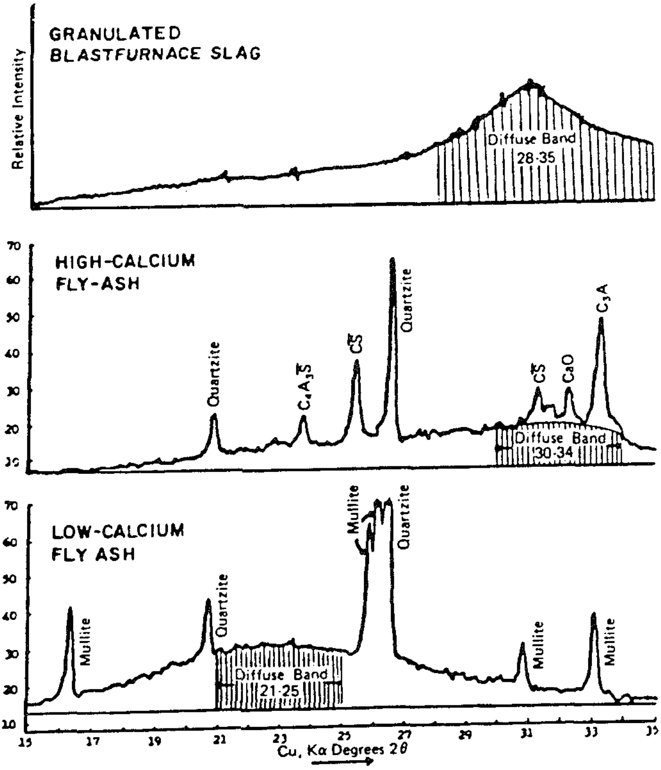

Figure 5. X-ray diffraction patterns of fly ashes and granulated blast furnace slag.[97]

4.2 Granulated Blast Furnace Slag

Granulated slag, obtained as waste product from both ferrous and non ferrous metal industries in finely ground form, has been used as mineral admixture, mostly as component of blended cements, called slag cements. In North America as well as in parts of Europe, it is also used as a supplementary cementing material, as an admixture in concrete. The generation of slags from the metallurgical industry is estimated around 40 million tons per year. More than 85% of the slags produced is used as a construction material for roads, raw material for cement, fertilizer, and pottery and as a soil stabilizer. Recently, with the growth in onshore and offshore construction activities, the use of blast furnace slag in concrete has gained momentum to improve durability of the concrete placed in marine environment. It has been more than 100 years since the hydraulic reactivity of slags was discovered and it was used for underwater concrete placement, especially in sea water.

Blast furnace slag is produced as a by-product in iron and steel industries. Air cooled slag dumped in heaps exhibits no pozzolanic or cementitious property even after pulverization to high fineness. However, when the slag is cooled quickly or quenched and then ground, it behaves like a pozzolan with some cementitious value and thus acquires the attributes of a suitable mineral admixture for use in concrete. The process of quenching is called *granulation* and the product is *granulated blast furnace slag.* Granulated slag is mixed with lime or portland cement clinker and ground, and the resultant products are called slag cements. For use as an admixture or as a blending agent, granulated slag is ground to the desired fineness, generally finer than portland cement.

In the industrially developed countries, slags are classified as blast furnace slag, converter furnace slag and electric furnace slag. The former two types are produced during the making of pig iron from iron ore, while the last type, electric furnace slag is generated from the steel making process using scrap iron as main raw material. Electric furnace slags have efflorescence and expansion characteristics like the converter slags and, thus, most of this production, about 2.5 million tons per year, is disposed of in land fills and reclamation areas.

The electric furnace slags are further classified into two categories, namely oxidizing and reducing slags due to the production process of slags. Oxidizing slag is produced in the process to eliminate the porosity and the impervious composition in molten steel by oxidizing, while the reducing slag is produced in the process to eliminate oxygen in molten steel and adjust the steel composition. Slags expand due to the volume increase associated with the hydration of free lime. The use of steel slag and non ferrous slags as mineral admixture is still in an infant state of development.

Ground granulated blast furnace slag (GGBFS) is, however, an accepted mineral admixture for use in concrete due to its glassy nature and chemical composition which make it pozzolanic and a cementitious material. The hydraulic reactivity of the quenched or rapidly chilled glassy GGBFS depends upon processing conditions, chemical composition, and particle characteristics. Slowly cooled highly crystalline slags are unreactive and are not marketed as cementitious materials.

Physical Properties and Particle Characteristics. According to the ASTM C989, the slag is classified in three grades, 120, 100, and 80, depending upon the mortar strengths when mixed with an equal weight of portland cement, and compared to that of pure portland cement mortar. The corresponding slag activity index standards are presented in Table 11. Majority of the GGBFS marketed in the U.S. is grade 120.

Table 11. ASTM C989 Slag-Activity Index* Standards for Various Grades

	Average of Five Consecutive Samples	Any Individual Sample
Minimum 7-day Index, %		
Grade 80	--	--
Grade 100	75	70
Grade 120	95	90
Minimum 28-day Index, %		
Grade 80	75	70
Grade 100	95	90
Grade 120	115	110

*SAI = slag activity index: compressive strength of standard ASTM C109 1:2.75 mortars with 50:50 BFS/portland cement proportions, and mortar flow of 110 ± 5%; referenced to equivalent standard portland cement mortars.

The particle shapes of GGBFS are generally equant. Granulation and grinding produces shards with conchoidal fracture surfaces, typical of broken glass. Compared to slag particles, fly ash particles are mostly spherical and have relatively a much smoother surface texture, thus fly ash addition produces better workability and finish of concrete mixes than slag addition. The particle size of GGBFS should lie between 10 µm and 45 µm with a considerable proportion of particles below 10 µm. It is reported that slag particles less than 10 µm contribute to early strength development in concrete up to 28 days, whereas 10 µm to 40 µm particles contribute to long-term strength. Blaine surface area required for slags to exhibit satisfactory cementitious and pozzolanic properties lies in the range of 4000 cm^2/g to 6000 cm^2/g. The slag produced after granulation in iron/steel plant is too coarse for use as mineral admixture as it consists of 50% particles larger than No. 20 mesh (840 µm). Grinding of slag is essential before it can be used as a mineral admixture.

GGBFS is now also used in combination with fly ash. Thus the benefits of using fly ash and slag separately are combined when the two are used together in concrete. Several studies have been made on the portland cement concrete containing both fly ash and GGBFS. In France and Australia, portland fly ash cement containing GGBFS is commercially available. Blast furnace slag cement (60% to 70% slag), in combination with 10% to 20% condensed silica fume (CSF), has been found to reduce expansion caused by alkali silica reaction, appreciably. Some studies[110] have shown that it is possible to make a concrete having 28-day strength of 94 MPa with 10% CSF and 30% slag used as replacement of cement in concrete. It has been demonstrated by different investigators that particle characteristics of slag and properties of the other blending materials such portland cement, fly ash, and condensed silica fume are among the other dominant factors that control the hydraulic reactivity and the performance of resulting concrete.

Chemical and Mineralogical Composition. Slags from iron/steel blast furnaces contain SiO_2 (33% to 36%), CaO (37% to 40%), Al_2O_3 (7% to 9%), Fe_2O_3 (1% to 10%), and MgO (10% to 11%) as major oxides. Of the various by-product mineral admixtures, slags are the nearest in chemical composition to portland cement. Nonetheless, they have a relatively higher silica and lower calcium content than portland cement. However, there are striking similarities in both chemical and mineralogical composition of slags and those of Class C or high calcium fly ashes. Not only are both essentially glassy, with glass content around 75%, but also the composition and reactivity of the glass appears to be similar.

Figure 5 shows that x-ray diffraction pattern of GBFS is quite similar to that of high calcium fly ash. The chemical composition of the glass in GBFS corresponds to melitite phase which is a solid solution phase between gehlenite (C_2AS) and akermanite (C_3MS_2). In a slowly cooled slag, these phases are mostly in crystalline form and are thus unreactive. However, in non crystalline state (glassy state), these phases significantly contribute to the reactivity of slag which goes up with increasing ratio of C_2AS to C_3MS_2 composition in glass.

One important difference between some high calcium fly ashes and granulated blast furnace slags is in the types of crystalline phases that are present. High calcium fly ash may contain reactive crystalline compounds such as free CaO, C_3A, C_4A_3 and alkali sulfates. However, all the crystalline compounds present in blast furnace slag are essentially unreactive. Some slags have slowly reactive dicalcium silicate (C_2S), crystalline phase in very small amount. No free MgO is present in slags. Rate of cooling the slag will basically establish the mineralogy of slag, slowly cooled slags give rise to unreactive crystalline phases whereas quenching produces reactive glassy minerals with relatively small amounts of crystalline matter. It may be noted that cooling does not alter the chemical composition of the slags. The strain in the glassy fractions of the slag may dictate the reactivity of the slag. There seems to be enough evidence to support this hypothesis.

Because of high calcium content as well as presence of reactive crystalline minerals, some Class C fly ashes possess self hardening characteristics just like cement. Their hydration reactions may start almost immediately after water is added. This may not be the case with slags which need some activator for starting their hydration. When slag is added to portland cement, the hydration of granulated blast furnace slag must await the hydration of the portland cement which provides alkalis and sulfates for *activating* the slag component. This initiates the hydration of glass present in slag which leads to the formation of cementing compounds.

Recent investigations have shown that it takes about three days before the contribution of the cementitious properties of the granulated slag to the blended cement becomes noticeable. Some slag hydration takes place immediately after water addition and a protective layer is formed on the surface of GGBFS which inhibits the water penetration into the slag particle and the further dissolution of ions from the slag. There are several compounds such as alkalis, gypsum, and lime $(CaOH)_2$ which serve as activators or accelerators for slag hydration. NaOH (caustic soda) has a greater effect than $Ca(OH)_2$ with increasing addition; gypsum accelerates the hydration still more with increasing addition and with age. However, gypsum is less effective as an activator without the presence of hydroxyl (OH) ions.

The addition of alkalis thus produces alkali activated slag (AAS) which sets and hardens much faster than portland cement. Extremely rapid hardening mixes can be produced by combining portland cement with slag, fly ash, and gypsum. Cement can be substituted by lime for economy. Alkali activated slags have found commercial uses in several countries round the world. Mostly sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3) or sodium silicate (Na_2SiO_3) are used as activators. In the early 1950s the U.S. Army Engineer Waterways Experiment Station used AAS cements, known as trief cements, in mass concrete construction. The usual composition was 1.5% NaCl, 1.5% NaOH and 97% slag. The water to binder ratio was 0.5. Thermal activation of slag without chemical activators is also possible.

The AAS concrete is characterized by quick slump loss in spite of the plasticizing effects of alkali solutions. However, the quick or flash setting can be prevented by continuous mixing due to thixotropic properties of AAS. The rate of strength development and ultimate strength are significantly enhanced and permeability of the concrete is appreciably reduced. To achieve the most optimum gains in workability, strength and durability, different additives like ground limestone, fly ash, and silica fumes are recommended for use in AAS concrete.

Various national and international standards allow different proportion of slag to produce slag cements, for example, up to 65% in the U.K. and the USA, 70% in Japan, and up to 80% in Germany, Russian Republics and Czechoslovakia. Supersulfated cement is extensively used in Germany, France, Belgium and Great Britain, particularly for underwater marine concrete construction. This cement is made by intergrinding a mixture of 80% to 85% GBFS, 10% to 15% $CaSO_4$ (anhydrite) and 5% portland cement clinker. A fineness of 4000 to 5000 cm^2/g is usual. For concrete made using this cement, water-cement ratio should not be less than 0.5 and aggregate-cement ratio not greater than 6. High sulfate resistance and low heat of hydration make this cement a suitable material for mass concrete construction in marine environment.

4.3 Condensed Silica Fume

During the last decade, the use of silica fume, also called microsilica, has significantly increased as a supplementary cementing material in concrete construction in North America, Japan and France. With the incorporation of condensed silica fume, a waste by-product from the silicon metal and ferrosilicon alloy industries, significant desired improvement in the rheological as well as mechanical properties of concrete has become possible.

Tjörn bridge in Sweden is the first major civil engineering structure in which silica fume (SF) was used. During the last 10 to 15 years, many structures all over the world have been constructed using SF in concrete. Among these is one of the most prestigious new structures in Paris, L'Arche de la Defense. France, Norway, the USA and Canada are some of the countries where SF has been extensively used and also researched as a mineral admixture in concrete. Unlike fly ash and blast furnace slag, the rate of annual production of SF is only a few million tons per year. In Japan the total amount of silica fume produced in 1992 was only 10,000 tons or less. Because of limited availability and current high price, silica fume, unlike fly ash and slag is used mostly as a property enhancing material rather than as replacement of cement in concrete.[66]

SF is a very fine powder with glassy spherical particles having diameters 100 times finer than portland cement. The particle size ranges from 0.1 µm to 0.2 µm. The silica (SiO_2) content in SF varies from 85% to 98%. Loose SF has a bulk unit weight of 240 kg/m^3 to 300 kg/m^3. SF does not suffer the variability in composition and heterogeneity in mineralogy typical of fly ashes. Typical particle size distribution of SF along with that of fly ash and portland cement is given in Fig. 6.[97]

Surface areas of the order of 20 to 23 m^2/g for condensed silica fume are reported in the literature. The extremely small size and spherical shape of glassy SF particles makes it highly reactive pozzolan which appreciably improves the properties of concrete both in fresh and hardened state. Because of the increased and accelerated pozzolanic reactivity of micro silica, calcium hydroxide released during the cement hydration is fast consumed to form cementitious materials. Each SF particle acts as a nucleation site for precipitation of calcium hydroxide. As a result, numerous small crystals, rather than a few large ones, are formed. The absence of large crystals of portlandite [$Ca(OH)_2$] which are weak and their replacement by smaller crystals can enhance the mechanical properties. The addition of SF contributes significantly to the improvement in the microstructure of the hydrated cement paste in the vicinity of coarse aggregate particles, called the transition zone. With the incorporation of increasing amount of silica fume in concrete, the thickness of transition zone decreases and also the accumulating water under aggregate particles is reduced. This results in improved strength and reduced permeability of concrete due to the reduction in the porosity of the transition zone and the refinement of the pore structure of the hydrating cement paste itself.

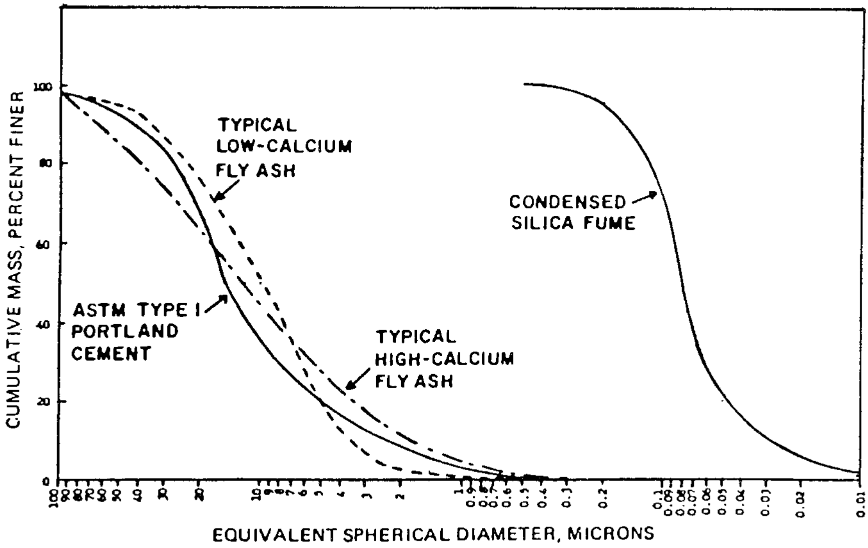

Figure 6. Particle size distribution plots of materials.[97]

Physical Properties and Particle Characteristics. Most of the silica fume presently used is gray in color with shades of darkness related to the carbon content. Some silicon and ferrosilicon plants equipped with heat recovery systems produce whitish SF that has a very low carbon content. SF is available in loose bulk form, densified form, slurry form and in the form of blended portland-SF cement. SF belongs to a superior class of pozzolan composed of glassy particles resulting from rapid condensation of gaseous SiO, which oxidizes rapidly when it comes in contact with air in the cooler part of the furnace.

5.0 EFFECT OF MINERAL ADMIXTURES ON PROPERTIES OF CONCRETE

Incorporation of mineral admixtures, particularly industrial waste by-products such as fly ash, blast furnace slag, and silica fume improves many properties of concrete significantly and favorably. Because of the spherical shape and small size of the glassy particles, the industrial by-product admixtures tend to fill the void space between relatively large cement grains which is otherwise occupied by water. In the water filled capillaries, the admixtures undergo pozzolanic reaction with $Ca(OH)_2$ released during cement hydration. As a result, pore refinement occurs as larger size pores are transformed into smaller size pores. There is also a marked decrease in the volume of pores and as a consequence of both the physical and pozzolanic effects of these admixtures, properties of concrete in both fresh and hardened state are affected. The extent of influence on concrete properties, however, depends on the type and amount of admixture used, concrete mix proportions, addition of chemical admixtures such as superplasticizer and air entraining agents, combined use of mineral admixtures, and many other factors. This section describes the effects of mineral admixtures on concrete mix proportions, water requirements, rheological properties of fresh concrete such as workability, bleeding and segregation and finishability, setting time, heat of hydration, rate of hydration and strength development, air entrainment, and on mechanical properties such as compressive strength, tensile strength and flexural strength, bond strength with reinforcement, modulus of elasticity, drying shrinkage and creep; and durability characteristics such as permeability, and resistance to deterioration by freezing and thawing cycles, scaling due to de-icing salts, attack by aggressive salt solution (sulfate attack) alkali silica reaction, corrosion of embedded steel in concrete, and resistance to abrasion and/or erosion. Mineral admixtures modify physical characteristics of fresh cement paste as well as the microstructure of the paste after hardening.

5.1 Concrete Mix Proportions and Water Requirement

Mineral admixtures are used in concrete as blended cement, as replacement of fine aggregate, and as partial replacement of cement at the concrete mixing plant. In a concrete mix, mineral admixtures can act in part as a fine aggregate and in part as a cementitious component due to their pozzolanic and cementitious reactions. In most field applications, mineral admixtures are used as replacement of cement in varying proportions from 10% to 80% by weight of cement.

Addition of fine particles of a mineral admixture, typically of the order of 1 μm to 20 μm size, would reduce the volume of voids in concrete mixes, thus requiring less water to produce a concrete of given consistency. Because of the smooth glassy surface texture of mineral admixture particles, internal friction between granular materials constituting concrete is reduced, which tends to improve consistency of mix. Very fine particles, as is the case with silica fume, tend to fill the void space between relatively large cement grains and thus release the entrapped water to enhance the fluidity of the mix. In two field applications 30% fly ash substitution for cement was found to reduce the water requirement by 7% at a constant slump. In many but not all the cases, less mortar would be required to maintain constant slump when fly ash is added to concrete mix. Similarly, the use of a granulated blast furnace slag with specific surface of 5080 to 6080 cm^2/g was found to reduce the water demand by about 6.4% for standard flow of a large number of portland cement slag mixtures containing 40% to 65% cement replacement by slag.

Not all the mineral admixtures reduce the water demand. In case of high volume replacement of cement by fly ash, the use of chemical additives such as superplasticizer (plasticizing agent) and air entraining agent is required to maintain constant specified consistency. Because of the increased specific surface area when high levels of mineral admixtures are used, the water requirement may sometimes be increased. Particularly when SF is used, very fine particles will show the tendency to adsorb water and thus lead to an increase in water demand. Many researchers have reported that, with the use of a fly ash containing a large fraction of particles coarser than 45 μm, or a fly ash with high amounts of unburned carbon exhibiting loss on ignition around 1% or more, water demand is rather increased to maintain constant fluidity. Also, some high calcium fly ashes may contain significantly large amounts of tricalcium aluminate (C_3A) and their use in concrete would result in an increased water requirement due to loss of consistency caused by the rapid formation of calcium alumino hydrates or sulfoaluminate hydrates including ettringite. The net effect of mineral admixture addition on water requirement depends upon several factors, in particular on type and amount of admixture, water to cementitious material ratio, mix proportions of concrete, as well as presence of other admixtures and chemical agents such as water reducer, set accelerator, superplasticizer, and air entraining agent in the concrete mix.

Condensed silica fume or rice husk consists of extremely fine particles with very high specific surface, and the investigations have shown that with their use in concrete, water required to maintain specified consistency increases in almost direct proportion to their amount present by weight of cement.

Aïtcin et al.[3] have reported that the addition of 10% SF in a lean concrete containing 100 kg/m^3 of cement reduced the water demand. However, this concrete exhibited poor durability against freeze-thaw attack. In normal structural concrete, even with 5% silica fume addition, the water demand is increased to maintain constant slump. For producing very high strength and durable concrete, silica fume up to 10% is added as an admixture and the use of a water reducer or superplasticizer to maintain the specified slump is found necessary. When no plasticizer is used, it has been suggested[112] that an additional 1 litre/m^3 of water should be used for every 1 kg/m^3 of SF addition to maintain constant level of fluidity.

By modifying the mix proportions, fly ash concrete could be made which has strength, both at early and late ages, comparable with that of non fly ash concrete mixes. It has been found that up to 60% cement can be replaced with subbituminous, Alberta fly ash, for comparable 28-day strength of plain concrete using superplasticizer or water reducing agent to maintain the specified level of workability. In the design of fly ash concrete mixes, coarse aggregate factor may be held constant at 1100 kg/m^3 for the limestone aggregate mixes and at 1175 kg/m^3 for the concrete mixes made with the gravel. Fine aggregate or sand, may be reduced to compensate for the volumetric displacements of the fly ash increments of 48, 66 and 84 kg/m^3 of concrete. Thus, to achieve the same effect as with 90 kg of cement, one would generally have to use at least 84 kg of Class C ash in conjunction with decrease in the sand to aggregate ratio. In general, it has been found that on 28-day strength basis, bituminous (Class F) fly ash in the range of 66 kg to 84 kg is worth 45 kg to a usual upper limit of 60 kg of cement in a cubic meter of concrete. On the other side, subbituminous (Class C) fly ash in the range of 66 kg to 84 kg appears to be worth 75 kg to about 90 kg of cement in a cubic meter of concrete. A plausible explanation for this difference is the observed increase in workability and the self hardening with the use of Class C, high calcium fly ash, in concrete. Proportioning fly ash concrete mixes on equal 28-day strength basis would generally require a cement replacement ratio greater than 1:1 by weight. The additional fly ash would replace a portion of fine aggregate thereby producing even a greater increase in the binder matrix to aggregate ratio. Therefore, improved workability will be achieved with a given water content.

5.2 Workability

Because of fine particle size and the spherical shape of particles of fly ash, workability including finishability of concrete mix containing fly ash is significantly improved. Bleeding and segregation are considerably reduced with the use of fly ash as a mineral admixture in concrete and thus pumpability of concrete is improved. The addition of silica fume increases cohesiveness and viscosity of concrete. Bleeding is appreciably reduced as some of the free water is adsorbed on the surface of SF particles. High strength SF concrete with W/(C + SF) ratio of 0.25 and 230 mm slump showed similar resistance to segregation as a non-SF concrete with W/C ratio 0.55 and 85 mm slump. With SF addition, particularly in rich concrete mixes or mixes with low W/(C + SF) ratio, the increase in cohesiveness and viscosity sometimes makes it more difficult to place and consolidate the concrete. It often becomes necessary to incorporate superplasticizer or to increase the required slump by 50 mm in order to obtain workability similar to that of non SF concrete. SF is mostly used as property enhancing material at addition levels up to 10% by weight of cement, and superplasticizer or water reducer is used for constant consistency.

When fly ash is used in the mix, workability can be increased to the point that sand content can be decreased and coarse aggregate content increased, thereby reducing the total surface area to be coated with cementitious material. This leads to the improvement in workability for the given amount of binder matrix. In general, fly ash is found to be particularly useful and valuable when used in lean mixes and in concretes made with aggregates deficient in fines, as it improves their workability and finishability.

5.3 Setting Time

Addition of mineral admixtures to portland cement generally results in set retardation. This is especially true of low calcium fly ashes with high carbon content. The high calcium fly ashes, which are generally low in carbon and high in reactive components, sometimes exhibit opposite behavior. Not all high calcium fly ashes cause quick setting. In a recent study[64] involving three different subbituminous coal ashes from Alberta, Canada, used at replacement levels of 40% to 60% by cement weight, it was observed that fly ash concrete achieved an initial set in 8 to 11 hours as compared to about 5 hours for non fly ash concrete. The final setting time varied from 10 to 13 hours while it was about 7 hours for control mixes containing no fly ash. The setting time of fly ash concrete mixes was a function of the type and amount of fly ash used. For producing acceptable ready made concrete mix containing fly ash for field use, it becomes necessary to regulate and control the setting time by application of set modifiers, i.e., set accelerators.

The initial and final set times of portland cement blast furnace slag mixtures containing 40% to 65% slag by weight were found to increase by about one hour compared to those of the reference portland cement. The observed increase in setting times is not of much significance, particularly for mass concrete construction and general building construction. However, for slip forming as well as cold weather concreting, setting time needs to be accelerated when mineral admixtures are used in concrete.

The addition of SF to concrete in the absence of a water reducer or superplasticizer is reported to cause delay in setting time, compared to non SF concrete of equal strength, especially when the SF content was high. Malhotra et al.[79] reported that the addition of 5% to 10% SF to either superplasticized or non superplasticized concrete with W/(C + SF) ratio of 0.4 did not exhibit any significant increase in setting time. However, when 15% SF was added with a high dose of superplasticizer, both the initial and final setting times were delayed by approximately 1 and 2 hours, respectively. The observed delay was mostly attributed to the relatively high dose of superplasticizer needed for the high amount of SF added to the concrete.

5.4 Heat of Hydration

Hydration of portland cement is an exothermic reaction accompanied by liberation of heat that results in temperature rise of fresh concrete. In mass concrete, sections thicker than 60 cm or so, depending on the type and amount of cement, thickness and type of formwork, ambient temperature and humidity conditions, the temperature rise at times may amount to 20°C to 50°C within 2 days to 5 days after concrete placement. On cooling at subsequent age, the concrete with initial temperature rise may crack due to thermal stresses induced in hardened concrete. Additions of mineral admixtures such as natural pozzolans, fly ash, blast furnace slag in concrete as replacement of cement, result in reduction of temperature rise due to heat of hydration almost in proportion to the amount of cement replacement. Low calcium bituminous fly ashes tend to reduce the rate of temperature rise more than high calcium subbituminous ashes as well as blast furnace slag and silica fume.

As a first approximation, the percentage reduction in heat liberation at 7 to 28 days may be taken at about one-half of the percentage of cement substitution by mineral admixture. Thirty percent substitution of cement by low calcium fly ash reduced the temperature rise of plain concrete from 47°C to 33°C after 4 days of concrete placement.[7] In a field test, a reduction in temperature rise in concrete sections, 2.5 m and 4.75 m deep, was reported to be about 15% at 30% replacement level of cement by fly ash. Cement replacement by fly ash in high proportions 40% to 75% or use of blast furnace slag cement with 40% to 80% slag offers an obvious advantage of mitigating or completely eliminating thermal stresses during hardening of concrete placed in massive structures. After long curing, the concrete containing mineral admixtures shows relatively higher ratio of flexural strength to compressive strength because of the superior aggregate-binder matrix bond. Therefore, the use of fly ash or blast furnace slag is recommended for concrete highway pavements as well as for normal reinforced concrete structures.

The actual heat evolution characteristics of any particular concrete placement depend upon the type and amount of admixture used, mix proportions, formwork, and the ambient environment. Early age rise in temperature of plain concrete has been found to adversely affect the late age compressive strength and durability of concrete because of the porous and weak framework of the gel matrix formed at early high temperature. However, when mineral admixtures such as fly ash, and blast furnace slag are added, thermal gradient is lower and healing of microcracks by the products of pozzolanic reactions, which are accelerated at higher than normal temperatures, takes place. Thus when concrete is exposed to high temperatures at early age, the use of mineral admixtures in concrete is obviously advantageous and favorable. Furthermore, the mineral admixtures which react slowly at normal temperature can benefit from the heat of hydration of portland cement which otherwise goes to waste in the surrounding environment.

In Bhakra dam (India), natural pozzolan in the form of calcined clay locally available at the dam site was used to reduce heat of hydration.

Recently mineral admixture such as fly ash has been used in the gravity platform concrete structure of Hibernia project in Canada. There are several examples of the use of large volumes of fly ash to retard the liberation of hydration heat and thus control the rise of temperature at early age in concrete for mass concrete structures such as dams, turbogenerator mats, and power houses.

It has been reported that partial replacement of cement by SF also results in reduction of heat of hydration without any reduction in strength. Tachibana et al.[118] showed that for a high strength concrete having 540 kg/m^3 cement content and 10% cement replacement with SF, heat was 9% less compared to the mix without SF. The addition of SF may accelerate the temperature rise during the first 2 days to 3 days, but a net decrease in temperature rise of SF concrete is observed at later ages (7 to 28 days) when compared to the corresponding plain cement concrete. At very early age, due to the fast pozzolanic reaction of SF, a greater amount of heat is liberated compared to portland cement. The ratio of heat liberated by pozzolanic activities of SF during the first 2 days to 3 days per gram of SF to that of portland cement is reported to be of the order of 1 to 2.

Mehta and Pirtz[91] have reported that with the use of 30% rice husk ash as cement replacement in a high strength mass concrete (40 MPa strength at 28 days), a drop of about 12°C in temperature rise at 28 days was observed compared to the reference concrete without the admixture.

5.5 Air Entrainment

Addition of mineral admixtures increases the demand for air entraining admixture (AEA) in concrete required to entrain a given amount of air for freeze-thaw durability. Concretes made with Class C (high calcium) fly ash generally require less air entraining admixture than those made with Class F (low calcium) fly ash to entrain around 6% air in concrete. Even with some subbituminous fly ashes, the average demand of air entraining agent is reported to be more than double that of the plain concrete. The unburned carbon in fly ash, especially when present as activated carbon, is suspected to increase the AEA demand significantly. Subbituminous fly ashes, even with low loss on ignition, may contain some activated carbon which enhances the AEA demand. The exact mechanism of increase in the AEA demand due to fly ash addition is still not understood.

The addition of silica fume (SF) has also been found to reduce the volume of air in concrete for constant dosage rate of an AEA. Carette and

Malhotra[11] have reported that it is difficult to entrain more than 5% air in concrete containing a high amount of SF, even when a superplasticizer is used. The concrete tested by them had a 0.4 W/(C + SF) ratio and a sulfonated hydrocarbon AEA. In a concrete containing 400 kg/m^3 of cementitious materials with 20% SF replacement, the requirement of AEA was observed to be about five times greater than similar concrete without SF. Additional demand for the AEA is less when a water reducer or superplasticizer is incorporated in the mix. In case of SF concrete, the increased demand for the AEA to entrain a specified air content is caused due to adsorption on the surface of microsilica particles and also probably due to the presence of carbon in SF. Because of the cohesiveness of SF concrete, the loss of air from fresh concrete during vibration is reduced, especially in the presence of water reducer or superplasticizer. Thus, the air stability in fresh SF concrete is significantly improved. The observed increase in the AEA demand with the incorporation of mineral admixtures, and particularly some fly ashes, to produce the specified volume of air in concrete has a negative impact regarding the utilization of fly ash in field applications on a commercial scale. The problem thus needs to be investigated for better understanding of the underlying reasons for the increased demand of AEA caused by mineral admixtures.

5.6 Hydration and Strength Development

Incorporation of mineral admixtures in concrete influences the rate of hydration of cement and thereby the strength development. In general, pozzolanic reactions initiate after the cement hydration begins when $Ca(OH)_2$ becomes available. Thus, with the replacement of cement by mineral admixture, early rate of hydration of cement concrete is retarded. The effect of pozzolanic reactions is generally manifested at late ages by increased strength and reduced permeability. The physical effect of adding fine particles of mineral admixtures results in more efficient dispersion of the flocculated structure of portland cement particles and may increase early hydration to some extent, particularly with fine aggregate replaced by the mineral admixtures in a concrete mix.

The rate of strength development of concrete containing mineral admixtures is dependent upon several factors such as the type and replacement level of mineral admixture, mix proportions, ambient temperature and curing conditions, and presence of other additives. A large volume of information is available on strength development characteristics of concrete containing fly ash, blast furnace slag cement, and silica fume, separately as well as combinations.

The two important factors which adversely affect both strength and imperviousness of concrete are the presence of large pores in the hydrated cement paste, and the microcracks at the aggregate-cement paste transition zone or interfacial zone. Due to the physical effect of filling the large voids with fine size mineral admixture particles and formation of the cementitious compounds by pozzolanic reaction products which cause pore refinement and also reduces microcracking in the transition zone, significant improvements in strength and durability are achieved. As compared to other admixtures, these effects become apparent with SF addition at very early age of hydration, within 1 to 2 days of concrete placement. Mixes containing fly ash exhibit the improvement in mechanical properties of concrete beyond the age of 6 to 8 weeks, depending upon the type and properties of fly ash used. For producing high strength concrete with replacement of cement by mineral admixtures, water reducer or superplasticizer is required to achieve the specified level of fluidity as the water to cementitious material ratio is rather low in these mixes. Both the rate of strength development and ultimate strength of concrete are of concern to the construction engineer. Thus, the potentials of mineral admixtures, when used in concrete, need to be exploited through proper understanding of the hydration mechanism of the binder matrix, i.e., portland cement + mineral admixture + water system.

The exact mechanism by which transformation of large pores into fine pores occurs in cement pastes containing mineral pozzolanic admixtures is not fully understood. It has been observed that compared to the C-S-H phase in hydrated portland cements, a less compact C-S-H is formed during hydration of cement pastes containing mineral admixtures. The transformation of high density phases and large pores in a portland cement paste system to low density products and small pores due to pozzolanic silica and lime, result in observed increase of strength and impermeability of concrete as postulated by several investigators.[27]

In the composite material concrete, the interfacial bond between the aggregate and hydrated cement paste, the density of the transition zone, and microcracking play an important role in influencing the mechanical properties and long-term durability of concrete. In normal portland cement concretes, the transition zone is generally less dense than the bulk paste and contains a larger amount of platelike crystals of calcium hydroxide, with C axis perpendicular to the aggregate surface. As a result, it becomes more vulnerable to microcracking induced by incompatible dimensional changes between the aggregate and cement paste due to normal temperature and humidity changes. The structure of the transition zone thus explains why it is the weakest zone in concrete and would thus control the properties of concrete. Because of their pozzolanic characteristics, mineral admixtures are known to exercise a beneficial effect on the structure and mechanical strength of the transition zone. Therefore, the combined effect of pore refinement and improved structure of the transition zone holds promise that concretes containing mineral admixtures can be stronger and more durable than plain concretes. Different mineral admixtures depending on their composition and properties, particularly fineness and pozzolanic reactivity, will influence the strength and durability of concrete with wide variations. A brief account of the effect of industrial mineral admixtures on the strength of concrete is described below.

Strength usually gives an overall picture of the quality of concrete and is directly related to the hydration characteristics of the hardened cementitious material paste. With highly active pozzolans, such as rice husk ash and SF, the pozzolanic reaction may start as soon as calcium and hydroxyl ions are available from the cement hydration. Some of the high calcium fly ashes also exhibit quick hydration because of their self hardening characteristics. However, in most cases, blast furnace slag and fly ash have relatively slower hydration and less early age strength. In the presence of rice husk ash with the high internal porosity of its particles, significant effects of the pozzolanic reaction on the compressive strength, even at early ages of 1, 3 and 7 days after hydration, are observed. It has been possible to develop industrial concretes containing 30% rice husk ash as cement replacement and a superplasticizer, with compressive strength of 90 MPa at 90 days.[90]

Condensed silica fume reacts at a slightly slower rate than rice husk ash, yet it is capable of producing concretes of very high ultimate strength. The extent of compressive strength increase, caused by replacing some cement with SF, depends upon the age of concrete as well as the cement and SF contents. Furthermore the time at which SF starts contributing to strength gain is a function of W/(C + SF) ratio as well as cement content of the concrete. In a study on the effect of SF addition on concrete strength, it was reported that at 1 day the reference concrete had higher strength. However, at 3 days and beyond, concretes containing the admixture (SF) showed higher strength than the reference concrete.[10] Ultimate compressive strength of the order of 100 MPa has been reported by several investigators using superplasticizer and 20% or more SF by weight of total cement. By using a special aggregate (cementitious aggregate) of given particle size distribution and extremely low W/(C + SF) ratio, compressive strengths of the order of 200 MPa are achievable.[6] SF addition accelerates the strength development of concrete at early ages and it is found favorable and advantageous for use in fly ash concrete which invariably has low early strength. Malhotra[78] has reported that concretes made with W/(C + SF) ratio of 0.6 and using SF at replacement level 5% to 15% by cement weight did not show any noticeable increase in strengths up to 3 days of curing. However, when W/(C + SF) ratio was reduced to 0.4, strength increase was observed at earlier ages of 1 day to 2 days of curing. At low W/(C + SF) ratio, the effect of SF on early age strength is quite marked and has been observed by several researchers. There is an optimum concentration of SF, mostly less than 15% to 20%, that can be used to replace cement to achieve maximum strength improvement both at early and late age.

Bituminous fly ash invariably contributes to the long-term strength gain of concrete, more than subbituminous ash, in spite of its relatively less effectiveness in early age strength. Swamy and Mahmud[115] have reported that concrete containing 50% low calcium bituminous fly ash as cement replacement and using a superplasticizer is capable of developing 60 MPa compressive strength at 28 days and a reasonable strength of 20 MPa to 30 MPa at 3 days. For a typical low calcium fly ash, it was reported that the pozzolanic reaction started at 11 days after hydration at 20°C and the significant effect on compressive strength was noticed after 28 days of curing. No significant contribution to strength development occurs up to 7 days with the use of low calcium fly ash in concrete. At 28 days and beyond the gain in strength of cement-fly ash mortar with 30% fly ash as cement replacement was observed to be about the same as that of reference portland cement mortar. High calcium fly ashes exhibit significant contribution to strength even at 3 days and strengths of similar magnitude as that of reference mortar at 7 days. It seems that the availability of hydroxyl, sulfate and calcium ions in the hydrated cement paste initiates and accelerates the hydration of high calcium fly ashes at early age and this process continues with the progressive growth of cement hydration.

High strength fly ash concrete has found applications in several field projects, for example, high rise buildings in the Chicago area of the USA and the Toronto area of Canada (Canadian National Tower in Toronto). High strength concrete containing 504 kg/m^3 portland cement, 59 kg/m^3 low calcium fly ash, and water reducing agent, with water to cementitious material ratio of 0.33 developed for use in the Water Tower Place and River Plaza in Chicago had about 70 MPa compressive strength at 50 days.[7] For field application in Texas, similar strengths were obtained from concrete mixtures containing only 400 kg/m^3 cement, 100 kg\m^3 high calcium fly ash, and water reducing agent with water to cementitious material ratio maintained at 0.33.[14] The test results of Rodway et al.[108] showed that 28-day strength of concretes made with 56% to 68% Alberta fly ash as cement replacement was about the same and in some cases slightly higher than that of reference concrete without fly ash.

In a recent laboratory study, Joshi et al.[64] tested a large number of fly ash concrete mixes made by using three different Alberta fly ashes, subbituminous fly ashes with intermediate calcium content, at the replacement levels of 40% to 60% by weight of cement. The mixes were superplasticized and air entrained to obtain 100 mm to 120 mm slump and 6±1% air content. The cementitious material in the mixes was varied from 380 to 466 kg/m^3, water to cementitious material ratio from 0.27 to 0.37, coarse aggregate ranged from 1012 to 1194 kg/m^3, and fine aggregate (sand) varied from 712 to 643 kg/m^3. A summary of the mix proportions and some test data along with 7-day and 28-day compressive strengths are presented in Table .12. The results indicated that with fly ash replacement levels up to 50% by weight of cement, concrete with 28-day strength ranging from 40 MPa to 60 MPa could be produced. A detailed information on high volume fly ashes is given in Ch. 12.

At 3 days, the fly ash concrete mixes developed compressive strength in the range of 13.7 to 28.6 MPa against 35.3 MPa for reference concrete without fly ash. At 7 days, the fly ash concrete had strength varying between 21.9 to 41.0 MPa compared to 44.1 MPa for reference concrete. However, at 28 days, compressive strength of fly ash concrete ranged between 37.6 MPa to 50.7 MPa against 58.7 MPa for plain concrete. In brief, whereas the highly active pozzolans start their contribution to strength development almost from the onset of portland cement hydration, the low calcium fly ash does not show large enough pozzolanic activity to affect strength until about two weeks after hydration. The high calcium fly ash (Class C) with calcium content more than 15% may start its self hardening and pozzolanic action as early as three days after preparation of samples.

Table 12. Proportions and Properties of Final Design Mixes Using High Volume Fly Ash[64]

Mix No.	Fly Ash+ (kg/m^3)	Cement (kg/m^3)	Coarse Aggregate (kg/m^3)	Fine Aggregate (kg/m^3)	$\frac{W}{C+F}$	AEA* (ml)	Superplasticizer X (ml)	Density (kg/m^3)	Slump (mm)	Air Content (%)	Compressive Strength (MPa)	
											7-Day	28-Day
FS40-I	186(S)	280(I)	1088	700	0.28	130	1125	2258	120	5.2	39.8	47.0
FS50-I	233(S)	233(I)	1088	700	0.28	130	900	2206	140	5.3	27.9	48.2
FS60-I	280(S)	186(I)	1088	700	0.28	130	785	2206	150	5.2	25.5	41.5
FS50-III	233(S)	233(III)	1088	700	0.28	130	1429	2175	110	6.8	41.0	49.9
FW40-I	186(W)	280(I)	1088	666	0.31	300	1000	2206	125	5.7	34.3	50.7
FW50-I	233(W)	233(I)	1088	666	0.31	300	1437	2311	110	5.0	34.4	48.1
FW60-I	280(W)	186(I)	1088	666	0.32	450	1250	2284	150	6.0	21.9	37.6
FF40-I	186(F)	280(I)	1198	590	0.28	150	1083	2167	130	7.0	29.6	42.1
FF50-I	233(F)	233(I)	1198	590	0.28	200	1511	2208	100	5.4	33.5	49.6
FF60-I	280(F)	186(I)	1198	590	0.28	150	1408	2167	150	6.0	24.6	43.4
C-I	***	380(III)	1088	700	0.36	100	2500	2285	170	4.3	44.1	58.7
C-III	***	380(I)	1088	700	0.32	70	1406	2285	100	5.0	46.8	53.9

+S = Sundance, W = Wabamun, F = Forestburg, W = Water, C = Cement, F = Fly Ash

*AEA: Air-entraining agent (ml/100 kg of cementitious material)

XSuperplasticizer (ml/100 kg of cementitious material)

(I): ASTM Type I Cement, (III): ASTM Type III Cement

***: Control mixes

The hydration characteristics of ground granulated blast furnace slag are quite similar to those of high calcium fly ash due to the observed similarity in their mineralogy. At 40% to 65% replacement level of cement by GGBFS, it has been reported that up to 3 days of age, the contribution of slag to strength of mortars is low. However, at 7 days, strength almost equal to that of reference mortar was achieved. At later ages GGBFS increased the strength of mortar significantly to values higher than that of the reference mortar made with only portland cement as binder. At 40% to 50% replacement level of cement by GGBFS having Blaine surface area of 6080 cm^2/g, mortar strength of about 60 MPa was achieved at 60 days compared to 47 MPa strength of the reference mortar at the corresponding age. Concretes made with cements containing 40% to 50% slag and having water to (slag + cement) ratio of 0.38 developed about 55 MPa strength at 28 days as compared to 48 MPa for the reference concrete.[36] With the use of alkali activated slags as mineral admixture in concrete, the rapid hydration of the binder would lead to high early strength even at a rate faster than rapid hardening ASTM Type III cement.[105]

Regarding the effect of natural pozzolans on strength development of concrete, their effect is similar to that of low calcium fly ashes because of their similar pozzolanic reactivity characteristics. Ceresto and Rio[122] (1971) found that at 40% cement substitution by the Segni-Latium tuff, natural pozzolan from Italy, gave 62%, 75%, 85% and 86% compressive strength of the control concrete mix containing 300 kg/m^3 cement content at the ages of 7, 28, 90 and 365 days respectively. The corresponding percentages of strength when Bacoli volcanic glass was incorporated as mineral admixture were 63%, 86%, 95% and 97%. In his study on mortars made with 10%, 20% or 30% Santorin earth by weight of cement, Mehta[94] found that no contribution to the 7 day strength was noticed with the use of admixtures. However, at 28 days, strength was higher than that of the reference mortar by 6% at the 10% substitution level, but was lower by 7% and 18% for the 20% and 30% substitution levels, respectively. After 1 year, the ultimate strength at the 30% replacement level was found to be similar to that of reference mortar, and it was 10% higher for the 20% substitution.

Thus, it is easy to recognize that the rate of strength development as well as ultimate strength of concrete made with mineral admixtures can be related with the progress of pozzolanic reaction by which the continual process of pore refinement and improvement in the structure of transition zone occur. In general, the effect of mineral admixtures on flexural strength, tensile strength, and bond strength with steel follows about the same pattern as on compressive strength, as these strength parameters are approximately proportional to compressive strength. It is the quality of the cement paste which is significantly improved with the introduction of mineral admixtures and this results in favorable effects on different types of strength of resulting concrete. The correlation factors of different types of strength with compressive strength at a specified age depend upon several factors such as type and amount of admixture used, mix proportions, curing conditions, and age of concrete.

Flexural strength and splitting tensile strength of concrete made with Class F type fly ash from Eastern Canadian bituminous coal was found to be slightly lower than that of the control mixes without fly ash.[69] However, with subbituminous fly ash used at replacement level of 40% to 75%, an increase of about 30% in flexural strength was observed at the age of 90 days.

Johansen[37] reported that concrete containing 5% SF and cured in air for 3 years can have a flexural to compressive strength ratio comparable to that of control concrete without SF. Similar results were observed with concrete containing 11% SF replacement and water reducer. On the other hand, the concrete containing 11% SF and no water reducer and other concretes containing 25% SF replacements and made with or without water reducers had lower flexural to compressive strength ratios than those of non SF concretes. In the context that mineral admixtures reduce the bleeding and increase cohesiveness of concrete, bond strength with reinforcing steel, as determined by pull out strength test, has been reported to improve significantly. With the addition of SF, bond strength was found to increase with an increase in SF content up to 16%, particularly for high strength concretes.[31] The observed increase in bond strength was attributed to the reduction of thickness and porosity of the transition zone between the cement matrix and reinforcing steel. Although some investigators have reported that the addition of SF up to 15% can improve the adhesion between fibers and cement paste, the overall toughness of the fibre reinforced cement may not show a corresponding improvement.[102]

5.7 Effect of Curing Conditions on Strength Development

In order to promote continued hydration and pozzolanic reactions in the concretes containing mineral admixtures, favorable conditions of temperature and humidity are found necessary. Several studies have been conducted to investigate the effects of moist curing, water curing, air drying (dry curing), and mass curing at normal temperature levels on properties of hardened concrete such as strength, permeability, and durability. Langley et al.[69] reported that minimum duration of moist curing for fly ash concrete was 3 days, after which normal curing as per construction practices may be employed without any significant adverse effects. Long-term strength development in mass fly ash concrete construction was reported to be less influenced by drying than the control specimens used in the laboratory.

During the dry curing of a concrete made with 40% subbituminous Alberta fly ash as cement replacement and cured at 50% and 10% relative humidity, a loss of about 30% and 60% of mixing water, respectively, was observed within 50 hours after concrete placement. It was further reported that in addition to strength loss due to reduced water content, the combination of low curing temperature and the cooling effect of evaporation of water at low relative humidity may retard the rate of hydration and, thereby, strength development.[33] The importance of curing concrete in an enclosed environment, particularly during cold weather conditions, in order to reduce the evaporation of mixing water during the early hours after concreting, is therefore emphasized.

A clear picture of the effect of curing regime on strength development of high volume fly ash concrete mixes is shown in the data presented in Table 13.[115] Increases of 50% to 100% of 28-day strength were achieved after one year under continuous moist curing of fly ash concrete compared to only 18% to 25% increase in strength of control concrete without fly ash subjected to the similar curing conditions. Under the other two curing regimes, one with 7-day moist curing followed by air drying, and the other with continuous dry curing, the relative increase in strength of fly ash concretes after 1 year varied between 6% to 22% of the 28-day strength of reference concrete.

The minimum duration of moist curing of silica fume (SF) concrete suggested by several researchers is 7 days after casting to develop proper strength and durability. In the long term study of SF concretes made with 10% SF as cement replacement, Carette and Malhotra[13] found that, moist cured control and SF concretes showed continuous gains in strength over the test duration of 3.5 years. On the other hand, air cured control and SF concretes had 20% to 25% lower compressive strength than that of the corresponding moist cured concretes. The decrease in compressive strength

Table 13. Rate of Strength Development as Percentage of 28-Day Strength[115]

Age in Days	Strength (MPa)								
	20*			40*			60*		
	Fog	Dry	7F+D	Fog	Dry	7F+D	Fog	Dry	7F+D
1	19	--	--	25	--	--	34	--	--
7	55	71	--	67	80	--	68	79	--
28	100	100	100	100	100	100	100	100	100
150	176	125	104	140	119	105	135	123	117
270	197	114	110	150	125	116	140	113	121
365	209	118	106	162	122	107	146	116	118

7F+D = 7 day fog followed by air dry curing
* = fly ash replacement value (%)

under dry curing was observed to be a function of W/(C + SF) ratio and was relatively high in SF concrete mixes with higher W/(C + SF) ratio.

Under dry curing conditions, the relative strength gains beyond 28 days of SF concretes were significantly slower than those of non SF concrete continuously moist cured and slightly lower under the corresponding dry curing conditions. The probable mechanism for reduction in strength under dry curing is attributed to non uniform shrinkage of concrete during drying. The moisture gradient that can develop during drying between the inner and outer regions of concrete member can lead to structural distress and reduction in compressive strength. This structural effect of dry curing is expected to decrease with an increase in the size of concrete members and is confined only to surface layers in massive structures. With dense and cohesive SF concrete, the drying affects only a small outer layer. In this region, excessive tensile stresses can develop since shrinkage strains are restrained by the inner concrete which undergoes less drying. These tensile stresses, in turn, would cause compressive stresses in the core area of the specimens, which superimpose on applied loads upon testing, and result in recording a slight reduction in strength. It is reported that the drop in compressive strength caused by such structural effect of drying cannot exceed twice the tensile strength of concrete.[71]

Curing conditions also have a predominant influence on other mechanical properties such as different types of strengths, modulus of elasticity, shrinkage and creep of concrete. Permeability and, as a result, durability characteristics of concrete are much dependent on the curing conditions of concrete made with mineral admixtures because the microstructure, porosity and the general framework of the hydrated binder matrix are altered by variations in curing conditions.

5.8 Modulus of Elasticity, Drying Shrinkage and Creep

The effect of mineral admixtures used as replacement of cement on modulus of elasticity of concrete follows about the same trend as on compressive strength in that it is generally reduced, particularly with fly ash, at an early age and is slightly increased at late ages. As compared to compressive strength gain, the increase in modulus of elasticity was less with the incorporation of fly ash in concrete at 90 days.[75] Similarly with SF addition to concrete, a slight gain in modulus of elasticity was observed even at 28 days or earlier. With SF addition, the porosity and microcracking in the transition zone between aggregate and hydrated cement paste are reduced due to the physical and pozzolanic effects of SF. As a consequence, a better composite action can occur in the concrete whereby the stiffness of the aggregate can contribute more effectively to the stiffness of the concrete. Deformation characteristics and volume stability of concrete are dependent on both strength of concrete and stiffness of the aggregate including their volume fraction. With the addition of mineral admixtures, the continued hydration and pozzolanic reactions tend to form more dense and compact binder matrix which results in improved volume stability.

As regards drying shrinkage, the incorporation of high calcium fly ash in concrete at replacement levels between 20% and 50% by cement weight has little influence on drying shrinkage.[120] Furthermore, Haque et al.[33] observed that with 40% to 70% cement replaced by subbituminous Alberta fly ash, drying shrinkage of concrete decreased with an increase in fly ash content. With Class F, low calcium, fly ashes although the initial values of drying shrinkage of concrete tend to increase, yet after about a year, the drying shrinkage of plain and fly ash concrete has been observed to be similar.

Concretes containing 40% to 65% blast furnace slag by weight of total cementitious material exhibited somewhat greater drying shrinkage than plain cement concrete. However, the study made in Japan has indicated that this can be remedied by correcting the optimum sulfate content of the total cementitious material to 2% to 2.5% expressed as SO_3 content.[36] The addition of SF as cement replacement has been reported to reduce the drying shrinkage of concrete and the extent of reduction depends upon the period of initial moist curing, and W/(C +SF) ratio. Johansen[37] conducted drying shrinkage tests on SF concretes moist cured for 1 or 28 days prior to drying at 50% R.H. The concretes had SF additions as 0%, 5%, 10%, and 25% and W/(C + SF) ratios of 0.37 and 1.06. No significant difference in drying shrinkage was observed for concretes with W/(C + SF) ratio less than 0.6. However, concretes made with 25% SF exhibited greater shrinkage than non SF concretes. Tachibana et al.[118] have reported that the 1 year drying shrinkage strain of SF concretes made with W/(C + SF) ratios of 0.22, 0.25 and 0.28 and containing 10% SF replacements, varied between 540×10^{-6} and 610×10^{-6} compared to 930×10^{-6} for the non SF concrete made with W/C ratio of 0.57.

Since creep is influenced by compressive strength and modulus of elasticity of concrete, higher creep strains were observed in fly ash concrete at early age loading when strength was low; however, the creep rate decreased at later ages. In their study on creep of concrete containing Class

F type, Indian fly ash, at replacement level of 15% to 25% by weight of cement, Lohtia et al.[75] found that up to 15% cement replacement by fly ash, creep was not much affected. However, beyond 15% replacement level, fly ash concrete exhibited slightly higher creep than the corresponding plain cement concrete. Creep recovery was also smaller than that of plain concrete at fly ash additions more than 15% level. The nature and trend of creep-time curves of plain and fly ash concretes were observed to be similar.

Tachibana et al.[118] conducted creep tests on high strength concretes containing SF and compared the values of their creep coefficients with that of normal strength concrete without SF. The tested mixes had the same composition as used for drying shrinkage tests reported earlier. The 180-day creep coefficient of SF concretes was approximately 0.42 compared to about 2.60 for plain cement concrete at the corresponding age. Since with SF addition strength development is significantly accelerated, the early age creep deformations of SF concretes are thus observed to be less than that of non SF concretes.

Creep is related to the removal of adsorbed water from hydrated cement paste and to the viscosity of the paste. With the progressive hydration and pozzolanic reactions, compressive strength increases due to the increase in the volume of cementitious materials and refinement of pore structure. In general, the increase in compressive strength of concrete reduces creep, and thus the effect of mineral admixtures on creep of concrete will exhibit a similar pattern as their effect on strength development of concrete. For the concretes containing mineral admixtures, Fintel et al.[28] have suggested that specific creep, creep per unit stress can have values between 0.003 f′ and 0.005 f′, where f′ is the 28-day compressive strength of concrete.

5.9 Permeability

The improvement in impermeability and general durability of concrete due to the addition of mineral admixtures such as silica fume, rice husk ash, blast furnace slag, and fly ash has been verified by several laboratory investigations and field observations. The addition of mineral admixtures can cause considerable pore refinement, i.e., transformation of bigger pores into smaller ones due to their pozzolanic reactions concurrent with cement hydration. By this process, the permeability of hydrated cement paste as well as the porosity of the transition zone between cement paste and aggregate are reduced. As stated earlier, strength and impermeability are inversely related to the volume of large pores >1,000 A° in the hydrated cement paste. Figure 7 shows typical pore size distribution for 28 days old portland cement pastes containing 10%, 20% or 30% of a low calcium fly ash, a reactive rice husk ash, and a granulated blast furnace slag. The specimens containing rice husk ash and 70% slag showed considerable pore refinement as compared to the reference portland cement paste. Like low calcium fly ashes, addition of natural pozzolans requires longer curing periods before the benefits from the pore refinement process on strength and permeability become evident. Mercury intrusion porosimetry technique is mostly employed to determine the pore size distribution of hydrated cement pastes containing different mineral admixtures.

At early ages, fly ash concretes containing both high or low calcium fly ashes at 50% replacement levels by cement weight are found to be more permeable than concretes without fly ash. This trend, of course, is found to reverse after about 180 days when pozzolanic activity of fly ashes becomes predominant and permeability is reduced.

The addition of SF as cement replacement reduces both water permeability as well as chloride ion permeability of concrete depending upon the SF content, cement content of the mix, and W/(C + SF) ratio. In a study to determine the water permeability coefficients of concretes containing 300 kg/m^3 of cementitious materials with SF used at 0%, 5%, 10% and 20% cement replacements, Sandvik[109] reported that with 10% and 20% SF addition, the permeability coefficients were too low to measure (less than 10^{-12} cm/S). With 5% SF addition, the permeability coefficient was measured to be 6×10^{-12} cm/s against 3×10^{-9} cm/s for similar non SF concrete.

In another study,[82] the addition of 10% SF to concrete containing only 100 kg/m^3 of cement was found to reduce the water permeability coefficient of concrete from 1.6×10^{-5} to 4×10^{-8} cm/s. This was comparable to that of non SF concrete having cement content of 250 kg/m^3. The influence of SF addition in reducing water permeability is found to be more marked than in increasing the strength of concrete, particularly in lean concrete mixes. The influence of SF addition on water permeability of concrete was observed to be small when the concrete contained more than 400 kg/m^3 of cement, i.e., in rich mixes.[30] It has been well recognized that of all the causes of lack of durability in concrete, the main one is excessive permeability. Since permeability is decreased with the addition of mineral admixture, durability of concrete against freeze-thaw attack, chemical attack (sulfate attack) alkali aggregate reaction and also resistance of concrete against the corrosion of embedded reinforcing steel, are significantly improved as discussed below.

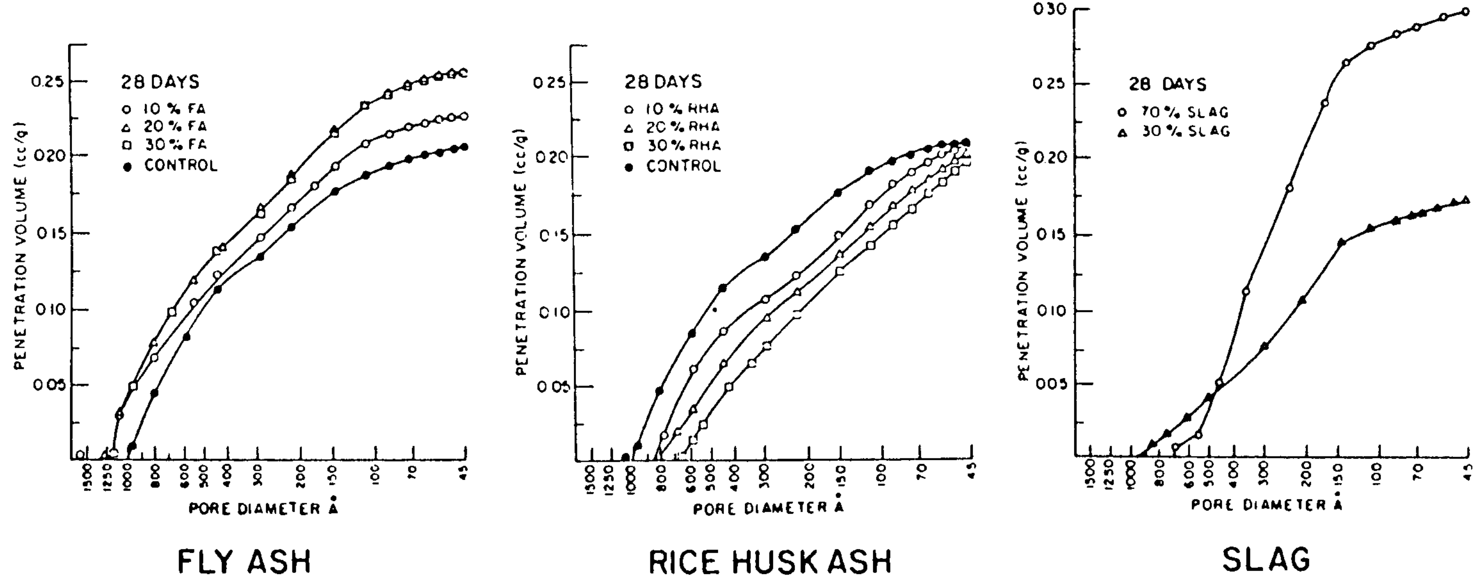

Figure 7. Effect of fly ash, rice husk ash or blast furnace slag additions on pore size distribution of hydrated cement pastes.[80]

5.10 Freeze-Thaw Durability

In cold weather concreting, it is a general practice to use air entrained concrete to improve the frost resistance of concrete. Based on several investigations, it is known that the resistance of air entrained concrete to freezing and thawing depends upon several factors such as the degree of saturation, air void system, type and content of cementitious materials, W/C ratio, curing conditions, rate of cooling, and minimum cooling temperature. Because of pore refinement due to the addition of mineral admixtures, the freezing temperature of water in small capillary pores is reduced and thus freeze-thaw durability of concrete at some intermediate low temperatures is improved.

The addition of fly ash does not affect the frost resistance of concrete significantly if the strength and air content are maintained constant. Joshi et al.[64] conducted freeze-thaw durability tests on air entrained and superplasticized fly ash concretes made with 40% to 60% Alberta subbituminous fly ash as cement replacement to produce high strength concrete mixes with W/C + F ratios of 0.28 to 0.36. They reported that most of the mixes exhibited relative dynamic modulus of elasticity values in excess of 60% after 300 cycles of freezing and thawing. However, the test specimens without air entrainment failed after less than 50 freeze-thaw cycles, indicating a low level of durability. They further reported that all the concretes containing fly ash showed some scaling damage after 150 to 200 freeze-thaw cycles and had about 2% weight loss at the culmination of the test. The effect of fly ash addition on increasing the air entraining agent demand to maintain 6 ± 1% air content was also reported by them.

The necessity of air entrainment to maintain and/or improve the durability of silica fume concretes was demonstrated by the tests reported by Malhotra.[78] The freeze-thaw durability values of concretes containing 0%, 5%, 10%, 15% and 30% SF replacements and having W/(C + SF) ratios of 0.4 to 0.6 were reported to be poor in the absence of air entrainment. On the other hand, air entrained concrete with SF replacement up to 15% was found to have good freeze-thaw durability irrespective of W/(C + SF) ratio and the procedure of testing (ASTM C666 procedure A or B). The poor frost durability observed for the concrete containing 30% SF and at a W/(C + SF) ratio of 0.42 was attributed to its high air void spacing factor of 570 μm compared to about 130 ± 30 μm for the other concretes. The addition of SF enhances the water tightness of the cement matrix and thus reduces the rate of water penetration. This reduction of water ingress rate, together with the decreased freezing temperature of pore water and the reduction of the degree of saturation improves durability of SF concrete to frost attack.

On the debit side, the reduced permeability of hardened cement paste with SF addition can retard internal moisture migration through the cement matrix whereby high internal hydraulic pressure can develop that may cause cracking and deterioration of concrete. In spite of the low amount of ice formed in SF concretes which may also have proper air spacing factor, the freeze-thaw durability may get impaired due to the possible thermally incompatible dimensional changes between aggregate and cement paste due to the difference in their coefficient of thermal expansion. Thus, at low temperatures, around -20°C, when freezing and thawing tests are done in water (ASTM C666 procedure A), differential tensile stresses due to thermal incompatibility as explained above are created at the interface between the aggregate and the cement paste and lead to cracking and loss of durability of concrete.

Bilodieau and Carette[8] have reported that the frost resistance of concrete in the presence of de-icing salts is slightly reduced when SF is used to replace 8% of cement weight. The tested concrete had W/(C + F) ratios between 0.4 and 0.65 and satisfactory air void spacing parameters. However, the difference in resistance to scaling due to de-icing salts of concretes containing SF and that of non SF concretes has been reported to be negligible for air entrained concretes with W/(C + SF) ratio less than 0.6. Hammer and Sellevold[121] reported that conventional concretes made with normal weight aggregate and W/(C + SF) ratios lower than 0.37 have good frost resistance in the presence of de-icing salts even when they are not air entrained. Similar results were observed for light weight aggregate concretes having W/(C + SF) ratio lower than 0.47. However, the addition of 5% to 10% SF as cement replacement was reported to reduce the scaling resistance of the concrete even when it was air entrained.

5.11 Resistance to Aggressive Chemicals: Sulfate Attack

The loss of durability by the attack of aggressive chemicals can be either due to the decomposition of cement paste or due to the destructive internal expansion caused by chemical reactions in the paste or by both combined actions. Deleterious chemicals such as acid solutions can react with $Ca(OH)_2$ to form water soluble salts that can leach out of the concrete, hence increasing the permeability of the concrete thus aggravating the attack by increased and faster ingress of harmful chemicals. Sulfates can react with $Ca(OH)_2$ to form calcium sulfoaluminate (ettringite) that can cause swelling and internal disruption of the concrete.[53]

With the incorporation of mineral admixtures in concrete, $Ca(OH)_2$ which is highly vulnerable to attack by harmful chemicals, is consumed progressively in pozzolanic reaction. It also leads to pore refinement and reduces the rate of molecular diffusion of aggressive elements through concrete due to the decreased permeability. The degree of chemical attack, especially sulfate attack is measured by changes in weight, length, relative dynamic modulus of elasticity or pulse velocity, and strength of specimens over period of time. The addition of mineral admixtures such as fly ash, blast furnace slag, and silica fume has been found to improve the sulfate resistance of concrete significantly. Joshi et al.[54]-[58] have reported that with the use of subbituminous fly ash from Alberta at 15% replacement level by cement weight, the sulfate resistance of cement sand mortar was significantly improved on exposure to Na_2SO_4 and $MgSO_4$ solution of concentration below 10%. For higher concentrations, the mortar mixes made with Type V, sulfate resistant cement, and 15% unclassified Alberta fly ash exhibited adequate sulfate resistance. Langan et al.[68] demonstrated the favorable effect of Alberta fly ash in improving the sulfate resistance of concretes containing up to 50% fly ash by weight of cement.

A systematic study with three fly ashes from the United States, representing a range of CaO contents 11% to 28,6% and using 10% to 100% fly ash by weight of the total cementitious material, was made by Von Fay and Pierce[119] to investigate the effect on sulfate resistance of air entrained concrete. The specimens were moist cured for 14 days and dry cured at 50% relative humidity for another 14 days period before they were immersed in 10% sodium sulfate (Na_2SO_4) solution or subjected to cyclic soaking and drying phases (accelerated test) in 2.1% Na_2SO_4 solution. Their test results showed that both low lime Class C and Class F fly ashes can be effective cement replacements in controlling sulfate expansion favorably. Class F fly ash was most effective in reducing sulfate expansion at the lower cementitious levels of 251.5 kg/m^3. At the higher cementitious level, 387 kg/m^3, Class F fly ash at 30% level was found to be most effective. The high lime Class C fly ash mixes generally exhibited more expansion than the control mixes at replacement levels below 50%, opposite to the behavior observed with low lime Class F mixes. For low lime fly ash, replacement levels were suggested to be greater than 30% to achieve the most improved sulfate durability, whereas for high lime Class C fly ash, the corresponding level was suggested to be greater than 75%. The replacement level was found to depend upon cementitious content of the mix. With lower cementitious content, 50% or more, while for richer mixes 50% or less Class C fly ash was suggested for improving the sulfate resistance of concrete.

Blast furnace slag has been used in concrete for underwater marine structures because of the improved resistance of concrete to the chemical attack including sulfate attack. Many researchers have found alumina content of fly ashes as well as of blast furnace slags has a similar effect on the sulfate resistance of resulting concrete. With low alumina content (15% to 16%) in fly ash, the concrete mixes made with 20% cement replacement by fly ash showed 8% strength gain on immersion in sulfate solution for about 5 months. However, with the use of fly ash containing high alumina (about 30% Al_2O_3), a strength loss of 23% was observed under similar conditions of immersion in sulfate solution.

The European slags are relatively high in alumina (13% to 15%), as compared to the American slags (8% to 10%). Whereas 70% or more ASTM Type I cement replacement by slag is recommended for sulfate resistance in Europe, it has been found in North America that even 50% Type I cement (12% C_3A content) replacement by slag would provide as good a sulfate resistance as by the use of Type V sulfate resistant cement.

The addition of SF as mineral admixture significantly improves the sulfate resistance and overall durability of concrete due to its efficient and fast pozzolanic reactions. Sulfate resistance of SF concrete is also improved by the increase of aluminum incorporated in the hydrates formed by SF reactions, thus reducing the amount of alumina available for ettringite formation. Ammonium sulfate solutions are found to cause more deterioration of concrete with or without mineral admixtures than the Na_2SO_4 solutions of corresponding concentration. Durning and Hicks[24] conducted tests to study the chemical resistance of concretes containing up to 30% cement replacement with SF. The concretes were air entrained and had W/(C + SF) ratios of 0.26 and 0.36. After moist curing for 28 days, the specimens were subjected to weekly cycles of immersion in aggressive solutions followed by drying in air. Acidic solutions containing 1% and 5% H_2SO_4, 5% formic acid and 5% phosphoric acid were used. The test results as presented in Table 14 show that increase in SF content can substantially delay the rate of degradation of concrete by chemical attack as determined by the number of cycles needed to cause 25% weight loss of the specimens.

Table 14. Mass Loss of Concrete in Acidic Solutions[24]

Silica Fume Replacement (%)	Exposure Environment	Cycles to 25% Mass Loss	Percent of Reference Concrete
0	1% Sulfuric Acid	13	
7.5		19	146
15		22	169
30		32	246
0	5% Acetic Acid	8	
7.5		17	213
15		32	400
30		>60	>750
0	5% Formic Acid	17	
7.5		32	188
15		>50	>294
30		>50	>294
0	5% Sulfuric Acid	4	
12.5		5	125
25		5.3	133
0	5% Phosphoric Acid	12	
12.5		13.6	113
25		17.3	144

5.12 Resistance to Alkali-Aggregate Reaction

Alkali silica reaction occurs when certain acidic aggregates containing reactive silica in the form of silicate or silicate minerals react with alkali metal ions (Na_2O and K_2O) in portland cement paste to form gel. The alkali-silica gel formed can swell in the presence of moisture and can cause internal disruption of concrete due to the expansive pressures induced by swelling of the gel. High alkaline portland cement having more than 0.6% Na_2O eq. (soda equivalent) is very vulnerable to attack by aggregates containing reactive silica in the form of opal (amorphous), chalcedony (crypto crystalline fibrous) and tridymite (crystalline). Although in most cases alkalis are derived from portland cement itself, alkalis can also be introduced by mixing water, admixtures, and salt contaminated aggregate, and de-icing salts. The reaction progresses slowly and the continuous formation of gel of unlimited swelling causes expansion and cracking of concrete.

When a part of the portland cement is replaced by a mineral admixture, the available alkali in the system is reduced by the amount of admixture added, provided the admixture itself does not contain soluble alkali. Thus, a partial replacement of high alkali cement by a mineral admixture is found to be effective in suppressing expansion due to the alkali silica reaction. The use of finely divided mineral admixtures not only improves the packing of cementitious materials but also reduces permeability of cement paste due to their pozzolanic action. The ion migration and availability of moisture needed for alkali-silica reaction are appreciably reduced, thereby improving the resistance of concrete to the expansive alkali reaction significantly. The large size ions of harmful elements, such as Na^+ from de-icing salts, cannot penetrate the hardened fly ash concrete because of reduced pore size and permeability. Therefore, alkali-aggregate reactions are retarded or minimized by use of fly ash in concrete. It has also been suggested that in the presence of a pozzolan, a non swelling lime-alkali silica may form in place of the swelling alkali silica gel. Both fly ashes and granulated blast furnace slags act as alkali-diluters, slags being more effective than fly ash in reducing damage due to alkali-silica reaction.

Numerous investigators have reported that up to 75% reduction in expansion, as measured by the ASTM C441 test for alkali-silica reactivity, can be achieved by replacing 36% to 48% volume of high alkali portland cement by fly ash. However, some high calcium fly ashes containing large amounts of soluble alkali sulfates might increase rather than decrease the alkali-silica reactivity. It may be noted that it is the soluble alkali and not the total alkali present in a fly ash which aggravates the reactivity. The results of study with twelve different Canadian fly ashes replacing 20% to 40% cement by weight in mortar mixes made with reactive opaline aggregate showed a reduction in expansion after one year ranging from 5% to 21% at cement replacement level of 20% by fly ash, 34% to 89% at 30% replacement level and 47% to 92% at 40% replacement level, respectively.[104] The alkali content of fly ash varied over wide limits. However, the alkalis present in fly ash were relatively less sensitive with reactive aggregates, due to their limited solubility in water and presence in combined form, than the free and water soluble alkalis of portland cement. Thus, with the incorporation of high volume of fly ash as cement replacement, alkali-silica reaction may be appreciably reduced. Reproportioning of such concrete mixes with high volume of fly ash and the use of superplasticizer as well as air entraining agent are found necessary for achieving acceptable early strengths in addition to their increased resistance to alkali-silica reaction.

Joshi et al.[65] in a recent study found that effective suppression of expansion due to alkali-aggregate reaction was achieved with the incorporation of Alberta subbituminous coal fly ash at replacement levels of 35% and higher by weight of cement. Concrete mixes containing up to 60% fly ash exhibited favorable behavior in alkali-aggregate reactivity tests.

Compared to fly ash, the additions of blast furnace slags would be less sensitive to the amount and variation in slag composition as far as their resistance to alkali-silica reaction is concerned. It has been shown that with 40%, 50% and 65% granulated blast furnace slag used as cement replacement for the ASTM test C227 with pyrex glass as reactive aggregate, the expansion of the control mortar bar specimens was reduced from about 0.3% to 0.07% or even less.[36] Damage in concrete due to alkali-silica reaction has been reported to be unlikely to occur if the acid soluble equivalent Na_2O (soda equivalent) content of the concrete is below 3 kg/m^3. In calculating the alkali content of the concrete, granulated blast furnace slags as well as silica fume are assumed to contain no available alkalis, whereas fly ashes should be assumed to have an available alkali content of 0.2% by weight.[35]

The recent observations of the concrete pavements made with reactive aggregates and 10% to 40% SF replacements and 140 to 405 kg/m^3 cement concrete have shown that SF concrete was in satisfactory condition after 10 years of service.[4] Diamond,[22] in his study, showed that the addition of 5% SF to a cement paste made with W/(C + SF) ratio of 0.4 reduced the concentration of Na^+ and K^+ ions and OH in pore solutions by approximately half after 10 days of hydration, as much as those found in similar 2.5 month old paste without SF. In addition to reducing the permeability of cement paste and decreasing the concentration of alkalis and OH ions in pore solution, the addition of SF reduces the Ca/Si ratio of C-S-H products and increases the degree of polymerization of C-S-H.[107] This would increase the ability of the lattice to accommodate more foreign ions, such as Na^+ and K^+ ions, hence the risk of alkali aggregate reaction is expected to reduce.

Natural pozzolans are also found to be quite effective in reducing the alkali-silica expansion at lower levels of cement replacement. For example, 20% cement substitution by Santorin earth (Italian pozzolan) was found sufficient to cause a significant reduction in the alkali-silica expansion. Only 10% rice husk ash by weight of cement was adequate for effectively suppressing the alkali-silica expansion in ASTM C441 test without any adverse effect on early strength.[88]

5.13 Corrosion of Reinforcing Steel: Carbonation of Concrete

In a hydrated portland cement paste, about 20% $Ca(OH)_2$ by weight of the hydration products is present to provide the reserve basicity for steel protection. The high alkalinity (PH > 13) of pore solution in concrete protects the passive iron oxide layer present on conventional reinforcing steel bars. This layer is vulnerable to the attack by chloride ions in concrete or by carbonation when the pH of concrete is reduced to 10 or 11. Once this passive layer is destroyed, a galvanic cell can form between different areas on reinforcing bars, causing reduction at anodic area. The rate of corrosion of embedded steel depends upon the electric conductivity of the concrete and the permeation of moisture and oxygen through the concrete.

Carbonation of concrete from atmospheric CO_2 is generally the first step in the process of corrosion of reinforcing steel bars embedded in concrete. Calcium hydroxide [$Ca(OH)_2$] carbonates to calcium carbonate ($CaCO_3$) and other cement compounds may also get affected producing hydrated silica alumina and ferric oxide. The effects of carbonation have been observed even at the low partial pressure 3×10^{-4} atmosphere of carbon dioxide (CO_2) in normal atmosphere. The mechanism of carbonation is attributed to solution of gas in the pore fluid, which forms carbonic acid (H_2CO_3), and the diffusion of gas through microcracks in the specimen, and subsequent solution and reaction. The rate of carbonation depends upon several factors such as permeability of the specimen, size of the specimen, ambient temperature and humidity conditions, moisture content of concrete, and amount of $Ca(OH)_2$ available for reaction. The possible deleterious effects of carbonation in concrete are, increase in permeability, increased shrinkage and cracking, and increase in corrosion potential of embedded steel reinforcement.

In a study on cement sand mortars made with 25% fly ash replacing cement and at W/C ratios of 0.35 to 0.55, Butler et al.[9] observed an increase in carbonation with an increase in W/C ratio. It was further observed that more carbonation occurred at lower water contents when the fly ash concrete was desiccated with $CaCl_2$. However in the case of non desiccated specimens, the effect of fly ash on carbonation at lower water contents was insignificant. In a study Joshi et al.,[65] found that up to about 7 days, the extent of carbonation measured by the affected depth from the outer surface in concrete, after subjecting the specimen to 4% CO_2 at 20°C and 50% R.H., was more in concrete containing fly ash than the control concrete without fly ash. However, after 90 days curing, the fly ash concrete had less carbonation effect than the reference plain concrete.

It has been reported by several researchers that the pozzolanic and cementitious reactions associated with mineral admixtures not only consume the free lime [$Ca(OH)_2$] present in the cement paste, but also decrease the permeability and air diffusivity of the system, thus improving the overall resistance of concrete to CO_2 attack. Enough hydroxyl ion concentration and free calcium hydroxide is always present in portland pozzolan cement pastes, even when very active silica rich pozzolans (rice husk ash or silica fume) are used. It is thus believed that the danger due to CO_2 attack should not be of much concern in concretes containing mineral admixtures such as fly ash, blast furnace slag, and silica fume.

With the additions of mineral admixtures at high replacement levels by cement weight, the pH of concrete can decrease since less cement is used. Moreover, the decrease in $Ca(OH)_2$ content due to pozzolanic reaction and the reduction of alkali pore water concentration contribute to the reduction of steel corrosion resistance of concrete. All these factors combined may reduce alkalinity of concrete, thus increasing the corrosion potential of steel in reinforced and prestressed concrete structures when concrete made with mineral admixtures is used. The exposure of concrete to seawater or deicing salts can result in chloride ion penetration through the hardened concrete.

With the use of SF in concrete, the diffusion coefficient of chlorides and the chloride content in concrete are reduced significantly. The chloride content can be reduced by increasing the W/(C + SF) ratio as well as by increasing the SF content. Electrical resistivity of concrete is significantly increased with the SF addition, particularly when the concrete has a high cement content. Several reported field observations demonstrate that in well cured, high quality SF and regular concretes, carbonation is not a problem and with adequate protective cover provided, there should not be any danger of potential corrosion of embedded steel reinforcement. The corrosion problems are, however, of much concern when poorly cured concrete of low or medium strength is made with mineral admixtures. Generally, the concrete containing mineral admixture having equal strength and quality as that of plain concrete may exhibit improved resistance to corrosion of reinforcement because of the more dense and compact framework of the cement paste and refined pore structure.

5.14 Abrasion-Erosion Resistance

The deterioration of concrete by external physical causes such as abrasive and erosive forces due to moving traffic, flowing water, wave action on water front marine structures, and cavitation pressures on the downstream side of spillway, is of specialized interest to the concerned engineers. The use of hard aggregates and low W/C ratio has been found to be quite effective in increasing abrasion-erosion resistance of regular concrete. With the use of mineral admixtures, especially silica fume, in concrete made with hard aggregates such as granite or basalt, the abrasion resistance of concrete is much enhanced. Not much information is available on this topic at present. However, it is believed that with the SF addition, not only the hardness and wear resistance of the cement paste itself is improved, but also the bonding between the paste and aggregate is significantly enhanced. Because of the improved bonding action, the tendency of the coarse aggregate to be plucked out of the cement paste by abrasive action is reduced. Similarly, the pitting on concrete surface due to the abrasive or erosive forces caused by flowing water is significantly reduced.

5.15 Resistance to High Temperatures

There are two distinct situations to be considered when concrete is subjected to elevated temperatures. In one case, the heating is done under open conditions with the contained moisture in concrete free to evaporate, while in the other case, the heating is done under sealed conditions with the contained moisture prevented from escaping. In mass concrete structures, the inner concrete during heating at high temperatures will have its moisture converted into steam and thus subjected to steam pressures in addition to other forces.[100]

It has been reported by various investigators that the behavior of concrete at high temperatures depends on several factors such as the heating conditions, level and duration of temperature exposure, concrete composition, moisture content of concrete, pore structure of the cement past, and the size of concrete member. The addition of mineral admixtures, especially SF, in concrete makes the pore structure of hydrated cement paste very fine and, as a result, the rate at which water vapor can move within the cement paste can retard, leading to the development of excessive vapor pressure that can cause damage to concrete. The deterioration of concrete at high temperature may appear in the form of cracking, strength reduction and sometimes excessive spalling, especially when the moisture content of concrete is very high.

Water is present in hardened concrete in several forms such as capillary water (free water), gel water or zeolitic water (adsorbed water), and chemically combined water. Schneider[111] has reported that free water is lost when the concrete is heated to 100°C and that adsorbed water starts to evaporate at 180°C. Water in the $Ca(OH)_2$ begins to dehydrate at 500°C and finally chemically combined in hydrated compounds C-S-H starts to evaporate around 700°C. At elevated temperatures, the observed spalling of concrete is believed to be caused by the decrease in strength of cement paste due to the decomposition and high tensile stresses caused by the restraint of paste by aggregate.

To guard against the risk of spalling, short steel fibers are incorporated into concrete at 2% to 3% by volume especially in high risk structures such as prestressed concrete pressure vessels, launching pads of space vehicles and runways for jet aircraft, concrete floors of boilers and chimneys, and highly stressed slender members. Damage of concrete, when subjected to elevated temperatures, is caused by the dense structure of high strength concrete itself, even without the addition of mineral admixtures, and is more intense when the contained moisture in concrete is restrained during heating. Addition of mineral admixtures in concrete, in general, has not found favor for high temperature applications, particularly in mass concrete construction where thermal gradients may cause aggressive deterioration because of excessive internal pressures and tensile stresses.

6.0 TEST METHODS FOR EVALUATION OF MINERAL ADMIXTURES

ASTM C311 provides methods for sampling and testing of fly ash for use as an admixture in Portland cement concrete and is mostly used in North America. Determination of compressive strength of portland cement mortars containing a given proportion of the mineral admixture under normal or accelerated curing conditions is still regarded as the most reliable method for evaluating the quality of mineral admixtures. For accelerated curing tests for mortars containing fly ash or blast furnace slag, a wide range of curing temperatures from 40° to 80°C has been employed. Mehta[96] reported a simple method involving compressive strength and water diffusion tests on 7-day 50°C cured mortars to assess the quality of different types of mineral admixtures.

The chemical methods used for evaluation of mineral admixtures as pozzolans have been summarized by Lea.[72] Atomic absorption involving fusion with lithium metaborate ($LiBO_2$) and solution in dilute nitric acid is generally used to determine the chemical composition of mineral admixtures. ASTM C311 can be used to determine physical properties of mineral admixtures such as specific gravity, fineness, moisture, and pozzolanic activity. Loss on ignition and available alkalis in mineral admixtures are also determined using ASTM C311 standard.

Carbon in fly ash sample is determined by weighting the CO_2 formed during ignition of the sample at 950°C in a tube combustion furnace using pure oxygen. The total carbon dioxide (CO_2) absorbed is adjusted for the amount resulting from carbonates by determining the CO_2 released by hydrochloric acid in a separate determination to assess fixed carbon content of the sample.[26]

Different countries over the world use different test standards to evaluate the mineral admixtures to determine their suitability for use in concrete for specific applications. It has been pointed out that for general use the chemical methods do not offer an efficient and reliable index of quality when different types of mineral admixtures are evaluated. Thus the use of physical tests for evaluation of mineral admixtures are recommended for general purpose applications as pozzolans in cement concrete.

7.0 ECONOMICS OF USE OF MINERAL ADMIXTURES

The most efficient method of disposing a waste by-product is to use it. However, this may not be possible all the time because of economic constraints. Industrial by-product mineral admixtures, particularly fly ash which is produced in abundance, can find productive use in concrete only when the concrete construction site is in close proximity to the available source of waste by-product. If the market for use is very far from the generating source, then the transportation costs escalate and it may become more economical to dispose the waste in landfills rather than use it as mineral admixture. It is worth pointing out that at present day costs haulage distances of 300 km for fly ash, as a replacement for cement, is considered economical in Alberta, Canada.

Thus the main governing parameter that determines whether or not a natural pozzolan or an industrial by-product is used in a particular application is the economic cost which primarily includes the cost of collection, handling, processing, and transportation. For the power generating/supply company, the transportation cost of the waste by-product, say fly ash, from the site of production to the market, combined with the labor charges associated with it, should be less than the disposal costs at a waste dump. As far as the consumer is concerned, the waste by-product should be significantly cheaper than the material being replaced, i.e., portland cement. This requires the adoption of efficient quality control and quality assurance programs of the waste by-products at production and supply sources so that a consistent supply of quality waste by-product at a reasonable rate is available to the users.

Waste industrial by-products need to be disposed in landfills and/or lagoons in an environmentally sound manner. When they are stockpiled on land, they cause air pollution and during rainfall or snow melt season, the migration of leachate plumes from the dumped wastes can cause pollution of subsoil and ground water. When the wastes are dumped into ponds or streams, toxic metals, which are usually present as trace elements, can be released to pollute the water and make it unfit for use. With the use of wastes as mineral admixtures in concrete, the problems and costs associated with the environmentally safe disposal of wastes can be reduced or sometimes entirely eliminated. Socioeconomic benefits, achieved by the utilization of industrial by-products as mineral admixtures in concrete, have now been well recognized by all those concerned with production, disposal, and utilization of wastes.

Portland cement is an energy intensive material. In North America, for producing 1 ton of portland cement, the fossil fuel input of the order of 3.7 million kJ is required. Since fly ash, silica fume and rice husk ash normally do not need additional energy input before use, it is evident that with their use for replacement of cement, energy saving in direct proportion to the amount of mineral admixture used as cement replacement will result. Blast furnace slags need to be dried and ground before use and it is estimated that the total energy requirement for this purpose is about 20% of that required for portland cement production. Using blended cements containing portland cement, gypsum, and large proportions of fly ash, rice husk, or silica fume, it has been estimated that up to 75% energy in cement production can be saved, while the strength and impermeability of the products remain suitable for many applications in the construction industry. Thus the use of mineral admixtures in concrete leads to energy saving as well as conservation of natural resources by way of saving the raw material used for cement production.

Many investigators have reported the economic benefits which accrue from the use of mineral admixtures in concrete. From 1940 to 1973, the Bureau of Reclamation used 360,000 tons of natural pozzolans in 7.1 million cubic meters of concrete, and about 275,000 tons of fly ash in 5.4 million cubic meters of concrete.[23][25] The principal reason for the use of pozzolans in concrete dams by the U.S. authorities was cost. Considerable savings are reported by the use of fly ash as a mineral admixture in concrete on global basis. For example, a cost saving of $225,000 was achieved by using 10,000 tons of fly ash in about 72,000 m^3 of concrete placed at Normandy Dam in the USA.[67] Several other world wide applications of mass concrete with the incorporation of fly ash as a mineral admixture demonstrate similar cost savings due to the resulting reduction in the amount of cement used in concrete.

8.0 CONCLUDING REMARKS

This chapter describes the use of mineral admixtures such as natural pozzolans, fly ash, granulated blast furnace slag, rice husk ash, and condensed silica fume, as supplementary cementing materials or as cement replacement materials or in producing blended cements, called pozzolanic cements. Fly ash is the most abundantly produced, readily available, most used and hence most researched material admixture for use in concrete. The majority of fly ashes are slow reacting pozzolanic materials and suffer from low values of early age strength and longer setting times. They increase the demand for an air entraining agent to entrain the specified amount of air in concrete required for freeze-thaw durability. Fly ash addition also affects the resistance of concrete to scaling due to de-icing salts. High volume fly ash concrete with up to 60% replacement level of cement by high calcium Class C fly ashes and sub bituminous Alberta fly ashes have been successfully produced using chemical admixtures such as superplasticizer, and air entraining agents. Most of the properties of concrete, both in the plastic state as well as the hardened state, are improved by the addition of fly ash. Considerable savings in cost and energy consumption are achieved by high volume utilization of fly ash in concrete. In fact, the waste by-product whose disposal is otherwise a costly liability is converted to a useful supplementary cementing material with its use in cement concrete. Proper quality control and quality assurance is, however, required at the fly ash production, storage and supply sources.

Blast furnace slags, waste by-products from iron and steel manufacturing industries, when granulated by sudden cooling and pulverized to fineness finer than portland cement, are relatively quicker reacting pozzolanic materials than fly ashes. The total energy consumed in drying and grinding of the slags is about 20% of the energy required for production of cement on equal weight basis. It has been possible to replace up to 70–80% of portland cement by blast furnace slag for producing durable and dense concrete. The use of blast furnace slag is mostly in the form of blended cement for the mass concrete construction and for underwater marine concrete structures because of its reduced heat of hydration and excellent resistance to sulfate attack. Alkali activated slag, when blended with portland cement, can produce a rapid hardening binder that sets and develops strength faster than rapid hardening cement (ASTM Type III). Such blended cement is found useful for speedy repairs of damaged or deteriorated concrete. The combined use of blast furnace slag and fly ash can overcome the problems encountered by only fly ash additions in concrete. However, the availability of granulated blast furnace slag is not that abundant and widespread as that of fly ash for commercial applications worldwide.

Condensed silica fume, micro silica in amorphous form, is an excellent and superior pozzolan compared to fly ash and slag. Because of its limited availability and cost, it is normally used in concrete as property enhancing material rather than cement replacement. With about 5% to 15% silica fume addition, considerable improvement in both early and ultimate strength and impermeability of concrete can be achieved because of the refinement of pore structure and improved quality of the paste in the transition zone between aggregate and binder matrix.

The combined use of SF (5% to 10%) and fly ash along with blast furnace slag may lead to the development of extremely high strength concrete with 28 day strength around 100 MPa and having excellent long term durability against extremes of weather as well as chemical attack. Compared to fly ash, silica fume addition increases the water demand to maintain specified workability and thus the use of water reducer or superplasticizer is found necessary for producing SF concretes of the required consistency. Because of very dense and compact structure produced with SF, high performance concrete for all types of situations can possibly be developed. As a caution, it is pointed out that the added SF should be homogeneously dispersed throughout the concrete mass during mixing and used with a dispersing admixture, and superplasticizer; otherwise, it may cause serious durability problems due to non uniformity in the pore structure of resulting concrete.

Rice husk ash, like condensed SF is a fast reacting pozzolan and consists essentially of silica (95%) in amorphous form. Rice husk ash is a promising potential mineral admixture in rice producing countries of Asia and China. In the U.S. rice husk ash production is around 100,000 tons from 510,000 tons of rice hulls and despite the fact that it has all the attributes of a good pozzolan there has been no systematic and wide spread development of the rice husk ash production as yet.

Natural pozzolans have been successfully used as pozzolans particularly to contain and reduce heat of hydration and alkali silica reaction in mass concrete structures such as dams. However, their use is limited to the areas where deposits of suitable pozzolans are located within reasonable distance. Transportation costs sometimes can be the main hindrance in using such materials. Calcined shale and clay and other processed natural pozzolans are employed for local use in mass concrete to control heat of hydration and long term strength and durability. Because of their very slow pozzolanic action, their use in the applications for early age strength of concrete is not usually acceptable.

In general, it is believed that improvements in strength and durability of concrete associated with the use of mineral admixtures are possible through pore refinement, transformation of large pores into fine pores, and reduction of porosity and microcracking in the transition zone between the aggregates and cement paste due to their fine size, and progressive pozzolanic reactions. Long term durability of concretes containing mineral admixtures and exposed to adverse environments still needs to be studied further. It is anticipated that the combined use of mineral admixtures including silica fume will compensate the deficiencies in early strength and durability encountered, especially by only fly ash or blast furnace slag incorporation in concrete. In future applications of concrete technology for different environmental conditions, the need for economic and improved mineral admixtures as supplementary cementing materials will attract the attention of the researchers and practicing engineers.

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11

Antifreezing Admixtures

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1.0 INTRODUCTION

Antifreezing admixtures are chemicals which are added to the mixing water of concrete in order to lower the freezing point of the aqueous solution. They have been used even at temperatures as low as -30°C. Most work has been pioneered by Russian scientists. Antifreezing admixtures have been used in Russia for cast-in-place concrete, reinforced concrete, precast monolithic structures, joints of precast units, and others at ambient air or ground temperatures below 5°C and minimum daily temperatures below 0°C and down to -30°C. In recent years, some interest is evident in investigations on antifreezing by American scientists.

The application of antifreeze admixtures is technologically simple, convenient, and beneficial for winter concreting. It is estimated that the use of these admixtures permits economy that is about 1.2 to 1.5 times beneficial compared to steam curing, concreting in enclosures, or heating the constituents. These admixtures may also be used in combination with other methods. By such procedures, some advantages can be realized in terms of lower amount of admixture, early commissioning of the structure and saving of energy.

More than forty years of experience has been accumulated in Russia in the use of antifreeze admixtures for unheated concreting, even in regions of severe cold climate.

The antifreezing admixtures function in two ways:

1. They lower the freezing point of the liquid phase of concrete; they are either weak accelerators or retarders of cement setting and hardening. Examples are electrolytes such as sodium nitrite[1] or sodium chloride,[2] weak electrolytes (e.g., aqueous solution of ammonia), and nonelectrolytes of organic origin, such as multiatomic alcohols and carbamide.[3]
2. As binary or ternary admixture systems, they accelerate hydration of cement and also possess antifreezing properties. This group comprises potash and additives based on calcium chloride (CC) and a mixture of calcium chloride (CC) and sodium chloride (SC), sodium nitrite (SN), calcium nitrite-nitrate (CNN), calcium nitrite-nitrate + urea (CNN + U) and others.

In addition to the two basic groups of antifreeze admixtures, others possessing weak antifreezing properties, but accelerating cement setting and hardening, and promoting a considerable amount of heat at early stages of hardening of concrete are used in winter concreting. These admixtures, (ferric sulfate and aluminum sulfate)[3] contribute to the rapid formation of a dense microcapillary cement structure. These additives, however, are not widely used.

Chemical substances used in Russia as antifreeze admixtures are given in Table 1. Most of these substances can be used for other purposes, and only calcium nitrite-nitrate and calcium chloride-nitrite-nitrate mixtures are specially formulated for use as admixtures. Admixtures based on calcium nitrite are being produced in the USA.[4]

The regions where the climate is relatively mild and the temperature of concrete does not go below - 10°C, carbamide may be successfully used. This antifreezing admixture plasticizes the concrete mix and ensures a uniform mix, but the hardening of concrete is not very much accelerated.[3]

Carbamide is utilized as one of the components of the complex admixtures CNNU or CCNNU (mixtures of urea with calcium nitrite-nitrate or calcium chloride-nitrite-nitrate).

Table 1. Antifreeze Admixtures Used in the USSR[1]

Substance	Abbreviation	Formula
Sodium chloride	SC	$NaCI$
Calcium chloride	CC	$CaCI_2$
Potash	P	K_2CO_3
Sodium nitrite	SN	$NaNO_2$
Urea	U	$CO(NH_2)_2$
Calcium nitrate	CN	$Ca(NO_3)_2$
Calcium nitrite-nitrate	CNN	$Ca(NC_2)_2 + Ca(NO_3)_2$[a]
Calcium nitrite-nitrate + urea	CNN + U	$Ca(NO2)_2 + Ca(NO_3)_2 + CO(NH_2)_2$[b]
Calcium chloride-nitrite-nitrate	CCNN	$Ca(NO_2)_2 + Ca(NO_3)_2 + CaCI_2$[c]
Calcium chloride-nitrite-nitrate + urea	CCNN + U	As above + $CO(NH_2)_2$[d]
Complex salt of calcium nitrate urea	CNU	$Ca(NO_3)_2 \cdot 4CO(NH_2)_2$
Mechanical mixture of calcium nitrate and urea	CN + U	$Ca(NO_3)_2 + CO(NH_2)_2$[e]

[a] Ratio of calcium nitrite to calcium nitrate (by mass) is 1:1 ± 10%.

[b] Ratio of CNN to urea (by mass) is 3:1 to 1:1.

[c] Ratio of calcium nitrite-nitrate to calcium chloride (by mass) is 1:1.

[d] Ratio of calcium chloride-nitrite-nitrate to urea (by mass) is 3:1 to 1:1.

[e] Ratio of calcium nitrate to urea (by mass) is 3:1 to 1:1.

The most effective antifreeze admixture combination functions within a wide range of temperatures so that the advantage of each component is utilized to the maximum extent.

The antifreezing admixtures perform their function, by lowering the freezing point of water. Hence, it is more practical to specify their dosage by mass of mixing water, and this becomes apparent when utilizing different water to cement ratios.

At the same dosage of admixture by weight of cement, the higher the water to cement ratio, the less concentrated will be the solution and this will reflect in the rate of hardening at temperatures below 0°C; such a problem will not arise when the dosage of admixture is specified with respect to the mass of mixing water. Therefore, the amount of antifreezing admixtures is given in all the Tables as a percentage by mass of mixing water. This is convenient in the preparation of additives used in the form of aqueous solutions.

For comparison purposes with other admixtures this dosage may be easily converted to that based on the mass of cement. For conversion purposes average W/C ratio may be taken as 0.5.

2.0 PREPARATION AND APPLICATION OF ANTIFREEZING ADMIXTURES

2.1 General

The antifreezing admixtures are, as a rule, stable substances which may be stored indefinitely in the form of solids or solutions. Special inspection of admixtures stored over a period of 5 years has shown that during this period no oxidation or reduction took place.

In storing substances characterized by higher vapor pressure (for example, urea, ammonia water), measures should be taken to prevent their evaporation.

2.2 Dosage; Delivery Conditions

The recommended dosages of antifreeze admixtures are given in Table 2 and are dependent on the design temperature. These are only average values because in addition to the temperature of concrete, they are influenced by the mass of the structure (surface modulus), technology of construction, cement type, temperature of water and aggregates and some other factors. Depending on these conditions the dosages given in Table 2 may vary by ± 10–15%. However, the maximum concentration of the solution, taking into account the moisture in the aggregate should not exceed 30% for potash, 25% for CNU, CN + U, CCNN, CCNNU and SC + CC and 20% for SN and CNN. The use of antifreezing admixtures in amounts given in Table 2 is allowable when concrete is at a temperature lower than that for which the admixture dosage is specified, provided it attains a critical strength (the strength of concrete at which it can be frozen without detriment to its specified properties); not less than 30, 25 and 20% of the design strength, that is, 20, 30 and 40 to 50 MPa, respectively.

The advantage of ammonia as an antifreezing admixture is that it has a very low eutectic temperature (at the dosage of 33.23% it is -100°C) and is readily available. But its toxicity and, to some extent, its strong retarding effect on the cement setting and hardening processes restrict its use. In the USSR ammonia was used in the form of ammonia water, at a concentration of about 10–20% for some hydrotechnical structures (having a low surface modulus) that are put into service after the end of the winter period.

Table 2. Recommended Amounts of Antifreeze Admixtures

Design Temperature of Hardening		Total Amount of Admixture (% by mass of mixing water)						
°C	SN	C+SC	CNU CN+U[a]	CNN[c]	CN+U[b] CNN+U[b]	CCNN[d] CC+SN[e]	CCNNU[b]	P
0 to -5	8	6+0 to 6+4	6	9	8	6	8	10
-6 to -10	12	7+3 to 8+5	12	16	15	12	15	12
-11 to -16	16	6+9 to 7+10	15	-	18	15	18	16
-17 to -20	-	5+12 to 6+14	20	-	22	18	20	20+
-21 to -25	-	-	-	-	-	25	25	25–30

[a] Ratio of urea to all other components (by dry mass) is 1:1.

[b] Ratio of urea to all other components (by dry mass) is 1:3.

[c] Ratio of calcium nitrite to calcium nitrate in CNN (by dry mass) is 1:1.

[d] Ratio of calcium chloride to CNN in CCNN (by dry mass) is 1:1.

[e] Ratio of Sodium nitrite to calcium chloride (by dry mass) may vary from 1:1 to 3:1.

The higher alcohols retard the hardening process. They are also expensive compared to others and hence of limited use in Russia.

Most of the antifreezing admixtures are multicomponent and are referred to as *complex* additives. Some of them, as for instance CNN and CCNN, are produced by the Russian chemical industry in the form of 25–30% solutions. The solutions are supplied in tanks, then pumped into storage bins, and before application are diluted to the required concentration levels.

2.3 Antifreeze Admixtures with Other Additives

Most of the antifreeze additives are retarders of hardening. However, as dosages of antifreezers used are much higher than those used for retarding purposes, cement hardening becomes accelerated and this sometimes makes concrete placing difficult especially when potash is used. The potash additive not only shortens the time of cement setting and hardening but also influences detrimentally the cement paste structure and frost-resistance of concrete.[5] Hence, potash is usually used in combination with setting and hardening retarders, such as sodium tetraborate ($Na_2B_4O_7$) or organic surface-active substances of the lignosulfonate category. The dosage of these retarders depends on the type of cement and the mount of antifreezer.

Cold weather concreting with the use of antifreezing admixtures does not exclude the use of other substances in combination such as gas-forming agents, air-entraining admixtures, water reducing retarders or superplasticizers. The dosages of air entraining and gas forming additives should be determined experimentally. Higher than normal amounts of these admixtures are used when combined with antifreezers. These additives may cause rapid coagulation. Air-entrainers should be introduced in the form of solution at a concentration of about 3%.

The double salt $Ca(NO_3)_2 \bullet 4CO(NH_2)_2$-CNU is supplied ready for use in polyethylene sacks. This salt is an anhydrous nonhygroscopic crystalline product that is introduced into the concrete mix together with the mixing water. As the process of CNU dissolution is exothermic, this additive can be prepared not only as a concentrated solution which is then diluted for use, but may also be prepared just before application so that the heat of solution can be used for curing purposes.

All other multicomponent additives are not supplied ready for use and the necessary mixture is prepared in situ using the recommendations of Table 2. A concentrated solution of each component is prepared in a separate bin, then the two components are mixed in a third bin (proportioned by volume, designed by density). When the dosage of one of the components of the complex additive (for example, lignosulfonates or sodium tetraborate) is much lower than that of the other, then the former is introduced into the bin containing the more concentrated solution. According to the safety requirements, the maximum dosage of lignosulfonate for mixing with NN + CC or CCNN should not exceed 10%.

To accelerate dissolution of the antifreezers, water is warmed up to 40 to 80°C but for carbamide the temperature should not exceed 40°C. Only fully dissolved aqueous solutions of these admixtures are permitted for use. Tanks for delivering and storage of calcium and sodium chlorides should be protected against corrosion by means of paint or bitumen coatings.

Delivering and storage of CCNN and CCNNU do not require any special anticorrosive protection. Concentrated solutions of antifreezing admixtures can be stored and transported without keeping them warm. The minimum storage temperature of a solution is however, specified according to its concentration and eutectic temperature.

With other additives, either simple or complex, the above measures are not required. However, protection against direct contact with the mucous membrane of the eyes and nasopharynx is imperative. Other measures are the use of rubber boots and gloves, washing of hands and fire protection of the tanks (for nitrite-nitrate and carbamide).

2.4 The Use of Antifreeze Admixtures in Reduced Amounts

Shortening of the time of cement setting attained by the use of large amounts of antifreezing makes the technology of winter concreting, involved and expensive. This necessitated the development of a new method of application of these admixtures. This method consists of using 1.5–2 times less admixture than that is specified normally. Table 3 gives the amounts of antifreezers that can be used depending on the average outdoor air temperature.

Table 3. Recommended Amounts of Antifreezing Admixtures

Average Outdoor Air Temperature (°C)	Total Amount of Admixture (% by mass of mixing water)		
	SN + CC	CCNN	CCNNU
0 to -5	4-6	3–5	4–6
-6 to -10	6–10	5–10	6–10
-11 to -35	10–15	10–15	10–15

The additive CNU is introduced at the same dosage as CCNNU but the allowable minimum temperature at which it can be used is limited to –30°C. For temperatures up to –10°C the ratio of the components in CNU is 1:1 and that at lower temperatures is 3:1 (by mass).

The CCNN:U ratio in CCNNU is 3: 1, ratios of SN:CC and CNN:CC are 1:1 by mass.

These additives have been used under the following conditions of winter concreting:

1. Antifreezing admixture dosages given in Table 2 are used together with light heating in projects. In this case the strength requirements for concrete are higher when the temperature is below – 10°C. The required strength in comparison with a 28-day compressive strength of normal moist-hardened concrete (R_{28}) is as follows: for a strength of 10–15 MPa, it should not be less than 50%; the corresponding values for 20, 30, and 40–50 MPa, are 40%, 30%, and 25% respectively.
2. This method permits (in winter) concreting at temperatures $T \leq -15°C$ corresponding to a frozen state but the strength will continue to increase with time and reach its design value at $T > -10°C$. In regions characterized by stable low temperatures during the whole winter, the use of this method permits putting into service, shortly after completion, structures made of frozen concrete, such as floors, access roads, road base courses, pavements of temporary roads and lanes, as well as constructions having a low surface modulus.

The method of early freezing of concrete without the use of antifreezing admixtures has the following disadvantages. The strength of such a concrete is lower by 20–40% and the frost resistance lower by 40–60% compared with the normally moist-cured concrete. The bond between reinforcement and concrete is lowered by 70% compared to normally moist-cured reinforced concrete. These problems may be avoided when the method of early freezing is combined with the use of antifreezers in amounts specified in Table 3.

By this method forced interruption of service on roads and floors during temporary thaws can be prevented. This is possible because in the amounts recommended, antifreezing admixtures accelerate considerably early hardening of concrete and ensure subsequent hardening at temperatures down to -10°C.

Admixtures given in Table 3 as well as calcium chloride may be recommended for foundations in permafrost regions where, the temperature of ground is lower than 0°C and the ice contained in the soil contributes to its strength. The bearing capacity of permafrost soil depends on soil temperature and degree of salinity.

Concreting in such soils is conditioned by the necessity to preserve their permafrost regime, and this is attained by means of water proofing. The required dosage of admixtures is to be found on the line corresponding to 0°C to – 5°C (Table 3). At soil temperatures up to -3°C the amount of the admixture should be the minimum given in Table 3, i.e., 3–4% by mass of mixing water, and at temperatures of –3 to –5°C, it should be 4–6%. At lower temperatures these percentages should be raised but should not exceed the value given in the next line (– 6 to – 10°C) of Table 3. In reinforced concrete, the amount of calcium chloride should not exceed 4% by mass of mixing water.

3. In this case, the antifreezing admixtures (electrolytes) not only accelerate concrete hardening and reduce the electric heating period but also raise the electrical conductivity of the liquid phase, thus allowing electric heating at a temperature below 0°C.

   In this method sodium nitrite, sodium nitrite-calcium chloride (1:1 by mass), a mixture of calcium chloride and sodium chloride, and CCNN, in amounts given in Table 4 may be used.

Table 4. Recommended Admixture Percentages for Winter Concreting With the Use of Electric Heating

Temperature of Concrete Cooling Before Electric Heating (°C)	Dosage of Admixture (% by mass of mixing water) SN	SN+CC	CC+SC	CCNN
0 to -5	6–8	3+2	0+4	5
-6 to -10	10–12	4+3	0+6	8
-11 to -15	14–16	7+6	2+6	12
-16 to -20	18–20	9+9	3+7	–

Note: The ratio of CNN to CC in the additive CCNN is 1:1. Additives containing urea are not to be used because of their volatility. Potash is not recommended because it lowers the frost-resistance of concrete.

2.5 Choice of Antifreezing Admixtures

Table 5 shows what admixtures should be used for various types of structure and operating conditions. Data from this table may also be used when the antifreezing admixtures are utilized in combination with other methods of winter concreting.

Table 5. Requirements of Concrete Containing Antifreezing Admixtures (+ denotes permitted and - denotes not permitted)

No.	Type of Structure, Conditions of Operation	Additives						
		CC+SC	CNU, CN+U, CNN+U	CC+SN	CCNN, CCNN+U	SN	P	CNN
1.	Prestressed structures	-	-	-	-	+	-	+
2.	Nonprestressed concrete reinforcement of diameter:							
	a. >5 mm	-	+	+	+	+	+	+
	b. <5 mm	-	+	-	-	+	+	+
3.	Concrete (nonprestressed)							
	a. without protection	-	+	-	-	+	+	+
	b. zinc coating	-	-	-	-	+	-	+
	c. other coatings (alkali-resistant paint or other alkali resistant protective coatings)	-	+	-	-	+	+	+
4.	Precast-monolithic structures consisting of blocks with a monolithic core	-	+	+	+	+	+	+
5.	Reinforced concrete subjected to:							
	a. noncorrosive gas media	-	+	+	+	+	+	+
	b. corrosive gas media	-	+	-	-	+	+*	+
	c. corrosive and noncorrosive water media, except as given in (d)	+	+	+	+	+	+*	+
	d. corrosive water media containing salts and alkali	-	-	-	-	+	-	+
	e. the zone of varying water level	-	+	-	-	+	-	+
	f. water and gas media at R.H. >60% (aggregate containing reactive silica)	-	+	-	+	-	-	+
	g. zones of stray constant currents from outside sources	-	+	-	-	+	+	+

*Allowed in combination with water reducer-retarder additives.

Notes:
1. The possibility of using additives of items 1 to 3 of this table should be modified to fulfil the requirements given in item 5. With antifreezing admixtures CNU, CN+U, CNN+U, SN and CNN only prestressed deformed bars specified according to GOST 10844-81 should be used.
2. Restrictions imposed on the use of concretes with additives listed in items 3, 5(d) and 5(f) as well as of concrete with potash admixture in item 5(e) of this table are also valid for concrete structures.
3. Under item 5 (b), the use of additives (except for SN and CNN) in media containing chlorine or HCl requires special consideration.
4. Structures periodically exposed to water, condensate or effluent liquids from factories are taken as structures operating at relative air humidity exceeding 60%.
5. The lack of experience has not permitted inclusion in this table of prestressed structures reinforced with thermally strengthened reinforcement of different classes.
6. Reinforced concrete structures for electric-powered transport and plants consuming constant electric current are not included because of the danger of electrolytic corrosion. The use in these structures of such antifreezing admixtures as calcium nitrite-nitrate and sodium nitrite-nitrate (especially in reduced dosages) is permissible.

2.6 Safety Precautions

The following safety measures should be observed in transportation, storage, and handling of antifreezing admixtures.

Crystalline NN is able to maintain fire or induce flame in inflammable substances and in some cases even by friction or a knock.

Sodium nitrite interacts and burns in contact with such organic materials as wood, cotton and straw. Mixtures of sodium nitrite and ammonia salts or cyanides may explode.

Crystalline sodium nitrite should not be stored with other salts, readily inflammable gases or liquids, organic substances, combustible materials, alcohol-based substances, or radioactive materials, or with caustic, corrosive, or explosive substances.

To prevent fire hazard in storehouses, smoking and use of open fire should be avoided, and the possibility of short circuits and sparking of the electric equipment should be excluded. The storehouse should be provided with fire extinguishers.

Liquid sodium nitrite is not flammable.

Urea and CNU are fire hazardous products. Urea has a flash point at 182°C. Urea and CNU should be stored in separate storehouses with fireproof walls of not less than the degree 1 fire-resistance.

Potash, calcium chloride and sodium chloride, CNN and CCNN are not fire hazards.

In places where the additives are stored or their solutions are prepared, food should not be served. Precautions should be taken against contamination of food and skin with the additives, especially when using SN, CNN and CCNN admixtures.

Plenum-exhaust ventilation or local suction should be provided in places where additive solutions and concrete mixtures are prepared. In places where the solutions of SN, CNN, CCNN, P, CN and CNU are prepared a 10–15 fold increase in air change should be ensured by the plenum-exhaust ventilation.

The laboratories in which the density of the additive solutions is determined should be equipped with exhaust chambers.

Persons with skin injuries (abrasions, burns, scratches, etc.) as well as with eye and eyelid injuries should not be permitted to work with these admixtures.

Operators preparing the additive solutions should work in overalls of water-repellent cloth, goggles, rubber boots and gloves.

Sodium nitrite and CNN are toxic. Accidental penetration of sodium nitrite (in the form of crystals or salt solution) into the organism results in dilation of blood vessels and formation of methemoglobin in blood.

Typical effects of poisoning are: weakness, nausea, giddiness, reduction in vision and onset of blue coloration of the tip of the nose, toes, and fingers, 10–15 minutes after the intrusion of the substance into the organism. If such effects occur immediate medical attention should be provided.

Longtime action of sodium nitrite and CNN can result in headache, weakness, easy tiredness, loss of appetite, loss of sleep, pain in feet and hands, inflammatory conditions in skin, arms and feet, chaps, and festers. Splashes of the additives on the skin should be immediately washed off with water. The following precautions are recommended.

Crystalline sodium nitrite should be stored in single buildings, and concentrated liquid sodium nitrite and CNN within fenced yards.

Tanks for preparation, storage and handling of aqueous solutions of sodium nitrite, CNN, CCNN and CCNNU as well as those used for storage and transporting of crystalline sodium nitrite should be provided with warning signs.

Solutions of sodium nitrite should be prepared in rooms specially designated for this purpose.

Crystalline sodium nitrite should be dissolved in closed, highly mechanized installations operated by few persons; the process of salt charging should be highly mechanized and proper sealing should be ensured.

The discharge of water solutions of sodium nitrite and CNN into tanks and concrete mixers should be performed only through pipelines; hand transportation of salt solutions to the site should be permitted only in exceptional cases, and in closed bins filled up to not higher than 3/4 of the height of the bin.

Discharge of solutions of sodium nitrite, CNN, CCNN, CNNU and CCNNU into reservoirs of sanitary and ordinary water management systems should be disallowed.

Aqueous solutions of sodium nitrite in acid medium ($pH < 7$) decompose releasing gaseous products and poison gases including NO and NO_2.

The allowable concentration of nitrogen oxides, in terms of NO_2, in the working place is 5 mg/m^3.

The decomposition of sodium nitrite may also occur when the solution is mixed with acids or salts exhibiting acid reactions (e.g., lignosulfonates-LS).

Safe preparation of the solution of the additives containing LS and $NaNO_2$ depends on the solution concentration of each of the two components, the sequence of introduction of the components into water, and temperature.

Dangerous amounts of gases are released during the preparation of concentrated solutions, at a higher temperature and when the LS (but not sodium nitrite) is dissolved first.

The additive mixture LS + $NaNO_2$ is not hazardous for health when the aqueous solution of LS is treated with sodium hydroxide to obtain $pH \geq 8$.

For safety purposes separate pipelines and pumps should be provided for solutions of sodium nitrite (concentrated or diluted); this would eliminate the possibility of even accidental mixing of the solutions of this salt with the LS-solutions.

Thoroughly cleansing of vessels before filling them with sodium nitrite solutions is imperative. Vessels which had contained acids or other products having acid reaction should be pre-steamed.

The above precautions described for the preparation using mixtures of LS are also valid when using CNN and CCNN.

Potash is a salt possessing strongly alkaline properties. Therefore, precautions should be taken against spilling of solutions (especially if they are concentrated) on the skin and the eyes. Longtime action of salt particles and intrusion of these into the organism triggers excitation of respiratory organs, conjunctivitis, ulceration of the mucous membrane of the nose and causes gastric and bowel diseases.

The additives CC, SC and U are not toxic. When solutions of these additives spill on the skin, the face or hands they should be washed thoroughly.

2.7 Preparation, Transportation and Placing of Concrete Mixes

Concrete mixes containing antifreezers (introduced with the mixing water) are made with cement of specified brand, and specified fine and coarse aggregate. The use of frozen aggregate is prohibited.

The temperature of the components of the concrete mix depends on the type and dosage of the antifreezer, conditions of transportation and the field of application.

When concrete is to be placed into joints, correction should be made for cooling effect of the mix in zones of contact.

When heated components are used, the technology of mix preparation is the same as that for usual concrete, except for cases where, instead of additives, water solutions are used.

When the mixes are cold the following order of mix preparation is recommended: the aggregate is discharged into the solution of the admixture and after 1.5–2 minutes of agitation, cement is added and 4–5 minutes of agitation thereafter, completes the process of preparation.

In case of rapid hardening of cement (using an antifreezer), when the required amount of concrete mix is not large, it is expedient to use the following technology: the dry mix of cement, sand and crushed stone is transported to the site and there the admixture solution of specified concentration is added; 3–3.5 minutes of agitation completes the process of preparation.

Concrete mixes containing antifreezers may be transported without heating, but appropriate protection against atmospheric precipitation and freezing is necessary.

The concrete mix delivered to the site should have the required temperature and workability. When these conditions are not fulfilled heating becomes necessary.

The temperature of concrete mix on site may vary within wide limits depending on the purpose for which concrete is designed, technology of preparation, type and dosage of admixture. However, the minimum temperature of the concrete mix should be five degrees higher than the freezing temperature of the aqueous solution of the admixture.

Placing of concrete mixes containing antifreezing admixtures should proceed uninterruptedly; if this is not possible the surface of concrete should be heated.

During snowfall and under strong windy conditions concreting should be performed within shelters.

2.8 Curing of Concrete with Antifreezers

After termination of concreting, the open surfaces of monolithic and reinforced concrete structures should be protected by a waterproof membrane against moisture loss, atmospheric precipitation and formation of salt on the surface. Provision for keeping concrete warm should also be provided.

The required strength of concrete after removal of forms should

- not be less than 80% of the design strength for prestressed structures;
- not be less than 70% of the design strength for structures exposed immediately to freeze-thaw cycles.
- be according to requirements of Table 6 for load bearing structures.

Table 6. Concrete Strength Required for the Removal of Forms

Length of Required Structure (meters)	Strength Under Acutal Load (% of design strength) >70	<70
≥6	100	80
<6	100	70

Forms (which carry no loads), hydro- and heat-insulation are removed when concrete attains its ultimate strength (see Sec. 2.1).

Some work has been done on winter concreting using antifreezing admixtures such as sodium nitrite and potash[1] using vertical slip-forms and calcium nitrate + urea and calcium nitrite-nitrate + urea, using horizontal slip-forms.[6] This technology permits mechanization, allows uninterrupted construction, saves time and lowers the manufacturing cost of walls by about 20% and labor consumption by ¼.

Concrete mixes containing admixtures of sodium nitrite and potash may be used in vertical slip-form construction of exterior walls of multistory buildings and interior stiffening walls (cores) of large-load-bearing walls of multistory buildings, attached and interior walls of monolithic lift and staircase blocks of multistory brick and framework buildings.

Concrete mixes with the addition of CNU or NNCU may be used in horizontal slip-form construction of monolithic walls of linear structures. The requirement is that concrete should be dense and this limits the W/C ratio to 0.5–0.55 and the workability (slump test) to 60–80 mm.

The dosage of additives should be determined experimentally using guidelines given in Tables 2 and 3.

The rate of construction and that of slip-form lifting, depends on the strength of concrete at the age of 1, 2, 3 and 7 days. Table 7 gives tentative values of early strength of concrete as a function of temperature.

Table 7. Strength Gain of Concrete at Early Ages for Vertical Slip-Form Concreting

Additive	Design Temperature of Concrete Curing (°C)	Strength (% of design value) 1 Day	2 Days	3 Days	7 Days
Sodium nitrite	-5 to -15	1–1.5	1.5–2.5	4–7	10–30
Potash	-15 to -35	1.5–3	3–7	5–15	20–50

Filling of slip-forms with concrete should proceed without interruption and with proper compaction; each layer should be placed before the beginning of setting of the preceding one. The initial moving of slip-form is performed immediately after it has been filled with the concrete mix. To maintain the required shape the compacted layer of concrete should acquire a minimum strength of 0.1–0.2 MPa and thereafter the slip-form movement could proceed uninterruptedly.

The optimum rate of slip-form movement should be determined in the laboratory. For concrete containing $NaNO_2$ and potash, the optimum rate of slip-form movement should be on an average 0.06–1 m/h in vertical slip-form concreting and 4–5 m/h in horizontal slip-form concreting.

3.0 EFFECT OF ANTIFREEZING ADMIXTURES ON CEMENT AND CEMENT COMPONENTS

3.1 Interaction of Antifreezing Admixtures with Calcium Hydroxide and Silicate Phases

The silicate phases of cement (alite, C_3S, belite and β-C_2S), as well as calcium hydrosilicates, are chemically inert to strong electrolytes used as antifreezing admixtures. Electrolytes in contact with alite and belite change the ionic strength of the solution, whereas the hydrolyzing salts not only change the ionic strength of the solution but also change the pH. When the admixtures do not contain the same ions as in the cement phases (i.e., Ca, Si or Al ions), they accelerate the hydration process chiefly by increase in the solubility of C_3S and β-C_2S. The admixtures such as calcium chloride, calcium nitrite and calcium nitrate that contain the same cations as C_3S and β-C_2S, accelerate hydration by nucleating action of such ions and this results in an intensification of the processes of crystallization of hydrate.[3]

The effect of carbamide and ammonia admixtures on silicate phases of cement is due to the ability of these admixtures to form complex salts with calcium hydroxide. Thus, the metastable solubility of these phases increases[7] and leads to acceleration of hydration. However, as these admixtures change the dielectric characteristics of the mixing water and adsorb on the solid phase, the retarding effect on the hydration of C_3S and β-C_2S prevails.

During the hydration of C_3S, calcium hydroxide is formed which is capable of reacting with most of the antifreezing admixtures with the formation of hydroxysalts.

The phase composition of hydroxysalts as well as the composition of double salt hydrates (products of interaction of C_3A and C_4AF with antifreezing admixtures) differs from that formed when the salts are used in small amounts. The salts promote densification of cement paste and change its microstructure and physical characteristics of concrete.

The properties and composition of calcium oxychlorides have been described in the literature.[8][9] In the system $Ca(OH)_2$-$CaCl_2$-H_2O, the formation of two types of oxychlorides $Ca(OH)_2 \bullet CaCl_2 \bullet H_2O$ (low-basic form) and $3Ca(OH)_2 \bullet CaCl_2 \bullet 12H_2O$ (high-basic form) are recognized.

The low-basic form of calcium hydroxychloride is stable at temperatures up to 100°C at calcium chloride concentrations from 32 to 38%. This compound crystallizes in the form of hexagonal prisms and plates.

The high-basic form of calcium hydroxychloride crystallizes as needles and prisms. The composition of hydroxychloride is $3Ca(OH)_2 \bullet CaCl_2 \bullet 12H_2O$.[8] This compound is stable up to a temperature 38.9°C in a 32% solution of calcium chloride. The XRD shows a strong peak at 2.16Å.

Formation of hydroxynitrates of two types is also recognized in the $Ca(OH)_2$-$Ca(NO_3)_2$-H_2O system. The properties and composition of calcium hydroxynitrates have been described.[10][11] The low-basic form of calcium hydroxynitrate $CaO \bullet Ca(NO_3)_2 \bullet 3H_2O$ is formed at 25°C and calcium nitrate concentrations from 45.3 to 57.7%.

At 100°C and calcium nitrate concentration of 57–70%, $CaO \cdot Ca(NO_3)_2 \cdot 2H_2O$, crystallizes whereas a compound of composition $CaO \cdot Ca(NO_3)_2 \cdot 0.5H_2O$ crystallizes at a concentration of 70 to 77%.

Figure 1 shows isotherms of calcium hydroxide solubility in calcium nitrate solution. X-ray and crystallographic data on $CaO \cdot Ca(NO_3)_2 \cdot 3H_2O$ have been described in a publication.[11]

X-ray data of the compounds $CaO \cdot Ca(NO_3)_2 \cdot 3H_2O$ are given in Table 8.

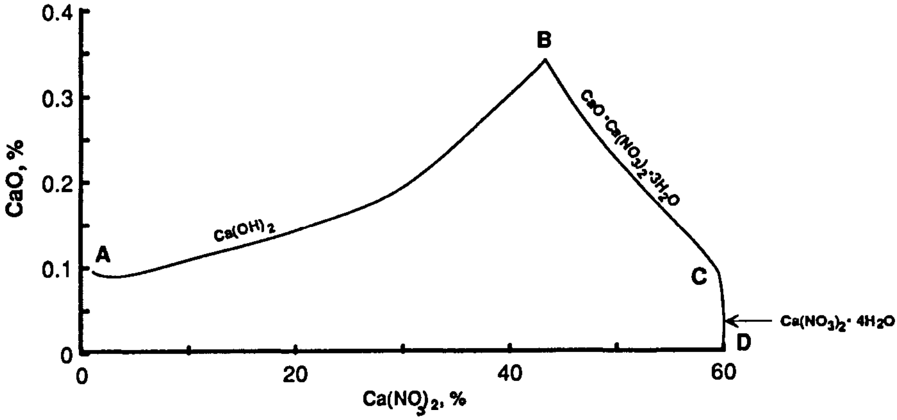

Figure 1. Isotherms of calcium hydroxide in calcium nitrate at 25°C.

Table 8. XRD Data on $CaO \cdot Ca(NO_3)_2 \cdot 3H_2O$

Interplanar Distance (Å)	Height of Diffraction Peaks (%)	Interplanar Distance (Å)	Height of Diffraction Peaks (%)
7.9	30	2.45	0.5
6.79	40	2.42	2
6.0	30	2.314	90
3.89	40	2.210	100
3.64	1	2.010	25
3.42	2	1.910	1
3.29	100	1.897	1
3.01	2	1.731	2–3
2.79	30	1.664	2
2.67	1		

The high-basic form of calcium hydroxynitrate ($3CaO{\bullet}Ca(NO_3)_2{\bullet}14$–$16H_2O$) is formed at temperatures in the range – 6 to – 20°C over a range of calcium nitrate concentrations of 20 to 45%.

The properties and composition of calcium hydroxynitrite $CaO{\bullet}Ca(NO_2)_2{\bullet}3H_2O$ are described by Rozenberg et al.[11] As a result of interaction between calcium nitrite (of concentration ranging from 19.5 to 40 per cent) and $Ca(OH)_2$ at temperatures – 10°C to + 20°C, only the low-basic form of calcium oxynitrite is formed. The crystals possess direct extinction, negative elongation and strong double refraction (bright coloration in polarized light).

3.2 Interaction of Aluminum-Containing Phases with Antifreezing Admixtures

Unlike the silicate phases, the aluminum-containing phases of cement (C_3A and C_4AF) and products of their hydration (calcium hydroaluminates and hydroaluminoferrites) show a tendency to form slightly soluble double salts-hydrates with antifreezing admixtures.

Properties and composition of the low form of calcium hydrochloraluminate (CHCA) $3CaO{\bullet}Al_2O_3{\bullet}CaCl_2{\bullet}10H_2O$ have been studied.[12][13] The thermogram of CHCA shows endothermic peaks at 160°, 330°, 810°C and an exothermic peak at 680°C. CHCA crystallizes in the form of hexagonal plates. The XRD of CHCA is characterized by strong diffraction peaks at 7.91 and 3.94 Å. This compound is formed from solutions containing calcium hydroxide, calcium aluminate and calcium chloride. Tricalcium aluminate and other aluminum-containing minerals of Portland cement clinker in contact with 2.25N calcium chloride solution also produce this complex. Small amounts of this compound are also formed when calcium aluminates interact with sodium chloride in the presence of calcium hydroxide.

Properties and composition of calcium hydrochloraluminate in the trichloride form $3CaO{\bullet}Al_2O_3{\bullet}3CaCl_2{\bullet}H_2O$ (CHCA-3) are described in Refs. 13 and 14. This compound produces a peak at 160°C in thermogram and the XRD strong lines at 3.66 and 2.55 Å. The CHCA-3 complex is formed by reacting 2.25N $CaCl_2$ with tricalcium aluminate at temperatures – 15°C to 20°C.

Properties and composition of low form of calcium hydronitroaluminate $3CaO{\bullet}Al_2O_3{\bullet}Ca(NO_3)_2{\bullet}10H_2O$ (CHNA) are described by Foret.[12] CHNA shows endothermic effects at 140, 280, 560, and 800°C. It crystallizes in the form of hexagonal plates. It shows strong XRD lines at 4.32 and 8.7 Å.

CHNA is formed either from diluted solutions of aluminate, nitrate and calcium hydroxide or by treating of calcium nitrate with tricalcium aluminate.

Properties and composition of calcium hydronitroaluminate of trinitrate form $3CaO \bullet Al_2O_3 \bullet 3Ca(NO_3)_2 \bullet 16–18H_2O$ (CHNA-3) have been described by Rozenberg et al.[15]

CHNA-3 shows an endothermic effect at 140°C; x-ray data of this compound are given in Table 9.

Table 9. XRD Data on CHNA

Interplanar Distance (Å)	Comparative Intensity of Diffraction Peaks (%)	Interplanar Distance (Å)	Comparative Intensity of Diffraction Peaks (%)
8.00	100	2.47	15
4.95	30	2.32	65
4.70	50	1.96	15
4.20	30	1.85	30
4.02	15	1.76	20
3.64	70	1.656	10
3.23	17	1.616	7
3.12	25	1.592	10
2.92	60	1.548	10
2.68	40		

CHNA-3 can be obtained by the interaction of tricalcium aluminate with calcium nitrate solution.

The composition and properties of the low form of calcium hydronitroaluminate $3CaO \bullet Al_2O_3 \bullet Ca(NO_3)_2 \bullet 10H_2O$ (CHNiA) are given by Ratinov et al.[16]

CHNiA is formed by the action of calcium nitrite with the Al_2O_3-bearing phases of cement. CHNiA may be crystallized by the action of sodium nitrite on C_3A in the presence of calcium hydroxide.

In the presence of calcium hydroxide, C_3A and C_4AF react with potash to form calcium hydrocarboaluminate $3CaO \bullet Al_2O_3 \bullet CaCO_3 \bullet 11H_2O$ (CHCaA). Simultaneously, the liquid phase becomes enriched in caustic alkali. The composition and properties of CHCaA are described in a publication.[17]

Thermograms of CHCaA show endothermic effects at 230 and 840°C. XRD shows peaks at 3.76 and 7.67 Å.

Similar double salt hydrates are formed with more low-basic aluminate phases contained in slags and alumina cements in the presence of calcium hydroxide.

3.3 Compositional Requirements of Cement for Use with Antifreezers

The knowledge of the above reactions permits formulation of requirements with regard to the mineralogical and chemical composition of cements used in winter concreting when used with antifreezing admixtures.

As the basic purpose of using these admixtures is to ensure rapid attainment of the design strength of concrete, the cement should possess high reactivity, irrespective of the ambient temperature. Portland cement of brand not less than 400–500 conforming to the Russian standards should be used.

The C_3A component reacts with the majority of antifreezers with the formation of double salts and lowers the admixture content in the liquid phase of concrete mix. Hence high-alite and low- and average-aluminate cements should be preferably used. The use of alumina cements, or nonshrinking, expanding, and self-stressing cements is not recommended.

The use of slag Portland cement may be permitted only after performing the necessary trials.

Paving concrete with antifreezing admixtures should be made with cement meeting the requirements of a standard. The use of slag Portland cement for this purpose is not recommended.

Because of the higher requirements of energy of activation of slag minerals, compared to normal cements, it is expedient to use antifreezers with a high quality slag portland cement in combination with electric heating.

It is desirable for winter concreting to minimize the mineral admixture content in portland cement, as it acts only as a diluent.

Slag portland cements may be used for winter concreting in conjunction with antifreezers for massive low-modular structures, when they are put into operation only after the spring-summer period.

The sulfate-resistant cement can be used with anti-freezing admixtures, but should be combined with electric heating.

There is no practical experience in the use of antifreezing admixtures with halogen-containing cements.

Taking into account the intensive strength gain of concrete made with alunite cement, it may be considered as a prospective candidate for winter concreting without heating.[18] It may be used in combination with other admixtures (plasticizing and air-entraining types) or in combination with electric heating.

If antifreezers are used in amounts of 3–5% by mass of mixing water for protecting steel, they are in essence, equivalent to concretes made with Portland cement with the antifreezing admixture CCNN.

4.0 EFFECT OF ANTIFREEZING ADMIXTURES ON PHYSICAL PROPERTIES OF CONCRETE MIXES

The effect of antifreezing admixtures on such physical properties of concrete mixes as bleeding, rheology, and placability, depends on the type and composition of cement, temperature, composition, and dosage of the antifreezer.

4.1 Bleeding

Bleeding and sedimentation of solid particles are not promoted by concrete mixes containing the most widely used antifreezing admixtures. This is due to the fact that these additives are strong accelerators of cement setting. In addition, antifreezing admixtures used in large dosages increase the viscosity of the liquid phase of concrete mixes and also lower the temperature.

Bleeding rises when antifreezers are used with strong retarders and plasticizers, or when sodium nitrite, carbamide, ammonia and some other additives which are weak accelerators or retarders are used. In such cases usual precautions are taken to minimize bleeding. They include changing the composition of concrete mix by increasing the sand content, lowering the fineness modulus of the sand, introduction of dispersing mineral additives, etc.

4.2 Rheological Properties of Concrete Mixes

Antifreezing admixtures, especially the calcium salts, behave as weak plasticizes of concrete mixes, and lower the W/C ratio by 3–5% with respect to the standard specimen, without changing the workability.

Mixtures of calcium chloride and nitrite with sodium chloride act as weak plasticizers.

A higher plasticizing effect is characteristic of the carbamide additive; it increases the flowability of concrete mixes even when used as a component of complex antifreezing admixtures, such as CNU, CNNU and CCNNU.

As carbamide also retards setting, its plasticizing effect (in complex additives) is more pronounced than that of additives containing no carbamide.

Other salts, used singly or as components of complex antifreezers, do not show any perceptible plasticizing effect. It is, therefore, preferable to combine these salts with plasticizers and superplasticizers.

By combining sodium nitrite with superplasticizers of the naphthalene-formaldehyde type or potash with lignosulfonates, the required concentration of superplasticizer can be decreased from 0.3 to 0.15%.[19]

The combination of calcium salt antifreezers with superplasticizers shows synergistic effect (Fig. 2).[30]

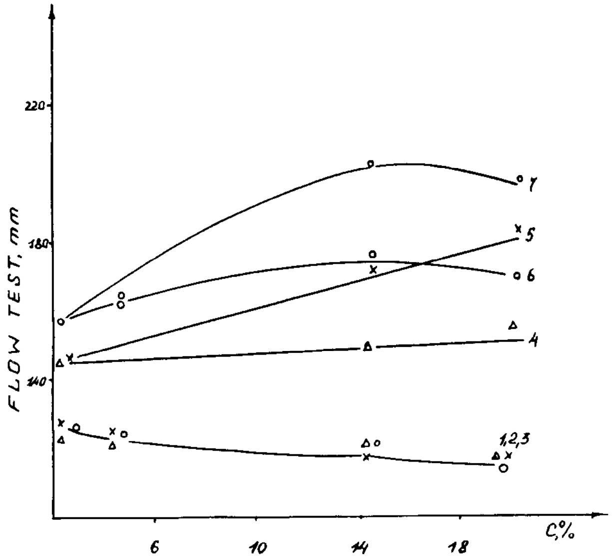

Figure 2. Plasticizing effect of different dosages of electrolytes and other admixtures on mortar. *(1)* CNN, *(2)* CC, *(3)* CCNN, *(4)* 0.2% LS + CCNN, *(5)* 0.5% superplasticizer + CNN, *(6)* 0.7% superplasticizer + CC, *(7)* 0.7% superplasticizer + CCNN. Dosage of organic admixtures is by mass of cement and that of inorganic admixtures is by mass of mixing water.

4.3 Dimensional Changes in Concrete

Concrete hardened at T ≥ 0°C, with calcium containing antifreezing admixtures (e.g., $CaCl_2$ with NaCl) exhibits 5–10% more shrinkage compared with the reference concrete without an admixture. Other admixtures influence the shrinkage only marginally.

In complex admixture combinations containing antifreezers and other additives, the effect of the latter on concrete shrinkage is about the same as when they are used separately.

4.4 Microstructure of Cement Paste

The cement paste structure is influenced by physical and chemical factors. In unheated winter concreting, the temperature of curing influences the rate of hydration and hardening of cement. At low temperature, less defective hydrate phases are formed and, consequently, the strength of reference concrete at temperatures 0 to 10°C is higher when compared, at the same degree of hydration, with that containing admixtures. This effect of antifreezing admixture is related to its influence on the hydration of silicate and aluminate components of cement.

The morphology of calcium hydrosilicates is not modified in the presence of antifreezing admixtures. This is not true for the microstructural features of hydrated alumina-bearing phases of cement. Double and basic salts form as well-shaped needle crystals. The rate of crystallization of these salts from oversaturated solutions is higher than the rate at which the hydrosilicates are released. As a consequence of this, the double and basic salts are able to form the initial structural skeleton and function as a microreinforcement for the hydrosilicate matrix of the cement paste.

In Fig. 3 the compressive strengths of cement paste (with and without antifreezers), hardened at different temperatures are compared on the basis of the degree of hydration of alite.

The curve of specimens with antifreezers shows higher strengths at the same degree of hydration. This cannot be explained only by the effect of the additive on the formation of hydro-oxy salts and double salt-hydrates. The main cause for the higher strength development in specimens with antifreezers is the formation of an initial structural skeleton which becomes enveloped by calcium hydrosilicates.

From the results in Fig. 3, it can be seen that to obtain specimens of cement paste of strength 10 MPa, 50% of alite should be hydrated.

Subsequent hydration of 30% alite increases the strength to 60 MPa. Observation shows that a considerable amount of hydration occurs in forming the initial skeleton structure and, thereafter, even small amounts of the hydrates forming on the skeleton give comparatively larger strengths. In the cement paste containing antifreezers, strength of the order of 10 MPa is obtained at 30% alite hydration. The skeleton may form earlier or the structure itself is stronger.

Table 10 shows the effect of antifreezers on the surface area of cement pastes. Antifreezing admixtures seem to increase the surface area and hence promote strengths.

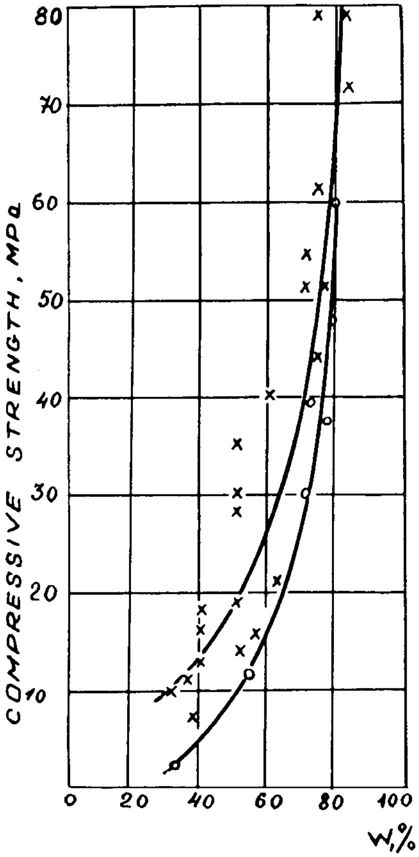

Figure 3. Relationship between compressive strength of cement and degree of alite hydration (% W) in portland cement. o-o-o = without admixture, x-x-x = with admixtures CNU and CCNNU.

Table 10. Effect of Antifreezing Admixtures on the Specific Surface of Cement Paste (m^2/kg)

Duration and Conditions of Hardening	Admixture	Concentration, % by Mass of Mixing Water	Specific Surface sp x 10^{-3}
28 days at -20°C RH = 100%	None	-	54
	CCNN	5	91
		10	145
	CC	5	115
		10	110
	CNN	10	87
		17	122
	Potash	5	69
		9	91
	Calcium nitrate	5	72
		10	115
		17	122
	Ferric chloride	5	106
28 days at -10°C and 28 days at +20°C, RH = 100%	CNN	25	80
	CCNN	25	91
	CCNNU	25	76
	Potash	25	60

The combined action of physical (dispersion) and chemical effects ensures formation of a dense structure, not only of the cement paste, but also of the zone of contact with the aggregate. This manifests itself in such concrete properties as increased impermeability, frost and salt resistance.

4.5 Creep of Concrete

The presence of antifreezing admixtures influences marginally the creep of concrete. The creep values may be lower than when normal accelerators are used. When other additives are used in combination with antifreezers, the same effects as described for shrinkage are observed.

4.6 Pore Structure of Cement Paste

Introduction of most of the antifreeze admixtures affects the pore structure of the cement paste. This effect manifests itself in a considerable shift of the curve of pore size distribution into the zone of gel pores and micropores at the expense of macropores. The overall porosity of concrete is unaffected.

These effects can be seen in Fig. 4. Sodium nitrite changes the pore structure to a lesser degree than other admixtures.

The tendency towards the formation of finer pores increases with the admixture dosage up to 20–25%. Further increase acts detrimentally as far as pore structure is concerned.

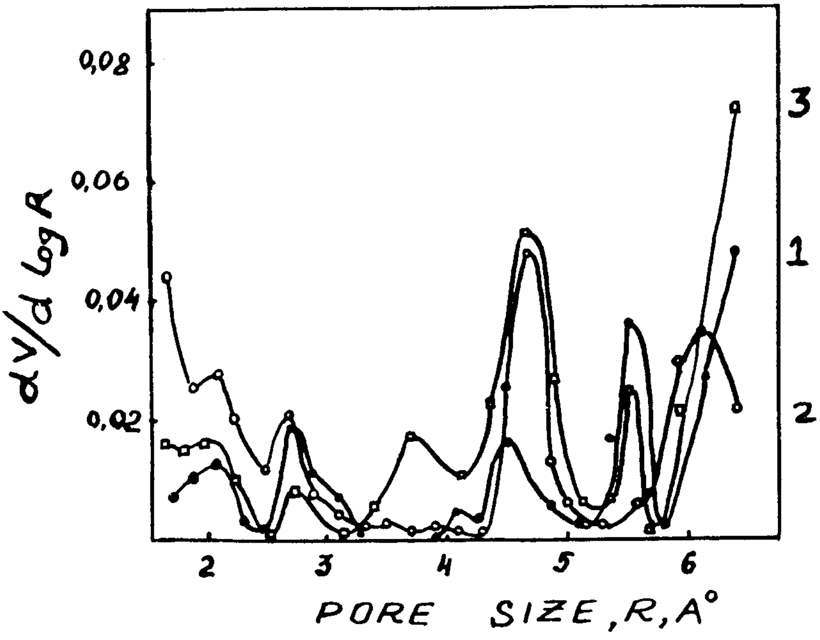

Figure 4. Porosity of cement paste in concrete. *(1)* without admixture, *(2)* with 15% CCNN, and *(3)* with 15% potash.

Antifreezing admixtures are often used together with organic surface-active substances such as retarders, plasticizers and air-entrainers. In such a complex admixture combination, each component acts independently on the pore structure of the stone. The use of such combination of additives of different types permits achieving an optimum pore structure with respect to mechanical and frost-resistance properties (Fig. 5). The resulting pores are enveloped by dense, well dispersed and stronger cement paste.[23]

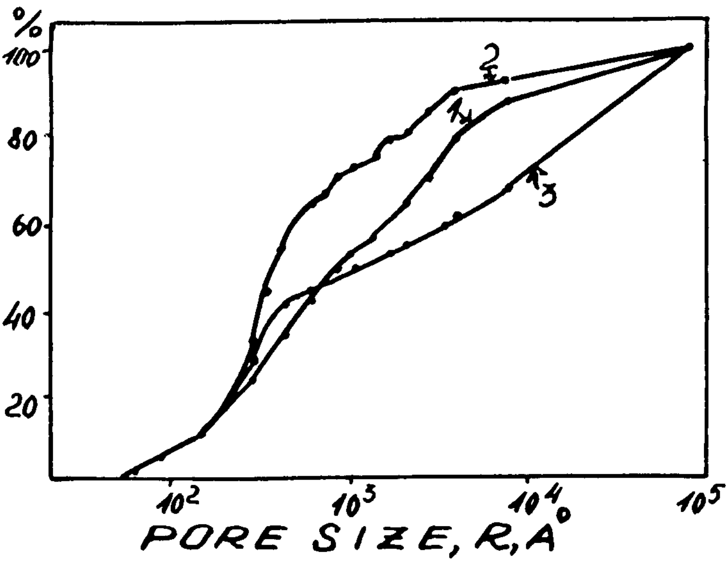

Figure 5. Integral porosity of mortar in concrete. *(1)* without admixture, *(2)* with 6% CCNN (by mass of mixing water), *(3)* 6% CCNN + 0.03% sodium abietate by mass of cement. The ordinate shows the percent porosity corresponding to various pore size ranges.

4.7 Permeability of Concrete

The shift in the pore size distribution curve of the cement paste in the presence of calcium-based antifreezers, towards the zone of microcapillaries and gel pores, improves the zone of contact between the cement paste and aggregates and, hence, increases the impermeability of concrete. It is further promoted in combination with superplasticizers. Sodium nitrite is not as effective as the calcium salts. Addition of potash does not result in the formation of finer pores and hence the permeability of concrete is increased, therefore potash has to be used in combination with water reducing admixtures.

4.8 Setting of Concrete

Antifreezing admixtures based on calcium chloride, potash and others reduce considerably the setting time of concrete. Therefore, when concrete has to be transported over a long distance, even at low air temperatures, these admixtures are used with organic or inorganic retarders.

Calcium nitrate, CNU, CNN and CNNU accelerate the setting processes marginally. Sodium nitrite does not influence the setting time to any significant extent, whereas carbamide retards the setting periods.

Tables 11–13 give the setting periods of cements containing some anti-freezing admixtures.

Table 11. Setting Time of Cement-Sand Mortar (1:2) Containing Antifreezing Admixtures at +20°C

Admixture		Setting Time (hr-min)			
		Portland Cement		Slag Portland Cement	
Composition	Amount by Mass of Water (%)	Initial	Final	Initial	Final
No additive	—	2-50	6-10	2-57	4-27
SN	8	2-35	4-35	3-58	7-43
	12	2-56	6-16	3-52	7-52
	16	3-18	6-18	4-30	7-45
	20	4-00	6-30	5-22	7-22
SC + CC	6 + 0	3-10	3-40	3-42	5-50
	7 + 3	2-28	3-13	4-02	5-40
	6 + 9	1-45	2-15	3-37	5-00

Table 12. Setting Time of Cement Paste Containing 10% of Potash and Surface-Active Additives at +20°C

Surface-Active Additive Amount, % by		Setting Time of Cement with the Admixture K_2CO_3 (hr-min)	
Type	Mass of Cement	Initial	Final
No additive	—	0-20	0-30
Lignosulfonate	0.5	0-30	2-02
	0.75	0-25	1-53
	1.5	0-45	5-00
	3.0	2-06	7-20

Table 13. Setting Time of Cement-Sand Mortar (1:2) Prepared with Portland Cement Containing Chloride Salt Admixtures and Lignosulfonate

Amount of Lignosulfonate % byMass of Cement	Setting Time (hr:min) of Cement Containing the Admixture NaCl + $CaCl_2$, Percent by Mass of Water (20°C)			
	7+3		6+9	
	Initial	Final	Initial	Final
0	1:45	2:15	0:10	0:22
0.25	6:02	8:00	0:29	3:25
0.50	6:32	8:02	0:30	6:05
0.75	7:17	14:12	0:39	2:20
1.00	8:15	15:21	0:43	2:33

4.9 Heat of Cement Hydration

Hydration of cement carried out at different temperatures indicates that a large amount of heat is produced in the presence of antifreezing admixtures. It is necessary to acquire data on heat effects as they permit adjustments of heat required in winter concreting. The amount of heat released by concrete containing antifreezers is shown in Figs. 6 and 7. The figures refer to results using portland cement of strength 53.2 MPa or high early cement of strength 60 MPa. In Fig. 6, curing of concrete was carried out simulating *thermos* curing, and the results in Fig. 7 were obtained isothermally at −10°C.

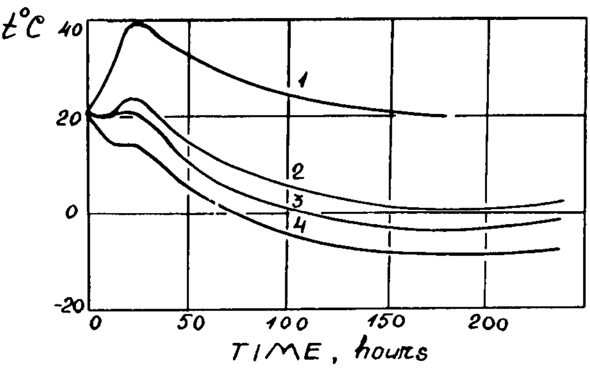

Figure 6. Temperature change in concrete with admixtures. *(1)* without admixtures at 20°C, *(2) (3)* with 6% SN at 0°C and -5°C respectively, and *(4)* with 14% SN at −10°C.

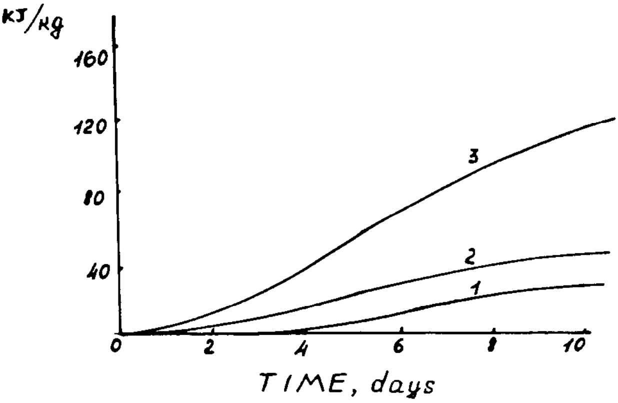

Figure 7. Isothermal heat release at −10°C in concrete containing admixtures. *(1)* 20% SN, *(2)* 6% CC + 14% SC, and *(3)* 20% potash.

The curves in Fig. 6 show the usefulness of combining the application of antifreezers with the thermos method. Cooling of concrete proceeds slowly and its temperature lies close to 0°C for a long period.

As the hydration of cement is accompanied by the release of heat, more ice will melt to form water in the presence of antifreezing admixtures. The amount of heat released depends on the mineralogical composition and surface area of the cement.

4.10 Thermodynamics of Ice Formation in Fresh and Hardened Concrete in the Presence of Antifreezing Admixtures

The action of antifreezing admixtures in fresh concrete and hardened concrete can be treated under three areas as follows. *(a)* As a solution with unset concrete acting as dispersed but discrete solid particles in the mass. *(b)* As a solution existing in a porous body formed from the completely hydrated cement. *(c)* As a solution existing in a partially formed porous body which is in the process of changing with time.

Ice Formation in Concrete Mixes Having a Coagulating Structure. The vapor pressure versus temperature curves for the ice-water transition with and without the presence of salt is shown in Fig. 8. The vapor pressure at any temperature decreases with salt concentration and the freezing point is similarly depressed. For dilute solutions Raoult's law relates the salt concentration to the vapor pressure from which a relationship between the freezing point depression (ΔT_1) and the concentration of salt (C_2) can be derived.

Eq. (1) $$\Delta T_1 = K_{cr} \bullet i \bullet C_2$$

where K_{cr} = Cryoscopy constant; 'i' is a correction coefficient for the lack of complete dissociation of the salt molecules. This equation is not as accurate at high salt concentrations due to incomplete dissociation of the molecules, but corrections may be made by using the appropriate activity coefficients.

Cooling of a normal salt solution will result in the formation of pure ice with a resultant increase in the concentration of the solution; ultimately the concentration of the solution becomes equal to E in Fig. 9 and the solution will freeze at the eutectic point.

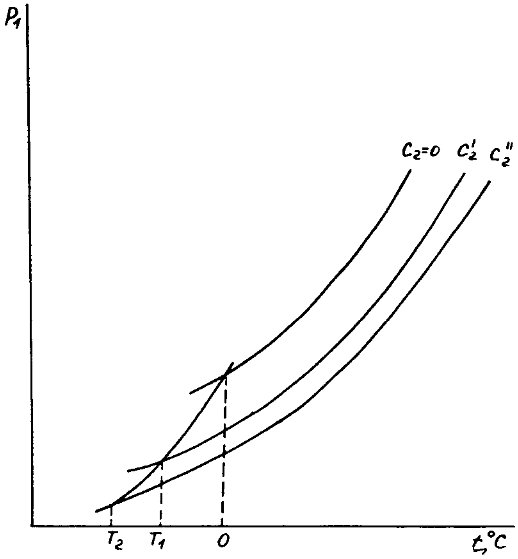

Figure 8. Relationship between vapor pressure (P) and freezing point of water (t, °C).

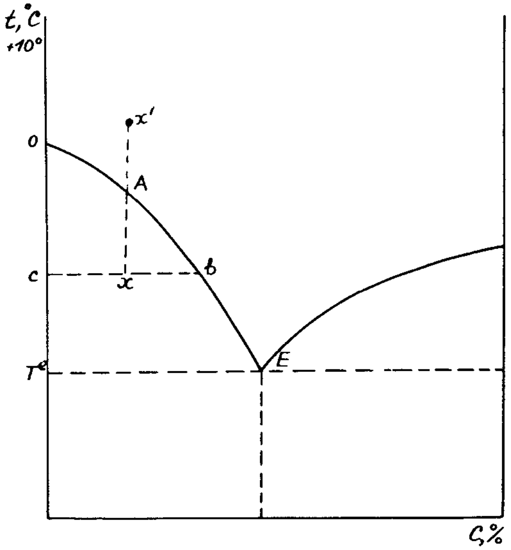

Figure 9. Water-salt equilibrium diagram.

Table 14 gives data on the eutectic points of the most frequently used antifreezing admixtures. As can be seen, the eutectic point varies depending on the type of admixture. Raoult's law however, is independent of the nature of the dissolved substance.

Table 14. Some Data on Antifreezing Admixtures*

Solution Concentration	Density of Solution at 20°C ($\rho \times 10^{-3}$ kg/m^3)	Temperature Coeff Solution Density ($\gamma \times 10^4$)	Freezing Point °C
Sodium Chloride (SC)			
2	1.013	2.4	-1.2
7	1.049	3.3	-4.4
12	1.086	3.9	-8.4
17	1.124	4.6	-13.1
22	1.164	5.1	-19.4
23	1.172	5.2	-21.2
Calcium Chloride (CC)			
2	1.015	2.3	-1.0
7	1.057	2.8	-3.6
12	1.102	3.3	-7.5
17	1.148	3.9	-13.0
22	1.198	4.4	-21.4
27	1.249	4.9	-36.1
31	1.293	5.3	-55.0
Sodium Nitrite (SN)			
2	1.011	2.3	-0.8
8	1.052	3.3	-3.9
14	1.092	4.2	-6.9
20	1.137	5.1	-10.8
26	1.183	6.1	-17.0
28	1.198	6.5	-19.6
Potash (P)			
2	1.016	2.4	-0.7
8	1.072	3.3	-2.8
14	1.129	3.9	-5.4
20	1.190	4.4	-8.9
26	1.254	4.9	-14.1
32	1.321	5.2	-21.5
38	1.390	5.4	-32.5
40	1.414	5.5	-36.5

(Cont'd)

Table 14. (Cont'd)

Solution Concentration	Density of Solution at 20°C (ρ x 10^{-3} kg/m^3)	Temperature Coeff. Solution Density (γ x 10^4)	Freezing Point °C
Calcium Nitrate (CN)			
2	1.014	2.2	-0.6
8	1.055	2.8	-2.3
14	1.116	3.4	-4.6
20	1.154	4.0	-7.6
26	1.220	4.6	-11.5
32	1.279	5.2	-16.1
35	1.311	5.5	-18.5
Urea (U)			
5	1.015	2.4	-1.9
10	1.030	2.7	-3.7
15	1.043	2.9	-5.1
20	1.060	3.2	-6.3
25	1.072	3.5	-7.4
30	1.085	3.8	-8.3
31	1.087	3.8	-8.4
Calcium Nitrate+ Urea (CNU)			
2	1.012	2.2	-0.6
8	1.037	2.7	-2.5
14	1.072	3.1	-4.3
20	1.107	3.6	-6.1
26	1.145	4.1	-7.9
32	1.185	4.6	-9.9
38	1.231	5.0	-12.3
44	1.274	5.5	-16.8
48	1.321	5.8	-21.7
Calcium Nitrite-Calcium Nitrate (CNN)			
2	1.016	2.2	-0.8
8	1.068	2.8	-3.3
14	1.119	3.4	-6.5
20	1.171	4.0	-10.6
26	1.222	4.6	-16.5
32	1.277	5.3	-24.2
35	1.298	5.5	-29.4

(Cont'd)

Table 14. (Cont'd)

Solution Concentration	Density of Solution at 20°C ($\rho \times 10^{-3}$ kg/m^3)	Temperature Coeff. Solution Density ($\gamma \times 10^4$)	Freezing Point °C
Calcium Chloride-Calcium Nitrite-Calcium Nitrate (CCNN)			
2	1.018	2.3	-1.2
8	1.070	2.9	-4.9
14	1.122	3.5	-10.9
20	1.175	4.1	-20.0
26	1.227	4.7	-34.6
30	1.263	5.2	-48.0

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* The last line for each of the chemicals refers to the eutectic point

In practice, the dosage of the antifreezing admixture is chosen such that the pore liquid is partly unfrozen. This is important especially if the salt content is high.

Thermodynamics of Ice Formation in a Capillary Porous Body; Model of Cement Paste. Hardened hydrated cement paste has a large volume of its pores in the small size range (less than 1000 Å). The vapor pressure of a liquid in fine pores above the meniscus (concave) is depressed and is inversely proportional to the radius. The freezing point of the liquid in such capillaries is also depressed (ΔT) and may be related according to the following equation:

Eq. (2) $$\Delta T_2 = \frac{2\sigma V_k T_o}{L_\gamma}$$

where σ and V_k are the interfacial energy and molecular volume of the liquid respectively. $\Delta T_2 = T_o - T_r$ is the difference between the freezing point of water in capillaries (plane surface) and that with a convex surface. L is the latent heat of melting of ice and γ is the capillary radius.

Cement paste has a wide pore size range (1000 to 15 Å) and water will freeze in these pores over a wide range of temperatures (-3 to -50°C). Some strongly adsorbed water does not freeze. The presence of antifreezng admixture in the pore liquid produces a further depression of freezing point in the capillary. This is important for the larger capillaries where ice formation occurs above -10°C. Combining these effects the net freezing point depression will be obtained by adding the two equations stated above.

The majority of antifreezing admixtures are non-surface active substances. The content of these substances in the capillaries is higher than on the capillary wall surface. On the other hand, the opposite effect occurs for the surface active materials. This effect can generally be neglected, but as in the case of carbamide, this effect becomes important. In the following equation when using carbamide the term

$$\frac{1}{RT\delta} \bullet \frac{d\sigma}{dC}$$

cannot be ignored.

Eq. (3) $$\Delta T = K_{cr} \bullet i \bullet C_2 \left(1 \pm \frac{1}{RT\delta} \bullet \frac{d\sigma}{dC}\right)$$

where ΔT = depression of freezing point, δ = coefficient adjusting for the change in concentration of salt adsorbed on the capillary wall, C = concentration of the salt, R = gas constant.

The thermodynamic considerations show that the antifreezing admixtures should be used in the form of electrolytes with or without the surface active materials. The surface active agents should not, however, be used alone.

Ice Formation in Hardened Concrete. In the discussion above, it was assumed that the hydration of cement was completed and that it was chemically inert to water and admixtures, but under actual conditions both assumptions are not valid. Firstly, the hydration of cement involves a systematic redistribution of pores in the paste resulting in the formation of finer pores. It has been shown that almost all antifreezers affect the pore structure of cement paste similarly. Consequently, the freezing point of water in these finer pores will decrease.

Potash is an exception in not promoting the formation of finer pores. It reacts with the aluminate phases and calcium hydroxide, promoting a rapid hardening of the mix. In this system the possible increase in the freezing point of water in the pores is offset by the enrichment of alkali in the pores. This caustic solution has the eutectic point of -78°C. Thus, potash can be used in winter concreting.

In order to understand the basic laws of ice formation in the hardening cement containing antifreezing admixtures, a knowledge of changes, not only in microstructure of concrete but also in the pore solution is necessary.

The silicate reactions consume a large amount of water whereas the formation of double and basic salts results in the consumption of admixtures. The composition of the pore solution and its concentration depend on the relative rates of these reactions and on the composition of the new compounds.

Experiments have shown that, at low temperatures, a certain amount of the antifreezing admixture becomes bound as double and hydroxysalts in the first 3–7 days of hardening.[22] By the 14th day, these reactions are almost completed. Cement hydration will, however, proceed for months. The absolute values of the rates of reaction depend on temperature, concentration terms, type of admixture, water-cement ratio, and cement composition. Strictly speaking in such metastable systems, computations based on classical thermodynamics are not applicable unless the following additional conditions are recognized.

a. A reference point is taken when the formation of double and basic salts is practically completed, i.e., consumption of the admixture by interaction with cement minerals and their products is completed.

b. When the temperature of concrete is between -10 and -20°C, cement hydration proceeds very slowly and, therefore, for short time intervals, it could be assumed that the system is in a quasi-equilibrium state.

With such limitations the thermodynamic approach is possible. This explains that with antifreezers (under isothermal conditions of low hypoeutectic temperatures) the ice formed during hydration should gradually melt. This conclusion was verified by applying several methods such as calorimetric, ultrasonic, and the techniques using attenuation of super high frequency waves.[22]

5.0 MECHANICAL PROPERTIES OF CONCRETE

5.1 Concrete Strength

The effect of most of the antifreezing admixtures on the microstructure of cement paste, pore structure, and zone of contact between the aggregate and cement paste manifests itself as improvements in physical and mechanical characteristics of concrete.

After the concrete mix is placed, the process of cement hydration proceeds over a long time at low temperatures and therefore concrete hardens slowly.

Data given in Table 15 show that antifreezing admixtures such as CCNN, CNU and a mixture of sodium nitrite and calcium chloride increase the compressive, tensile, flexural and impact strengths of concrete compared to the reference specimen. The ratio of tensile to compressive strength is unchanged.

Table 15. Strength of Concrete with Antifreezing Admixtures (28 Days at -20°C + 28 Days of Normal Moisture Curing)

Admixture	Amount of Admixture (% by mass of mixing water)	Compressive Strength (MPa)	Flexural Strength (MPa)	Tensile Strength (MPa)
CCN N	10	38.8	4.3	2.4
	15	35.7	4.4	2.4
CCNNU	10	40.0	4.7	2.65
	15	38.5	4.6	2.6
SN + CC	10	36.0	4.5	2.5
	15	34.2	4,2	2.4
CNU	15	36.0	4.4	2.5
Without admixture	-	36.0	4.3	2.4

It is also observed that even sharp temperature changes from -20 to 30°C, or even down to -50°C and then up to 20°C, do not induce destructive processes once the concrete possesses the necessary critical strength (see Sec. 2.0). This is evident from Fig. 10 which shows that curves of strength gain of test specimens after thawing are parallel to each other and the 28-day strength is higher than that of the reference specimen.

The introduction of antifreezing admixtures in low amounts does not cause any decrease of the tensile and compressive strengths of concrete by freezing at -30 to -35°C (Tables 16 and 17), but if the temperature drops to -50°C, the final strength after concrete has hardened at a temperature above 0°C decreases by 20%.

Data on the traditional application of antifreezing admixtures have permitted tabulating the kinetics of the gain of strength as a function of temperature (Table 18).

In Table 18, the temperature ranges for which the antifreezing admixtures are applicable are also shown. The data in this table serve as a guide for the proper choice of an admixtures and for choosing the shortest period of curing before the structure is exposed to service conditions.

At temperatures not lower than -10°C, these data are also applicable for the kinetics of strength development in concrete containing antifreezing admixtures used in combination with early freezing or the thermos method.

Average results on the duration of hardening of concrete (made with Portland cement and containing antifreezers) for attaining the critical strength, are shown in Table 19.

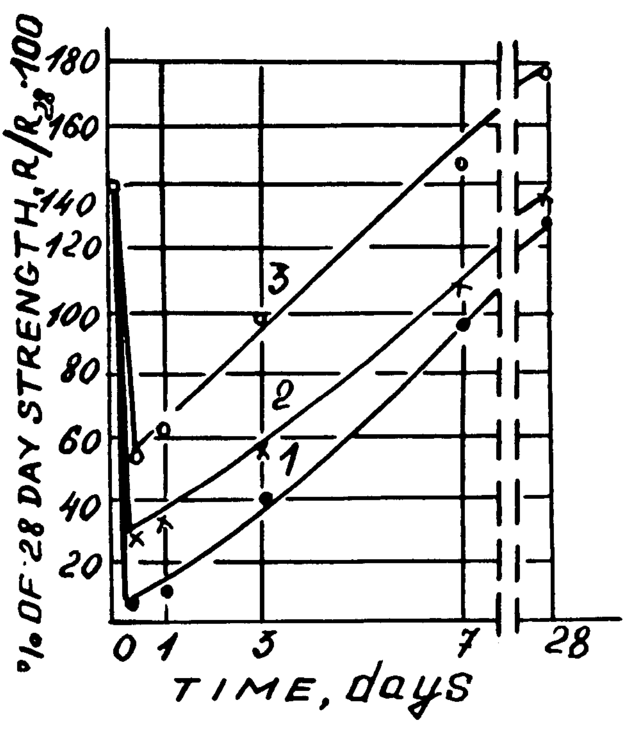

Figure 10. Rate of strength development (percentage of 28 day strength of standard specimen) in concrete with 15% CCNN from –2° to 4°C after 56 days at –30°C. Strength before freezing: *(1)* 0, *(2)* 5 MPa, and *(3)* 11 MPa.

Table 16. Constructional and Technical Characteristics of Concretes Frozen at Early Age. (Regime: 30 days at T = -30°C +28 Days at-10°C + 28 days under normal moisture conditions)

		Characteristics					
Admixture	Amount of Admixture (% by mass of mixing water)	Compressive Strength Before Freezing R_{comp} (MPa)	Compressire Strength R_c (%)	Flexural Strength $R_{f\cdot t}$ (%)	Tensile Strength $R_{t\cdot a}$ (%)	Impact Strength A_{imp} (%)	Wear Resistance W (%)
CCNN	15	0	106	103	~02	101	95
CCNNU	15	0	99	105	104	102	93
SN + CC	15	0	100	98	99	104	89
No additive	—	0	61	63	64	—	—
CCNN	15	5,5	100	138	136	116	90
CCNNU	15	6.5	107	129	130	118	66
SN+CC	15	5.7	105	133	132	113	74
No additive	—	6.2	69	73	60	—	—

1. Concrete was made with hydrophobic portland cement of brand M 400.
2. Reference specimens were hardened for 28 days under normal moisture conditions. R_c = 33.7 MPa, R_{fl} = 3.66 MPa, $R_{t\cdot a}$ = 2.12 MPa, A_{imp} = 12.4-104 J/m³, and W = 93 N/m². The strength of reference specimens is taken as 100%.

Table 17. Strength of Concretes Hardened Under Different Temperature Regimes

		Compresse strength, % of standard strength (38.7 MPa)		
Admixture	Amount of admixture, % by mass of mixing water	14 days at T = -35°C + 14 days at T = -10°C	14 days at -35°C + 28 days under normal moisture conditions of curing	14 days at-35°C + 14 days at -10°C + 28 days under normal moist-curing
CCNN	7	6	68	85
	10	8	118	103
	15	13	135	111
	20	23	120	102
	25	40	112	88
CCNNU	7	4	81	88
	10	8	107	90
	15	8	110	91
	20	13	103	86
	25	23	110	85
SN+CC	7	9	73	67
	10	9	80	75
	15	15	86	89
	20	18	87	79
	25	20	79	77
CNU	7	2	62	67
	10	3	67	70
	15	4	64	73
	20	4	69	80
	25	5	68	76
Potash	25	22	70	69
SN	25	13	55	66
No additive	-	0.5	44	50

Table 18. Gain of Strength of Concretes Made with Portland Cement and Antifreezing Admixtures

Admixture	Temperature of concrete hardening, °C	Compressive strength, % of strength of 28-day normal moist-cured specimens,under hardening at negative temperatures, days			
		7	14	28	90
SN,	-5	30	50	70	90
CNN	~10	20	35	55	70
	-15	10	25	35	50
CC+SC	-5	35	65	80	100
	-10	25	35	45	70
	-15	15	25	35	50
	-20	10	15	20	40
CNU,	-5	35	50	80	100
CN+U,	-10	20	35	60	80
CNN+U	-15	15	25	35	60
	-20	10	20	30	50
CC+CN	-5	40	60	90	105
	-10	25	40	65	90
	-15	20	35	45	70
	-20	15	30	40	60
	-25	10	15	25	40
CCNN,	-5	50	70	95	105
CCNN+U	-10	30	45	70	90
	-15	20	35	45	70
	-20	15	30	40	60
	-25	10	15	25	40
Potash	-5	50	65	75	100
	-10	30	50	70	90
	-15	25	40	65	80
	-20	20	35	55	70
	-25	15	30	55	60

Note: For high brand slag portland cement, the value of concrete strength is determined by multiplying the given value by a factor of 0.8.

Table 19. Curing Period for Attaining Critical Strength for Concretes with Antifreezing Admixtures

Admixture	Temperature of hardening of concrete,	Curing period for concrete brands: days		
	°C	M-200	M-300	M-400
SN, CNN	-5	7	6	4
	-10	12	9	7
	-15	19	14	11
CC+SC	-5	6	5	4
	-10	9	7	5
	-15	19	14	10
	-20	58	45	28
CNU, CNU+U, CNN+U	-5	7	6	4
	-10	12	9	7
	-15	19	14	10
	-20	28	19	14
CNNU, CNNU+U, CC+SN	-5	5	4	3
	-10	9	7	5
	-15	11	9	7
	-20	9	7	5
	-25	14	10	7
Potash	-5	3	2	1
	-10	7	5	4
	-15	9	7	5
	-20	10	8	6
	-25	14	10	7

5.2 Elastic Characteristics of Concrete

The improvement of elastic properties of concrete containing antifreezing admixtures can be seen from data given in Table 20.

The modulus of elasticity is a structure-sensitive characteristic of concrete. This is confirmed by a lower modulus of elasticity in concrete containing potash.

5.3 Bond Between Steel and Concrete

Antifreezing admixtures either do not influence the bond strength between steel and concrete (e.g., potash or $NaNO_2$), or increase it by 10–

20%. The differences in bond strengths are particularly high when concretes (with and without antifreezing admixtures) undergoing freezing at an early age are compared; the bond strength between steel and concrete may decrease by 50–70% because of the destruction process. In the presence of antifreezing admixtures (low dosages in combination with the method of early freezing), this is prevented and high bond strengths are obtained.

Table 20. Elastic and Extensibility Characteristics of Concretes Containing Antifreezing Admixtures

Admixture	Concentration, % by mass of water	Dynamic modulus of elasticity $E \times 10^{-4}$, MPa	Conventional ultimate extensibility $E_{conv} \times 10^5$
No additive	-	4	5.6
CC+SC	10	4.25	5.95
SN	15	4.2	5.75
SN+CC (1:1)	15	4.2	6.2
CN	15	4.3	6.8
CNU	15	4.3	6.5
CNN	15	4.4	6.8
C~NU	15	4.25	7.1
CCNN	15	4.65	6.75
CCNNU	15	4.3	7.1
Potash	15	3.5	4.5

6.0 DURABILITY

Durability of concrete is its ability to preserve service properties during a length of time limited by design considerations.

The effect of antifreezers on durability varies and depends on the type of admixture and other inclusions (such as air-entraining agents, plasticizer, etc.), environmental conditions, chemical, mineralogical and physical properties of the cement and the type of aggregate.

6.1 Carbonation of Concrete

Increase of impermeability and moisture capacity of concrete due to increased microporosity of cement paste and improvement of its zone of contact with the aggregate in the presence of antifreezers lowers the degree of carbonation although the solubility of CO_2 in water increases with the drop in temperature. When potash is used calcium carbonate and calcium hydrocarboaluminate are formed. These salts may clog pores.

Mixtures of antifreezing admixtures with plasticizers or superplasticizers either densify the concrete or lower the rate of carbonation.

Gas forming and air-entraining additives, when used with antifreezers, do not increase carbonation of concrete because of the formation of closed pores.

6.2 Sulfate Resistance

The sulfate resistance of concrete is its ability to resist the action of liquid sulfate media, generally in the form of sodium sulfate.[26] All antifreezing admixtures do not influence the sulfate resistance similarly. Calcium salts reacting with the aluminate phases of cement and cement paste, form the double salts and lower the sulfate resistance, whereas the salts of alkali metals (potash, sodium nitrite) increase this resistance. Thus the effect of antifreezers on sulfate resistance is in many ways different from their effect on frost resistance (Fig. 11).

The low sulfate resistance of concrete with additives containing calcium salts is due to ettringite being the least soluble compound of the complexes such as hydrosulfo-, hydrochloro-, hydronitro- and hydronitrialuminates. In the presence of sulfate ions, substitution reactions occur in the double salts, resulting in the formation of ettringite.[27]

At low dosages of admixture (0–5%) by weight of mixing water, these reactions do not lower the sulfate resistance because of their more significant effect on the structure and strength of concrete. Consequently at a sulfate concentration of about 5×10^{-3} kg/l (in terms of SO_4^{2-}) concrete containing CNN and CCNN admixtures has the same degree of sulfate resistance as the standard specimen. At higher concentrations the sulfate resistance of concrete is decreased.

Surface-active substances, such as plasticizers, superplasticizers, and air-entraining additives contribute to the sulfate resistance of concrete,[26] but in aggressive sulfate media, at a sulfate ion concentration above 5×10^{-3} kg/l they may not be as effective in combination with calcium salts (when used in large dosages). Thus, if a construction or structure is designed to withstand sulfate attack, it would be necessary to limit the application of such additives unless sulfate resistant cement is used.

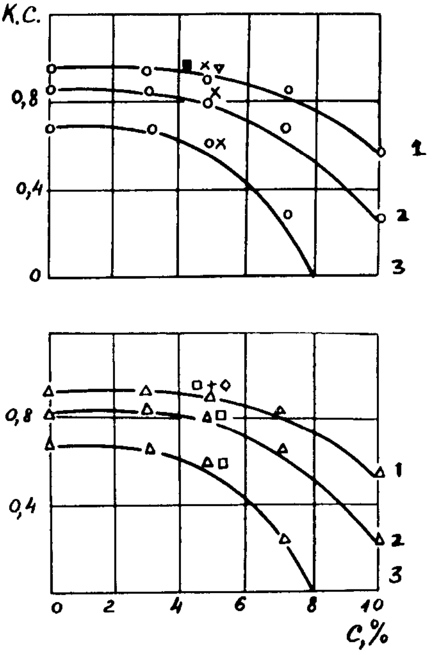

Figure 11. Corrosion resistance (KC) as a function of admixture concentration (C) tested after 1 year in a solution of Na_2SO_4. Sulfate ion concentration (kg/ℓ) = *(1)* 5 x 10^{-3}, *(2)* 10 x 10^{-3}, and *(3)* 30 x 10^{-3}. KC is the ratio of strength of specimen exposed to aggressive solution to that of specimen exposed to water. Admixtures: ▽ = SN, ○ = SN + CC, × = CC, △ = CNN, □ = CNN + CC, + = CNN + CU, ◇ = CNN + CC + U, and ■ = SC + CC.

6.3 Alkali-Aggregate Reactions

The use of antifreezing admixtures containing hydrolyzing salts of sodium and potassium (sodium nitrite or especially potash) is prohibited when alkali-aggregate reaction may occur.

The use of antifreezing admixtures in combination with plasticizing, superplasticizing, or air-entraining admixtures may result in a somewhat reduced rate of alkali attack, but is not enough to allow the limitations imposed by the use of sodium nitrite and potash.

Calcium salts do not cause alkali-aggregate expansion because they react with the amorphous silica to form slightly soluble calcium hydrosilicates that cover the aggregate grains with a protective film.

6.4 Seawater Attack

In sea structures the effects of both chloride and sulfate ions should be considered. The chloride ions may cause corrosion of the reinforcement. The use of inhibitors should be considered for such structures. Of various substances, sodium nitrite may be considered as the best additive because it functions as an inhibitor and also improves the sulfate resistance of concrete. To prevent leaching of this additive it is recommended for use in dense concretes, i.e., concrete made with plasticizing or superplasticizing admixtures.

6.5 Resistance of Concrete to De-Icing Salts

The most widely used de-icing chemicals consist of sodium, calcium and, very rarely, magnesium chloride. Therefore, the discussion on the effect of seawater on concrete can be applied to the de-icers also. The essential differences are the dosage of de-icing agents and the exposure conditions. Roads (on which de-icing salts are applied) carry heavier loads and thus are exposed to different conditions compared to sea structures.

De-icers promote frost and salt attack on concrete and also corrosion of steel reinforcement. Antifreezing admixtures used in road construction should be able to improve the frost- and salt-resistance of concrete and protect the steel reinforcement against corrosion. Under such conditions calcium nitrite, CNN and CNNU should be considered as useful admixtures.

6.6 Corrosion of Steel Reinforcement

With respect to corrosion of steel reinforcement, anti-freezing admixtures may be divided into three groups. The first group of inhibitors causes no corrosion. This group consists of sodium nitrite and calcium nitrite-nitrate mixture and is most effective when the steel reinforcement is protected by a sufficiently thick layer of concrete. The second group is represented by potash, calcium nitrate, urea, and CNU, and the third group, by calcium and sodium chlorides. Figure 12 shows potential-current curves for different admixtures. Chloride-ions are strong depassivators of steel, whereas nitrites passivate steel. Hence, the use of a combination of calcium chloride and sodium or calcium nitrite inhibits sufficiently, the corrosion of reinforcement in dense concrete (curves 7 and 8 in Fig. 12).

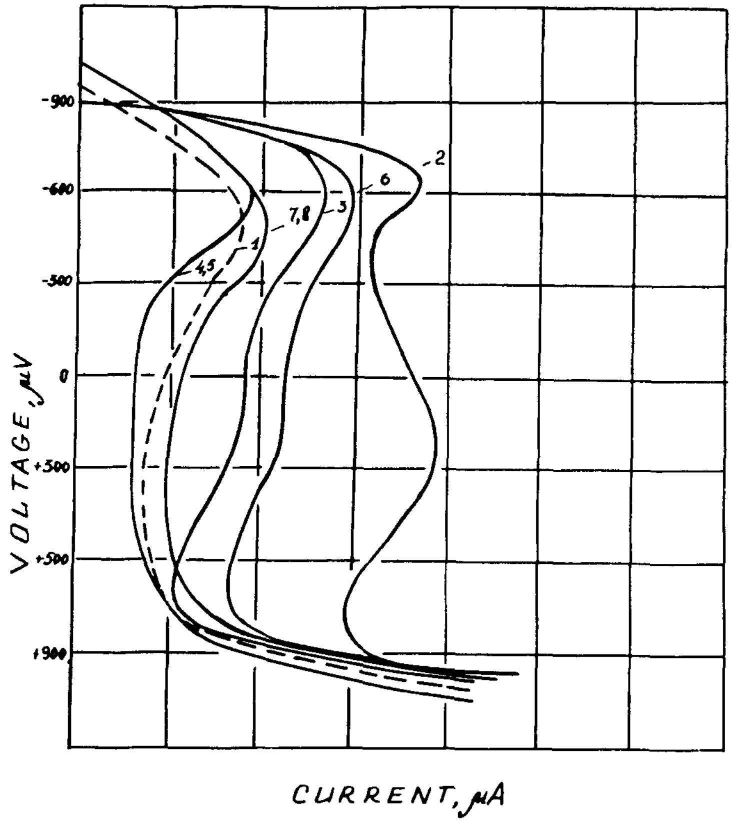

Figure 12. Effect of CCNN and its components on anode polarization of steel in concrete saturated with 3% solution of sodium chloride. *(1)* no admixture, *(2)* calcium chloride, *(3)* calcium nitrate, *(4)* calcium nitrite, *(5)* CNN, *(6)* calcium chloride + calcium nitrate, *(7)* calcium chloride + calcium nitrite, and *(8)* CCNN.

Experimentally it has been established that an adequate protection of the reinforcement against corrosion is ensured with $Ca(NO_2)_2$:$CaCl_2 \geq 0.5$, by weight (Fig. 13).

These data, substantiated by numerous experimental studies, have resulted in the development of a complex additive based on CCNN in which the ratio of calcium nitrite to calcium nitrate is 1 with the same ratio between CNN and calcium chloride. At ratios of $Ca(NO_2)_2$:$CaCl_2 > 0.6$, better protection can be achieved.

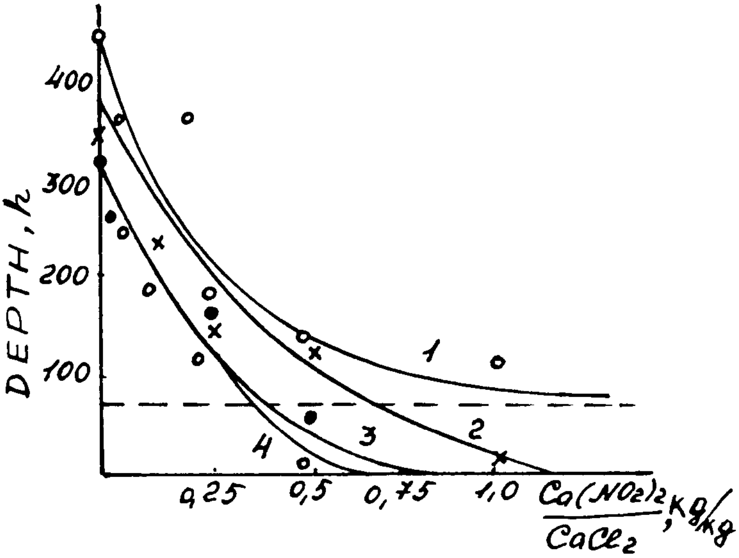

Figure 13. Relationship between the depth of steel corrosion (h) and the ratio $Ca(NO_2)_2$:$CaCl_2$. Concrete protection is 1.5, 5, 20 and 30 mm for *(1)*, *(2)*, *(3)* and *(4)* respectively. The dashed line is for the reference specimen with cover 20 mm thick.

With the use of CCNN and CCNNU admixtures, there is less possibility that the protective effect of calcium nitrite will be lowered. This is because calcium nitrite and calcium chloride have similar diffusion coefficients and activation. Therefore, if the admixture is leached out, the ratio between these two components should remain unchanged. However, since calcium chloride becomes more rapidly and more fully consumed to form calcium hydrochloraluminate than calcium nitrite through hydronitrialuminate, this ratio, changes with time in favor of a higher mount of corrosion inhibitor.[3][16] In addition, $Ca(NO_2)_2$ has a solubility of 15.88% at −5°C and at + 20°C it is 28.71%.[28] Such a high solubility ensures the existence of adequate concentration of nitrite ions in the pore liquid of concrete and is sufficient to protect steel against corrosion under the action of calcium chloride.

When it is required to protect the reinforcement of concrete against corrosion under the action of aggressive chloride and sulfate ions penetrating into the structure from outside, the use of inhibitors is recommended.

Calcium nitrate does not cause corrosion of steel. In addition, as this admixture, like CNU, densifies concrete, there is less possibility for the corrosion of reinforcement, but when heat-hardened steel is used in prestressed concrete, the use of calcium nitrate is prohibited as it intensifies the process of corrosion. Recently, in Russia, new steel reinforcement has been developed (GOST 10844-81) for use in the presence of nitrates.

Potash, due to its high alkalinity, passivates the steel reinforcement.

At the same W/C ratio, the addition of plasticizing, superplasticizing, or air-entraining admixtures to antifreezing admixtures does not influence steel corrosion. By lowering of the W/C ratio, the probability of corrosion is decreased because of the increase in the ohmic resistance and decrease in the accessibility of oxygen to the reinforcement.

6.7 Frost Resistance of Concrete

There are two main hypotheses to explain concrete failure under conditions of cyclic freezing and thawing.[28][30] According to one hypothesis, the main cause of failure is the local tensile stresses caused by the formation of ice. According to the other the failure is caused by the hydraulic pressure of the pore liquid squeezed out by ice. The most unfavorable pores have radius in the range of 30 to 1000 Å. Both these hypotheses consider that the ice formation is the main cause of destruction.

The antifreezing admixtures, calcium salts as well as carbamide, increase the frost and salt resistance of concrete (see Figs. 14 and 15). This is due to the improvement of the pore structure of cement paste and the zone of contact between the paste and the aggregate, as well as by the prevention of ice formation. Besides, the ice separated from highly concentrated solutions possesses a scaly structure and is weaker than that crystallized out from water or highly diluted solutions. Carbamide and other surface active substances are occluded by ice and this impairs the mechanical properties of ice. This explains why concretes with complex admixtures containing urea, CNU, CNNU and CCNNU are characterized by higher frost resistance than those containing calcium nitrate, CNN and CCNN (Table 21).

By the introduction of the above antifreezers, frost resistance of concrete under alternate freezing in water and thawing increases on an average by 1.5–2 times and that under conditions of alternate freezing in 5% sodium (or calcium chloride solution) and thawing 5–7 times (Figs. 14 and 15). The fact that, in concrete containing the above admixtures, frost and salt resistances are substantial, makes it desirable to use such concretes for roads where de-icing chemicals are applied.

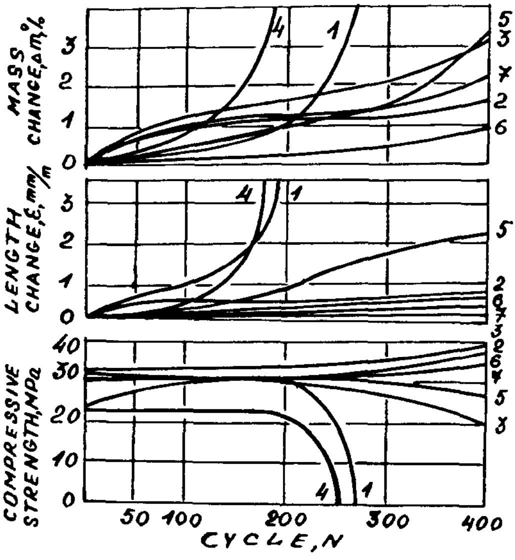

Figure 14. Frost resistance in terms of weight loss, length change and compressive strength. The concrete was cured at –20°C for 28 days and then for 28 days at 20°C. *(1)* no additive, *(2)* 9.7% CC + 6.5% SC, *(3)* 22% SN, *(4)* 22% potash, *(5)* 25% CNU, *(6)* 25% CCNNU, and *(7)* 25% SC + SN (1:1).

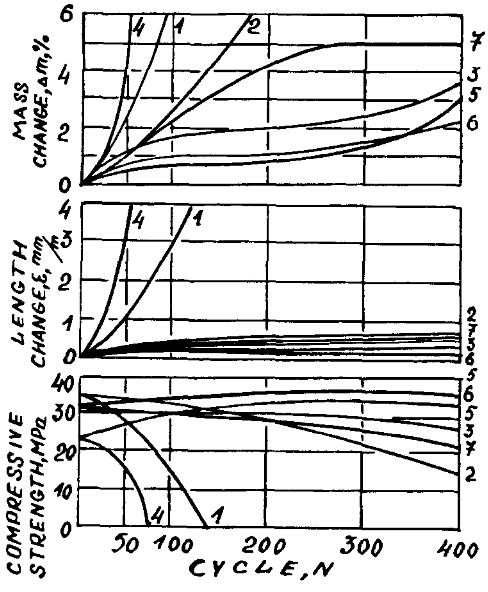

Figure 15. Frost resistance of concrete with additives—alternate freezing at –20°C and thawing in 5% solution of NaCl. (Other details as in Fig. 14.)

Table 21. Frost-Resistance of Cement-Sand-Mortars Containing 15% of Antifreezing Admixtures*

Admixture	Coefficient of Frost Resistance ($K_{fr\text{-}r}$)** After X Cycles X = 50 at -60°C	X = 350 at -20°C	X = 500 at -20°C	X = 750 at -20°C
No additive	0.2	0.78	—	—
Potash***	—	—	—	—
SN	0.24	0.87	0.41	—
CN	0.96	0.94	0.88	0.79
CNU (3:1)	1.40	0.94	0.94	0.89
CNU (1:1)	1.65	0.97	0.95	0.96
CCNN	0.93	0.96	0.82	0.81
CCNNU (3:1)	0.90	1.04	0.97	0.87
CCNNU (1: 1)	1.01	1.02	1.03	1.02

* Composition of specimens: cement-sand 1:3, w/c = 0.55.

** From the change of specimen strength at flexure.

*** Specimens with 15% potash failed after 5 to 10 cycles of freezing and thawing at -60°C and after 100 to 150 cycles at -20°C.

Combined admixtures with antifreezing and air-entraining additives have additional frost and salt resistance. Similarly, concrete with a combination of antifreezing admixtures with plasticizers and superplasticizers which lower the W/C ratio has a very good resistance.

Antifreezing admixtures based on calcium salts show frost resistance not only at -20°C but also at -50 and -60°C. When antifreezing admixtures are used with the method of early freezing, an increase in the frost resistance (compared with that of normal moist-cured standard concrete) is observed (Table 22).

After 1.5 to 2 years of uninterrupted storage of specimens under conditions of complete water saturation, frost resistance of concrete with or without antifreezing admixtures becomes similar. The main cause of the levelling-off of frost resistance under these conditions is a partial washing-out of the admixtures and this must be taken into account in hydrotechnical construction. Unlike the calcium salts, sodium nitrite admixture slightly increases the frost resistance while potash lowers considerably both frost resistance and salt-resistance of concrete (see Table 21). The lowering of concrete durability is caused mainly by the increase of pore size. The use of potash, even with air-entraining or gas-forming admixtures, is not recommended in concrete structures where high frost resistance is required.

Table 22. Porous Structure, Strength and Frost-Resistance at -50°C of Concrete with Antifreezing Admixtures Hardened at Different Regimes*

Type of Cement	% of CCNN by Mass of Mixing Water	Hardening Regime**	Moisture Content (wt %)				Index of Average Size of Pores (λ)	Concrete Strength (MPa) $R_c/R_{fl.t}$	Number of Cycles at T = 50°C	Coefficient of Frost-Resistance	
			Adsorbed Moisture	Moisture in Microcapillaries	Moisture in Macrocapillaries	Water Absorption (vol %)				$K_{fr.at\ c.}$	$K_{fr.at\ f.t}$
Average-aluminate portland-cement	0	III	1.38	1.23	5.57	15.3	2.36	28.4/4.2	18	0.78	0.52
	6	I	1.26	2.90	3.26	13.8	1.09	25.5/4.5	70	0.85	0.60
	6	II	1.79	1.42	4.37	13.0	1.21	28.6/5.0	50	0.82	0.30
Low-aluminate portland-cement	0	III	1.12	1.32	5.30	14.9	2.23	20.3/3.85	18	0.82	0.51
	10	I	1.57	3.36	2.60	13.4	1.69	28.0/4.25	70	0.84	0.41
	10	II	1.92	1.93	3.49	12.2	1.72	31.3/4.1	50	0.77	0.29

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* Concrete composition: cement:sand:crushed stone 1:2.3:3.1; w/c = 0.65.

** Hardening regime:

I. 21 days at -20°C + 14 days at -10°C + 14 days at +5°C + 28 days at +20°C.

II. 21 days at -20°C + 28 days at +20°C.

III. 28 days at +20°C.

6.8 Efflorescence

Some of the admixtures, such as accelerators of setting and hardening (sodium salts), tend to form efflorescence as a result of the migration of the solution to the surface and subsequent evaporation.

When antifreezing admixtures are used in large dosages efflorescence appears mainly by the use of sodium nitrite, sodium chloride and complex inorganic antifreezing admixtures. When these admixtures are used, it is advisable to mix them with lignosulfonate for reducing the efflorescence.

The formation of efflorescence may also be influenced by the changing conditions of heat and mass transfer, particularly by covering the surface of concrete with mats, polymer films, etc.

When aesthetic view is important, it is recommended that the above measures be combined by using calcium and potassium salts as antifreezing admixtures.

7.0 NEW DEVELOPMENTS

In the last ten years, further progress in research and the development of antifreezing admixtures has taken place.

Several novel admixture formulations include superplasticizers such as sulfonated naphthalene formaldehyde (SNF) and sulfonated melamine formaldehyde (SMF). The main advantage with such admixtures is that they are capable of reducing water requirements significantly and consequently lower amounts of antifreezing admixtures can be used. The quality of concrete is also improved.[31]-[34] In addition to superplasticizers, other admixtures have also been investigated. Examples are plasticizers, air-entraining agents, and the alkali by-product from the manufacture of caprolactam (ChSPK) or its modification (ChSPK-M). The active component in ChSPK and ChSPK-M is the salt of adipic acid.

The data in Table 23 show that such complexes in concrete yield slightly lower strengths than a combination of superplasticizer and an antifreezing agent, but they are more economical to use.

There has been an increasing interest in investigations on the possibility of using such antifreezing admixtures as sodium acetate (SA)[34][35] and sodium formate (SF).[35] A study of the formulations containing SA + SNF has indicated that in small amounts, they are as effective as a mixture of SN + SNF at -15°C (Table 24).[34] Concrete containing SA + SNF also has good frost resistance.

Table 23. Effect of Complex Antifreezing Admixtures on Strength Development in Concrete at -5°C[35]

Admixtures	Strength, % of design value (Days)			
	7	14	28	90
SN + 0.7% SNF	80	90	110	130
SN + 3% ChPK	60	75	90	110
SN + 3% ChSPK-M	70	80	100	120
CN + 0.7% SNF	60	80	90	100
CN + 0.3% Ch SPK	35	50	75	100
CN + 3% Ch SPK-M	40	60	80	100

CN= Calcium Nitrate; SN=Sodium Nitrite; Amount of SN and CN is 6% by weight of mixing water

Table 24. Strength Development in Concrete with Complex Antifreezing Admixtures[34]

Admixtures	Temperature(°C)	Strength (% of design value) at Days			
		7	14	28	90
SN + 0.4% SNF	-5	70	80	90	110
	-10	40	60	70	100
	-15	20	30	50	90
SA + 0.4% SNF	-5	60	70	80	100
	-10	30	50	60	70
	-15	10	20	30	50

Admixture combinations of various chemicals and different dosage proportions have been investigated. For example, effective antifreezing systems have been suggested in which the SA:AF ratio is 1:3 to 3:1 by weight.[35] Other formulations containing a mixture of calcium nitrite and sodium sulfate[36][37][40] and SN+SS[39] have also shown to possess effective properties as antifreezing admixtures. It has also been shown that a mixture of SA + SF is as effective an admixture as the individual SA or SF compounds and also more economical to use. The compressive strength of concrete at 28 days (-10°C) containing a mixture of sodium calcium nitrite or sodium nitrite+potash (SN + P) is higher than that containing only calcium nitrite,[36] but at -5°C, the compressive strength of concrete with calcium nitrite is higher than that with the binary admixture formulation (Fig. 16). The higher strengths obtained with admixtures containing sodium sulfate can be attributed to its accelerating action because its eutectic temperature is only -4°C.

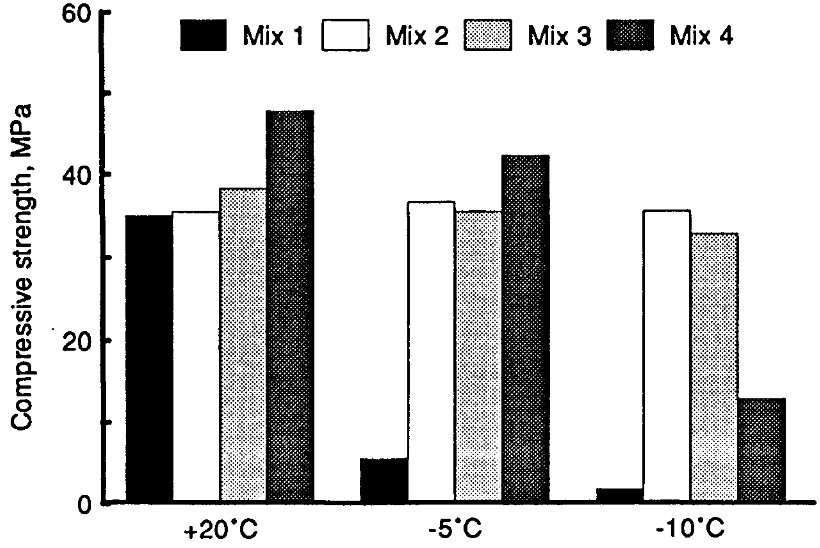

Figure 16. Compressive strength of concrete at 28 days. (Salts %'s are based on the mixing water: w/c = 0.39). *Mix 1:* Without admixtures; *Mix 2:* 15% sodium nitrite + 5% calcium nitrite; *Mix 3:* 15% sodium nitrite + 0.15% potash; *Mix 4:* 15% calcium nitrite.

Good mechanical properties were also obtained at -5°C using admixture combinations of SN and calcium nitrite (by mass of mixing water) in proportions of 3:1.[36]

In Russia, a new technology involving intense mechanochemical processing of cements or their mixtures with mineral admixtures in the presence of powdered superplasticizers has been developed. As a result, the so-called l*ow water requirement binders (LWRB)* have been produced.[41] The difference between LWRB and other binders is that very low water cement ratios of the order of 0.15–0.18 are possible with LWRB. Consequently, very high strengths are obtained with LWRB. Table 25 illustrates the effectiveness of LWRB.

Table 25. The Strength Development in Concretes Containing LWRB and Mineral Admixtures[42]

Binders	Mineral Admixture	W/S Ratio	Strength at 28 Days (MPa)	
			Flexural	Compressive
Portland Cement	————	0.27	5.4	41.7
Portland Cement with 0.7% SNF	————	0.23	6.7	53.4
LWRB, 100%	————	0.15	10.2	87.8
LWRB, 50%	Sand	0.16	7.0	61.0
LWRB, 50%	Slag	0.17	6.7	59.3
LWRB , 30%	Fly Ash	0.18	6.8	53.1

LWRB with SN as an antifreezing admixture has been successfully applied for winter concreting operations at temperatures below -10°C. The amount of SN used was twice as low as normally used with other formulations.[43] It has also been suggested that in some instances, LWRB may be used without other additives, at a temperature range of 0°C to -10°C.[43] The concrete made with LWRB has also a high frost resistance.[44] Some work on these lines was completed at an American Laboratory in Illinois.[45]

A new type of building material incorporating alinite has been developed. The main component of this additive is a chlorine-containing compound of $3CaO\bullet SiO_2$. During the process of hydrolysis and hydration of alinite cement in a liquid phase, calcium chloride offers a very low eutectic temperature of -55°C (Table 14). As a result, the freezing temperature of water is lowered significantly. Alinite cement has been successfully used in road building where a large monolithic concrete was fabricated without reinforcement.[46]

If alinite cement has to be used in reinforced steel concrete with an antifreezing additive, corrosion inhibitors such as SN, CNN or calcium nitrite have to be incorporated in the formulation. However, the amounts of these admixtures could be only about 50% of what would normally be used in other formulations. In such systems, in the initial stages, the liquid phase contains the nitrite ions whereas the chloride ions enter the liquid phase gradually. As a result, in the early stages of hardening of concrete, the ratio of nitrite to chloride is high enough to promote passivation of steel reinforcement. Because of the presence of chloride, the alinite cement is more active by 30% than portland cement at 5°C and by 15–20% at a temperature of -5°C (Fig. 17).[46] This cement is not recommended for use in prestressed concrete.

8.0 STANDARDS AND SPECIFICATIONS

Standards and specifications on antifreezing admixtures used now in Russia are given in Table 26.

Table 26. Standards and Specifications on Antifreezing Admixtures (Russia)

Admixtures	Title and Number
Calcium chloride	Calcium chloride, GOST 450-77 Minchimprom
Clacium nitrate	Technical calcium saltpeter TU 6-03-367-79, Minchimprom
Anhydrous potassium carbonate (potash)	Potash, GOST 10690-73
Sodium chloride	Sodium chloride, GOST 13830-68 TU 6-01-540-70, Minchimprom TU 6-13-5-75, Minchimprom
Sodium nitrite	Sodium nitrite, GOST 19906-74 TU 3810274-79, Minneftechimprom
Urea (carbamide)	Urea (carbamide), GOST 2081-75 GOST 52206-74
Calcium nitrite-nitrate	TU 6-03-704-74, Minchimprom
Calcium chloride-nitrite-nitrate	TU 6-18-194-76, Minchimprom
Complex salt of calcium nitrate and urea (CNU)	TU 6-03-349-73, Minchimprom

Conditions of supply of these additives are given in Sec. 2.2. Compliance with standards and Specifications is ensured by the supplier and as a rule is not controlled by the user. Considering the high stability of composition and properties of antifreezing admixtures no chemical analysis is made in the course of storage and transportation.

The dosage can be regulated by knowing the concentration of antifreezing admixtures delivered as aqueous solutions (Table 14). Table 14 contains data on the freezing point of water in the aqueous solution of the admixtures. This information assists in finding out whether there is any need for warming the tanks during transportation or storage.

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12

High-Volume Fly Ash and Slag Concrete

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1.0 HIGH-VOLUME FLY ASH CONCRETE

1.1 Introduction

Low-calcium fly ash (ASTM Class F) has been used in concrete as replacement for portland cement for the construction of mass gravity dams since 1935.[1] The primary aim in the use of fly ash was, and has been to reduce the heat of hydration. The low early-age strengths obtained by the use of fly ash are not critical as the compressive strength requirements are generally of the order of 20 MPa at 90 days or one year. In earlier years, the percentage of fly ash used was limited to about 30 per cent. In 1965, Mather[2] reported an investigation in which he studied the effects of 60% solid volume replacement of cement with fly ash. For water-to-(cement + fly ash) ratio (W/C+F) of 0.50 and 0.80, he reported three-day strengths of 4 and 1.5 MPa, respectively. In recent years, large volumes of fly ash have been incorporated into the construction of roller-compacted concretes, and the low-early age strengths are not of concern.[3]

In 1985, Malhotra and others initiated studies on structural concrete incorporating high volumes (> 50%) of low-calcium fly ash. The purpose of this research was to develop concrete with adequate early-age strength and workability, low temperature rise and high later-age strength. This was successfully achieved by using a higher-than-normal dosage of superplasticizer.[4]-[19]

This chapter summarizes the results of major investigations dealing with the development of high-volume fly ash concrete, and discusses its applications and limitations.

1.2 Mechanism of Hydration

Feldman et al.[4] and Berry et al.[5] have performed investigations to explain the mechanisms of development of the physical and mechanical properties and hydration reactions in high-volume fly ash cement pastes and mortars. ASTM Type I cement and ASTM Class F fly ash were used in these investigations. Feldman et al. performed investigations on fly ash/ cement pastes at W/C+F of 0.30 and 0.35, and tested several hundred specimens (50-mm cubes, 0.9 x 31-mm discs, and 31.8 x 69.9-mm diameter cylinders) involving compressive strength, modulus of elasticity, pore size distribution, total porosity, and thermographic analyses. The following explanations were offered for the high-early strength of the high-volume fly ash/cement paste.

1a. The blended pastes at early ages have high effective water-to-cement ratio, allowing greater degree of hydration of the cement.

1b. The fly ash commences reaction with the $Ca(OH)_2$ between 3 and 7 days.

1c. Cement matrix and residual unreacted fly ash form a good mechanical bond.

1d. The formation of a relatively homogeneous hydrate product with low $Ca(OH)_2$ content or the formation of low C/S ratio CSH produces a stronger body.

2. The volume of the pores >0.9 μm of mixture containing high volumes of fly ash after 7 days of hydration is the same as the volume of pores of control mixture, also after 7 days of hydration. This suggests that durability properties may be adequate (Figs. 1 and 2).[4]

3. Considerable amounts of $Ca(OH)_2$ and fly ash remain unreacted in all the fly ash mixtures after 91 days of hydration (Figs. 3 and 4).[4]

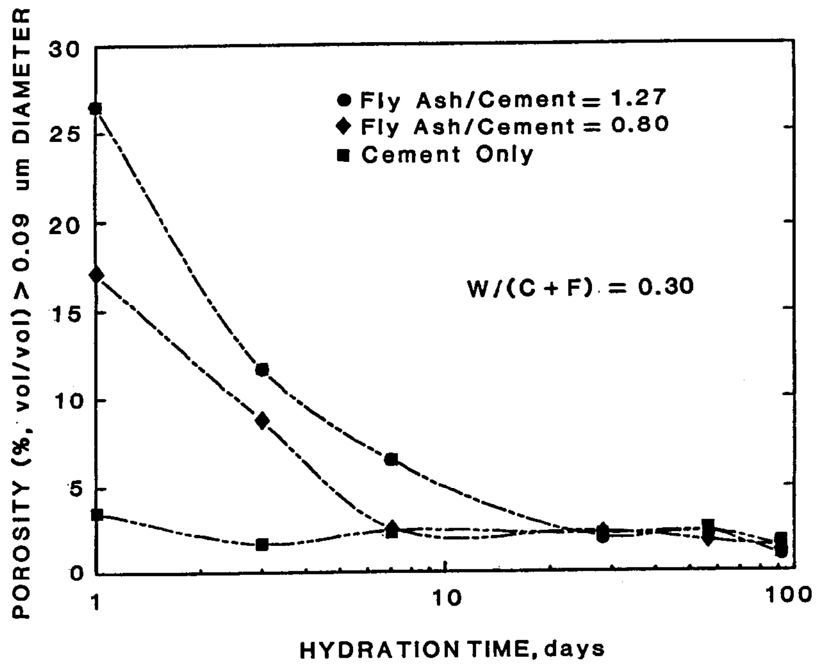

Figure 1. Volume of pores (>0.09 μm dia) versus hydration times for pastes with water-to-cementitious material ratio of 0.30.

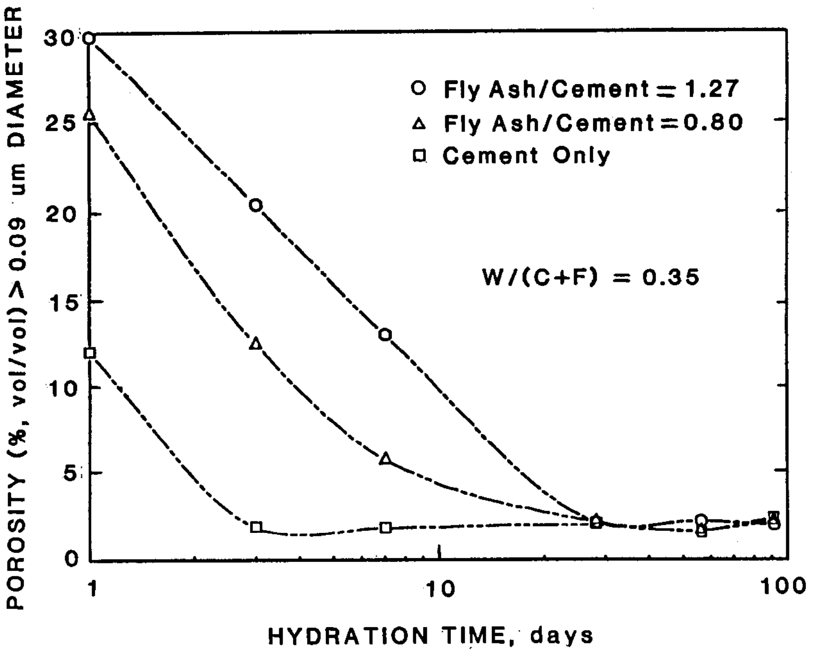

Figure 2. Volume of pores (>0.09 μm dia) versus hydration times for pastes with water-to-cementitious material ratio of 0.35.

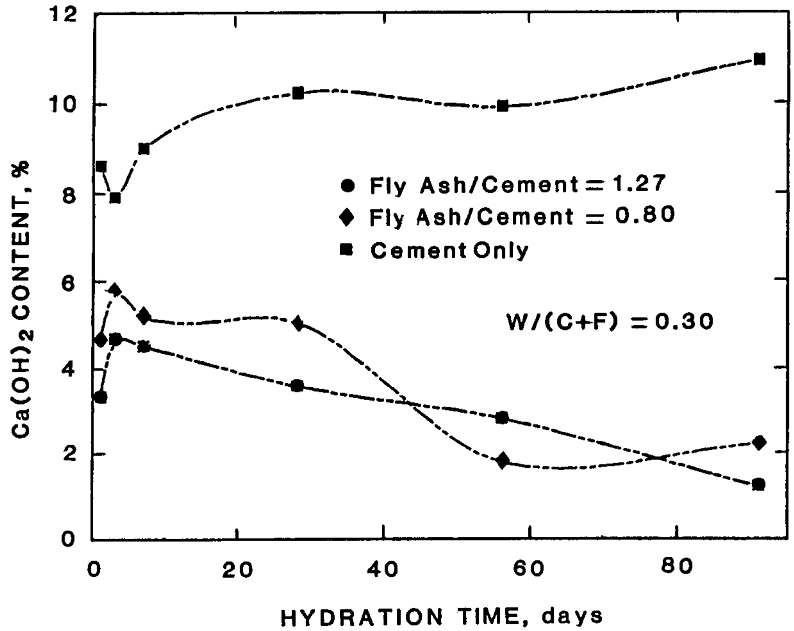

Figure 3. Calcium hydroxide content versus hydration times for pastes with water-to-cementitious material ratio of 0.30.

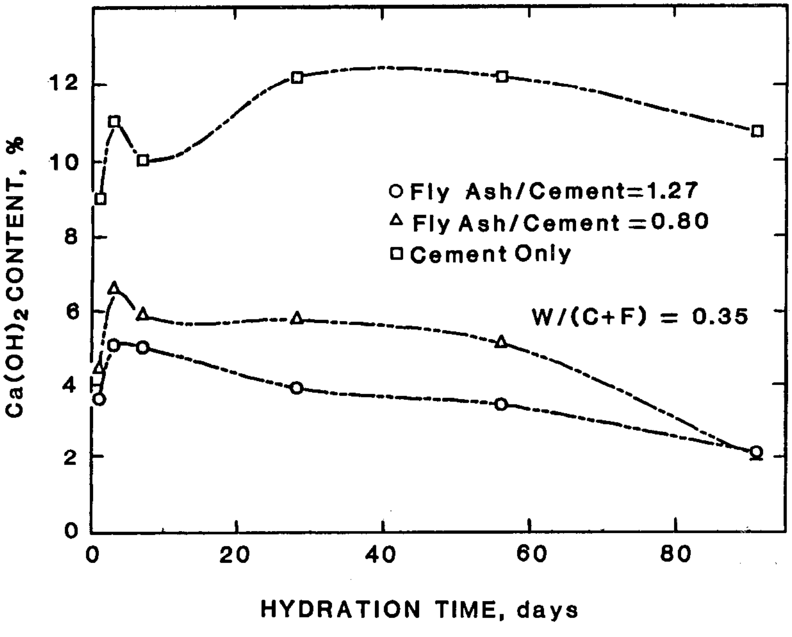

Figure 4. Calcium hydroxide content versus hydration times for pastes with water-to-cementitious material of 0.35.

Investigations performed by Berry et al.[5] were complementary to those performed by Feldman et al. In their studies, Berry et al. investigated the mechanisms of hydration in high-volume fly ash/portland cement binder materials at curing ages from 2 to 365 days. Two series of superplasticized mortars and pastes, one made with portland cement only, and the other with a mixture of 42% portland cement and 58% fly ash by mass, were prepared at a water-to-cementitious material ratio of 0.30. Test specimens at the ages of 2, 5, 10 hours and 1, 3, 7, 14, 28, 56, 91, and 365 days were characterized physically and tested for compressive strength (mortars only) and pore volume. Morphology, solid phase composition, degree of hydration, calcium hydroxide, and pore fluid composition by high-pressure extraction were determined. The following conclusions were drawn:

Overall, in the high-volume fly ash system, physical and chemical factors combine at all ages to densify and bind the paste. In the early stages, the physical effect of space filling and the chemical contribution of the formation of ettringite or related sulfoaluminate production are important factors in strength development. In the longer term, hydration reactions dominate as silico-aluminate binders are generated by reactions involving fly ash. The following observations indicate that chemical mechanisms are involved in late-age strength development in the portland cement-fly ash paste:

i. Levels of bound water substantially in excess of those consistent with the hydration of portland cement are present in the fly ash paste at ages beyond 28 days. This is taken to indicate the formation of silanol groups in the fly ash glass components.

ii. The pore water solutions at curing ages beyond 1 day have high concentrations of sodium, potassium and hydroxyl ions. These conditions are ideally suited to hydrolytic attack on fly ash glasses to produce silanol and related species.

iii. There is considerable evidence for a dynamic mass transfer of Na and K between solid and solution phases. This would be consistent with ion-exchange mechanisms occurring at silanol and siloxane sites in partly hydrolyzed fly ash glasses, or in gels precipitated from siloxane oligomers.

It is suggested that a mechanism similar to the alkali-activation of alumino-silicates originally proposed by Purdon in 1940 is active in the fly ash pastes with the pore water acting as a vehicle for transfer of alkali ions from cement or fly ash into the fly ash glasses. Many glass types are known to be hydrolyzed by strongly alkaline solutions with the formation of hydroxylated polymeric gels containing silanol, ionic Si-O^-...Na^+, or Al-OH groups. Similar reaction products have been found in previous work where fly ash was subjected to acidic hydrolysis.

Though the early attack on the fly ash glasses may derive from pore solutions of high Na^+ and K^+ contents, it is probable that exchange with Ca^{2+} ions may subsequently proceed with the precipitation of C-S-H gel-like materials. These secondary processes may be responsible for the apparent decline in bound water content and the indicated gel-shrinkage responsible for the increase in pore volume at late ages.

While this investigation has indicated the importance of one or more chemical mechanisms in the action of fly ash in portland cement systems, it has also raised many questions about the role of alkali ions in the pozzolanic process. Further work is needed to elucidate the complex reaction sequences and processes that are undoubtedly involved.

1.3 Mixture Proportions

Like normal portland cement concrete, the mixture proportions of high-volume fly ash concrete will depend upon the strength level required. In general, the cement content varies from 100 to 180 kg/m^3 with W/C+F ranging from about 0.30 to 0.40. The water and fly ash contents are kept at about 115 and 220 kg/m^3, respectively, and slumps in excess of 150 mm are achieved with high dosages of superplasticizers. In many studies, the maximum size of coarse aggregate has been kept at 19 mm, but high-volume fly ash concretes have been made using 25 and 39 mm maximum size aggregate. The high percentage of fly ash in the concrete mixture does not pose any serious problems for the entrainment of 5 to 6 per cent air in concrete except that large dosages of the air-entraining admixtures are required. However, this has no adverse effect on the properties of fresh and hardened concrete.[6] Nevertheless, exploratory investigations should be performed to ensure that air-entraining admixtures used are compatible with the type of cement and fly ash incorporated into the concrete mixture. A typical mixture proportion for the high-volume fly ash concrete is shown below:

	Batch Quantities
ASTM Type I Cement:	150 kg/m^3
ASTM Class F fly ash:	210 kg/m^3
Water:	115 kg/m^3
Coarse aggregate (19-mm max):	1275 kg/m^3
Fine aggregate:	620 kg/m^3
Air-entraining admixture:	720 mL/m^3
Superplasticizer:	4.0 L/m^3

The physical properties and chemical analysis of some of the fly ashes used are given in Table 1.

Table 1. Physical Properties and Chemical Analysis of Various Fly Ashes Used in High-Volume Fly Ash Concrete

	Fly Ash A	Fly Ash B	Fly Ash C
Physical Properties			
Fineness - passing 45 µm, %	78.8	82.7	80.6
- Blaine, m^2/kg	--	289	326
Specific Gravity	2.38	2.53	2.05
Chemical Analysis			
Insoluble residue	--	--	--
Silicon dioxide (SiO_2)	45.1	47.1	55.6
Aluminum oxide (Al_2O_3)	22.2	23.0	23.1
Ferric oxide (Fe_2O_3)	15.7	20.4	3.48
Calcium oxide (CaO), total	3.77	1.21	12.3
Magnesium oxide (MgO)	0.91	1.17	1.21
Sulphur trioxide (SO_3)	1.40	0.67	0.30
Sodium oxide (Na_2O)	0.58	0.54	1.67
Potassium oxide (K_2O)	1.52	3.16	0.50
Loss on ignition	0.32	2.88	0.29

1.4 Properties of Fresh Concrete

Time of Setting. Data have been published on the initial and final times of set of high-volume fly ash concrete.[11] In these investigations, the times of set were determined in accordance with ASTM C 403, at 23 ± 1.7°C and 50% relative humidity; the test results show that the initial times of set of 7½ hours are comparable to those of the control concrete, whereas the final times of set were retarded by about 3 hours when compared to that of the control. Other investigations have shown that undue delays in setting could occur for high-volume fly ash concrete made with certain fly ashes.[14] These delays appear to be related to the problem of compatibility between the cementitious materials and the very high dosages of the superplasticizers. The set-retardation, though not significant in general, may pose some scheduling problems in winter construction; on the other hand, the delayed set can be of benefit during summer months. Some typical test data are shown in Table 2.[11]

Table 2. Properties of Fresh Concrete

Mixture Series	Batch No.	Temperature, °C	Slump, mm	Unit Weight, kg/m^3	Air Content, %	Setting Time h:min.	
						Initial	Final
A(Control)	1	22	90	2375	5.9	7:20	8:40
	2	22	125	2410	4.9		
	3	23	90	2400	5.6		
	4	23	90	2410	5.0		
B(Fly Ash L)	1	24	175	2430	4.8	7:30	11:30
	2	21	200	2410	5.0		
	3	21	200	2420	4.7		
	4	21	200	2395	5.2		
	5	22	225	2375	5.2		
	6	23	200	2415	4.0		
	7	24	200	2400	4.6		
	8	25	175	2365	5.6		
	9	22	175	2410	3.8		
C(Fly Ash S)	1	25	175	2340	4.9	8:40	11:40
	2	25	150	2350	4.9		
	3	26	200	2345	4.6		
	4	24	190	2365	4.4		
	5	25	130	2420	3.7		
	6	23	200	2330	4.9		
	7	23	150	2340	4.5		

Bleeding. Bleeding tests performed on high-volume fly ash concrete have shown that this concrete bleeds very little according to the test performed (ASTM C 232). This is due to the very low water content (≈115 kg/m^3) used in this type of concrete.[11] This would necessitate additional curing in hot weather to avoid plastic shrinkage cracks.

Entrainment of Air in Fresh Concrete. No difficulty has been encountered in the entrainment of air in high-volume fly ash concrete, though the dosage required is considerably more than that for portland cement concrete without fly ash.[11][14] However, the fly ashes used in the high-volume fly ash concrete systems have relatively low carbon content. It may be difficult to entrain high percentages of air in the above system if the fly ash has carbon content >6%, but the judicious selection of an air-entraining admixture can overcome this problem.[14]

Density of Fresh Concrete. The density of high-volume fly ash concrete is of the order of 2400 kg/m^3, and is comparable with the density of portland cement concrete without fly ash. Considering that the specific gravity of fly ash is generally lower than that of portland cement (2.6 vs 3.1), the density of high-volume fly ash concrete is considered high, and this is due to the reduced water content due to the use of superplasticizers.

Dosage Requirement of Superplasticizers. Because of the very low water-to-cementitious material ratio (≈0.30) of the high-volume fly ash concrete, the use of superplasticizers becomes mandatory. The dosage required will depend upon the slump to be achieved; for flowing concrete, the dosage is of the order of 1.5 per cent of the total cementitious material (≈5 kg/m^3). There is also a question of compatibility between the superplasticizers and portland cements in the presence of fly ashes. Exploratory investigations should always be performed to ensure that there is no undue delay in the setting time of concrete when using the high-volume fly ash concrete system.[11][14]

1.5 Properties of Hardened Concrete

Temperature Rise. Because of the very low cement content, the temperature rise in the high-volume fly ash concrete during the first few days after placement is very low. For example, the peak temperature measured at mid-depth of a high volume fly ash concrete block (1.5 x 1.5 x 1.5 m) at 2 days was 31.3°C when the ambient and placing temperatures were 24° and 12°C, respectively.[12] Figure 5 shows a comparison of computed and measured temperature distributions at mid-depth of the block. In another instance, in a concrete block measuring 9 x 7 x 3 m, the peak temperature of 37.5°C was reached after 7 days, when the placing and the ambient temperatures were 12°C and 24°C, respectively.[12] Figure 6 shows a comparison of the measured and completed temperature variations with time of the centre of the block. In another research project, the maximum temperature of 54°C was reached at the mid-height of a large high-volume fly ash concrete monolith, 2.5 x 4.0 x 5.0 meter in size, after 7 days of placement. The ambient and placing temperatures were 22 and 21°C, respectively.[17] Thus, the high-volume fly ash concrete is ideally suited for the construction of massive structures such as concrete dams; furthermore, the placement of concrete can be done in one continuous lift rather than in 1.5 or 2.5 m lifts as in the current practice. This can result in substantial savings in construction costs.

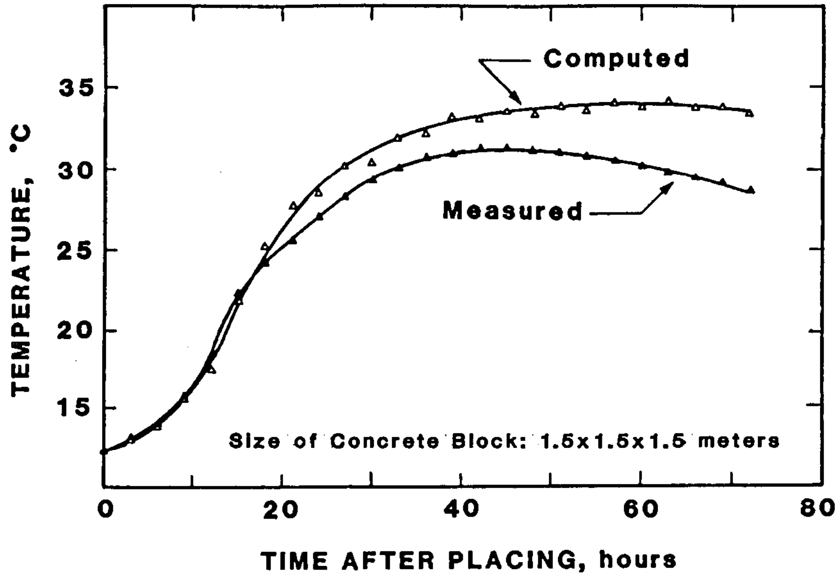

Figure 5. Computed and measured temperature with time at mid-height of 1.5 x 1.5 x 1.5-m concrete block.

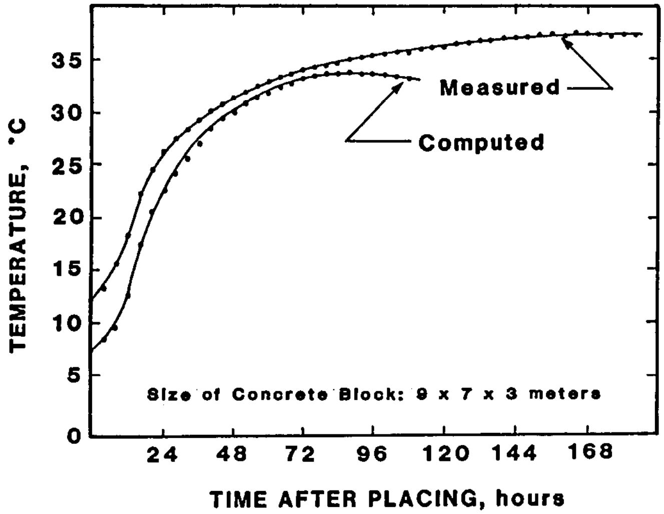

Figure 6. Computed and measured temperature with time at mid-depth of 9 x 7 x 3-m concrete block.

Strength Properties. The high-volume fly ash concrete exhibits adequate strength development characteristics both at early and later ages. For example, the one-day compressive strength of high-volume fly ash concrete can vary from 5 to 9 MPa, depending upon the type of cement. These strength values are more than adequate for formwork removal at normal temperatures, and are comparable to the strength developed by portland cement concrete with about 250 kg/m^3 of cement. The later-age compressive strength, in some instances, has been shown to reach about 60 MPa at one year. The 28-day flexural and splitting-tensile strengths of the high-volume fly ash concrete are about 15 and 10 per cent of the corresponding 28-day compressive strength, and are comparable to the values for the normal portland cement concrete. Figure 7 shows typical compressive strength development in a high-volume fly ash concrete.[14]

The compressive strength about 8 MPa or lower at one day may not be adequate for early form removal especially in winter concreting. However, this can be achieved by the use of ASTM Type III, "High-Early Strength Cement." By the use of this cement, compressive strengths of the order of 15 MPa at one day can be achieved.[8] In Canada and the USA, a number of ready-mixed concrete producers routinely use this cement for high-rise projects, and the premium for ASTM Type III cement as compared with ASTM Type I cement is only marginal. It is known that several cement companies, both in Canada and the USA, market ASTM Type I cements which meet the strength requirements of ASTM Type III cements. Figure 8 shows typical compressive strength development data for high-volume fly ash concrete made with ASTM Type I and Type III cements.

The compressive strength development of air-cured high-volume fly ash concrete preceded by 7 days of initial moist curing, as compared with the continuously moist-cured specimens, follows the same trend as the control concrete, i.e., the strength of the former concrete (air cured) is somewhat lower than the latter concrete (moist cured) Fig. 9.[12]

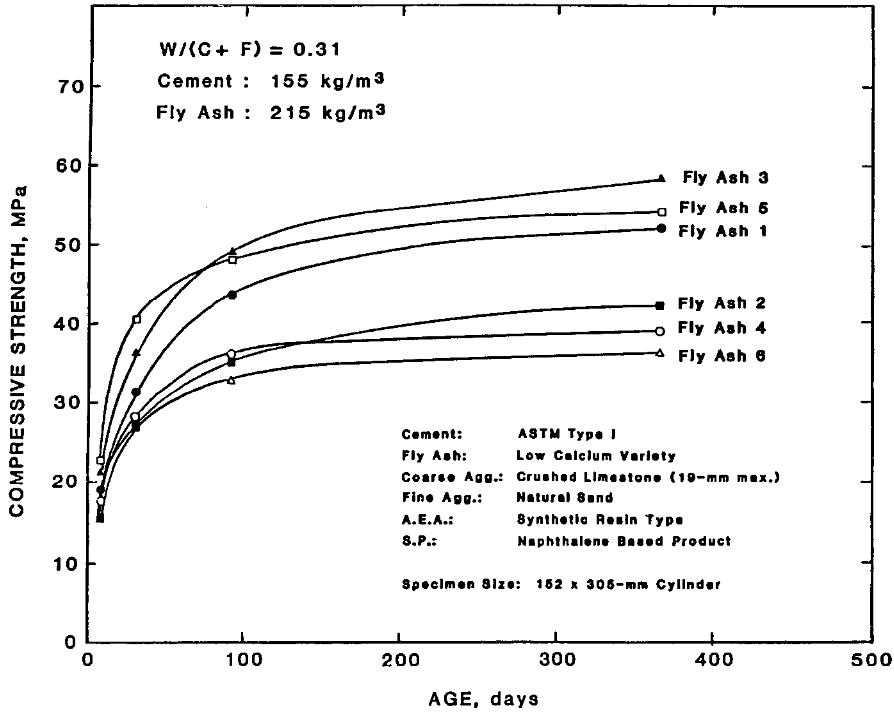

Figure 7. Compressive strength development of high volume fly ash concrete.

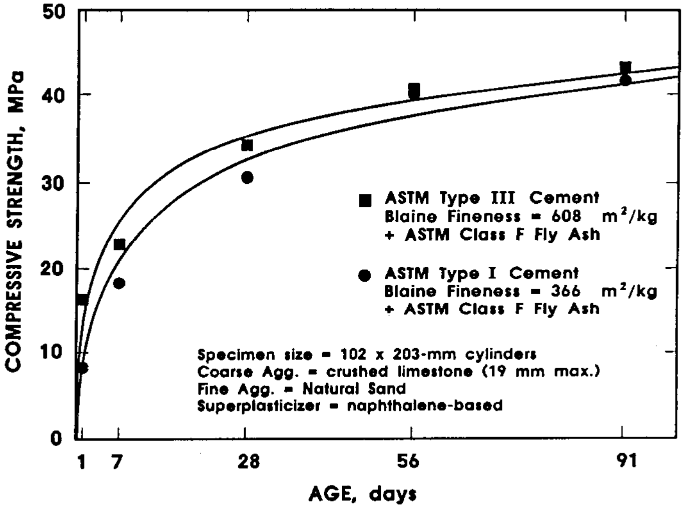

Figure 8. Compressive strength development with age of concrete made with ASTM Type I and III cements.

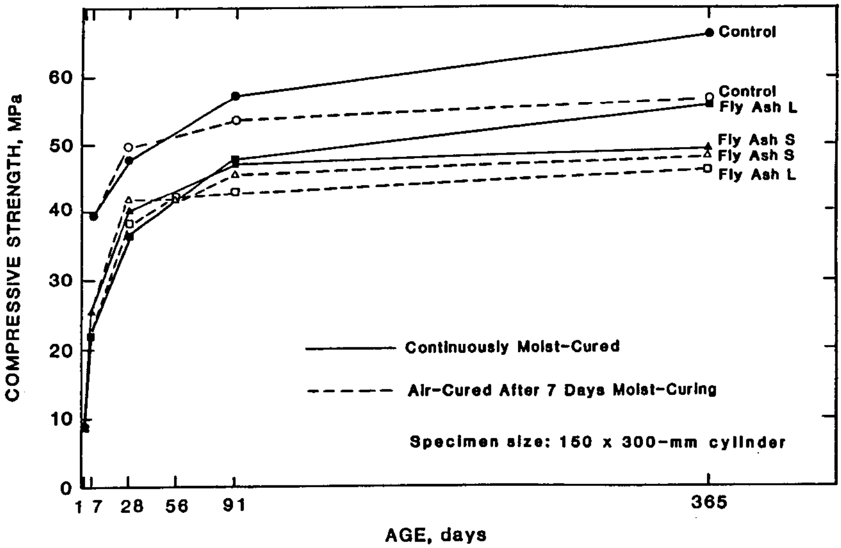

Figure 9. Compressive strength development of test cylinders under moist-cured and air-cured conditions.

In-Situ Strength Development of High-Volume Fly Ash Concrete. Investigations have been performed to determine in-situ strength development of high-volume fly ash concrete.[17][18][19] In one investigation, six concrete mixtures of various compositions were investigated.[18] The first five mixtures included a control mixture, mixtures with and without slag and or silica fume, and mixtures incorporating a cementitious materials content of 485 kg/m^3 of concrete. The sixth mixture was a typical high-volume fly ash concrete incorporating a cement content of 150 kg/m^3 concrete and 200 kg/m^3 of fly ash. The concrete was obtained from a commercial ready-mixed concrete plant. For each mixture, three types of structural elements simulating a thick-wall (0.5 x 2.5 x 1.5-m high), a thin-wall (0.25 x 3.1 x 1.5-m high) and a thick column (2.0 x 1.2 x 1.35-m high) were fabricated for testing under field curing conditions. Cores, 100 x 200-mm in size, were drilled at ages up to one year for determining the in-situ strengths of various concrete elements. In addition, a number of 150 x 300-mm cylinders were cast from each mixture for long-term strength testing.

The mixture proportions and the strength data for the test cylinders and the drilled cores are shown in Tables 3 and 4.[18] Figure 10[18] shows the plots of compressive strength development of concrete incorporating portland cement and high volumes of ASTM Class F fly ash. The test data show excellent in-situ strength development of high-volume fly ash concrete. The in-situ strength, as measured by drilled cores, equal or exceed the control concrete and concrete incorporating slag and or silica fume (Table 4).

Table 3. Mixture Proportions of Concrete Mixtures and Properties of Fresh Concrete (Non Air-Entrained)[18]

Mixture No.	Quantities, kg/m^3						
	Water	Cement	C.A. (S.S.D.)	F.A. (S.S.D.)	S.P. (L/m^3)	S.R.A. (L/m^3)	Slump, mm
1 (CSSi)	143	315	1142	744	7.5	0.45	250
2 (CS)	133	317	1145	749	7.0	0.46	110
3 (C8Si)	130	449	1149	758	11.0	0.84	225
4 (C12Si)	132	427	1139	754	14.9	0.90	200
5 (CF)	102	150	1222	811	7.1	0.66	210
6 (C)	130	485	1143	762	3.4	0.94	150

+From reference 18.

NOTE: C.A. - Coarse aggregate, F.A. = Fine aggregate, S.P. - Superplasticizer,
S.R.A. - Set retarding admixture
S.S.D. - Saturated, surface dry

Mixtures 1 and 2 contained 135 and 167 kg/m^3 slag respectively
Mixture 1, 3 and 4 contained 35, 39 and 59 kg/m^3 silica fume respectively
Only Mixture No. 5 has fly ash in the amount of 200 kg/m^3
The unit weight varied between 2410 and 2464 kg/m^3
Water/cementitious ratio varied between 0.27 and 0.29

Table 4. Summary of Compressive Strength Test Results

	Compressive Strength of 150 x 300-mm Cylinders, MPa						
	Age, days	1-CSSi	2-CS	3-C8Si	4-C12Si	5-CF	6-C
Moist Cured	1	36.7	34.5	38.4	43.5	8.3	44.4
	3	55.8	45.1	56.5	63.7	21.9	52.5
	7	69.6	57.9	66.9	77.7	33.7	58.5
	28	79.9	71.6	81.6	90.6	54.7	70.1
	91	81.1	75.7	84.3	92.2	69.5	85.0
	182	85.9	83.1	87.5	94.3	80.7	94.6
	365	88.6	82.7	91.5	103.7	97.5	100.8
Air Cured	1	39.6	34.8	47.8	53.4		45.9
	3	54.7	46.3	59.0	68.7	19.9	53.0
	7	62.1	53.0	68.5	73.5	28.3	59.5
	28	79.5	69.5	76.8	85.0	43.4	64.7
	91	82.1	62.9	80.6	91.7	57.6	79.4
	182	83.4	71.1	84.6	89.2	71.9	83.1
	365	85.7	74.6	85.2	98.1	75.4	88.0
Thick-Wall Element A (0.5 m x 2.5 m x 1.5 m)	Compressive Strength of 100 x 200-mm Cores, MPa						
	1	51.0	43.4	57.5	61.6		38.7
	3	62.4	51.1	66.2	-	24.3	50.8
	7	60.9	58.5	62.8	72.5	29.9	49.0
	28	69.2	64.8	70.6	74.8	52.1	57.2
	91	74.2	68.9	69.8	72.8	87.5	76.2
	182	73.3	70.2	76.4	81.0	92.1	80.2
	365	79.7	76.1	80.2	87.5	98.2	86.5
Thin-Wall Element B (0.25 m x 3.1 m x 1.5 m)	1	48.5	46.0	57.0	67.2		47.4
	3	60.7	53.2	65.7	-		52.0
	7	63.8	57.8	65.8	66.5		57.5
	28	73.1	68.6	72.3	75.9	N/A	64.3
	91	83.3	70.8	76.3	71.5		85.7
	182	80.7	70.3	80.2	84.8		86.7
	365	81.7	84.8	82.9	88.1		98.2
Thick-Column Element C (2.0 m x 1.2 m x 1.35 m)	1	41.7	45.6	58.4	69.4	7.8	41.7
	3	64.3	55.0	63.5	-	27.13	47.5
	7	63.2	57.2	63.4	71.8	4.049.	51.4
	28	69.4	63.4	66.8	75.8	9	59.9
	91	70.8	63.3	69.1	72.9	82.5	75.6
	182	69.6	69.4	71.4	78.7	87.0	74.3
	365	78.5	76.2	79.2	80.8	95.6	88.2

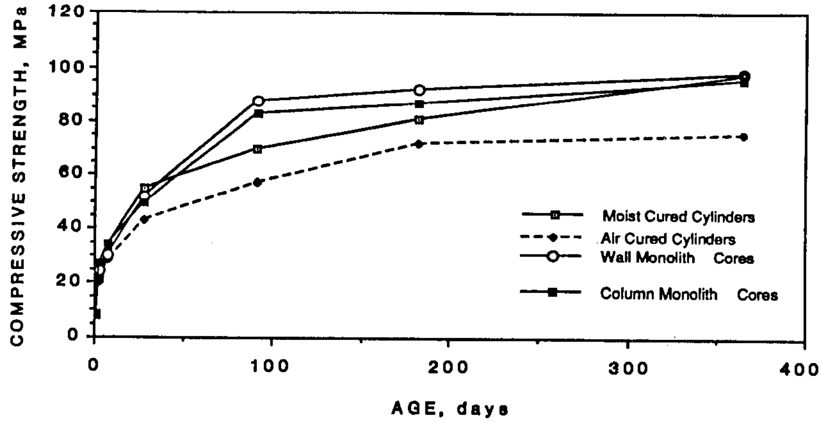

Figure 10. Compressive strength development of test cylinders and drilled cores from various types of concrete monoliths made with high-volume fly ash concrete.

Bisaillon et al.[17] and Langley et al.[19] have also reported data on in-situ strength development of high-volume fly ash concrete. Bisaillon et al.[17] used both drilled cores and pulse velocity measurements to estimate in-situ strength of concrete blocks measuring 2.5 x 4.0 x 5.0 meters. Langley et al.[19] determined the in-situ strength development by drilling and testing cores from large blocks measuring 3.1 x 3.1 x 3.1 meters in size. In each of the above investigations, the compressive strength of the drilled cores was comparable to or greater than the strength of the cores from the control concrete blocks.

Young's Modulus of Elasticity. The Young's modulus of elasticity of high-volume fly ash concrete made with limestone aggregate generally exceeds 30 GPa, and is thus somewhat higher than the modulus for comparable strengths of portland cement concrete. The higher modulus is probably due to the large percentage of aggregates, and in addition, due to the unhydrated fly ash particles acting as a fine filler material in the concrete.

Creep Characteristics. The creep characteristics of high-volume fly ash concrete are shown in Fig. 11.[14] The creep strain at one year ranges from 150 to 400 x 10^{-6} which is comparable to or lower than that of the portland cement concrete of comparable strength.

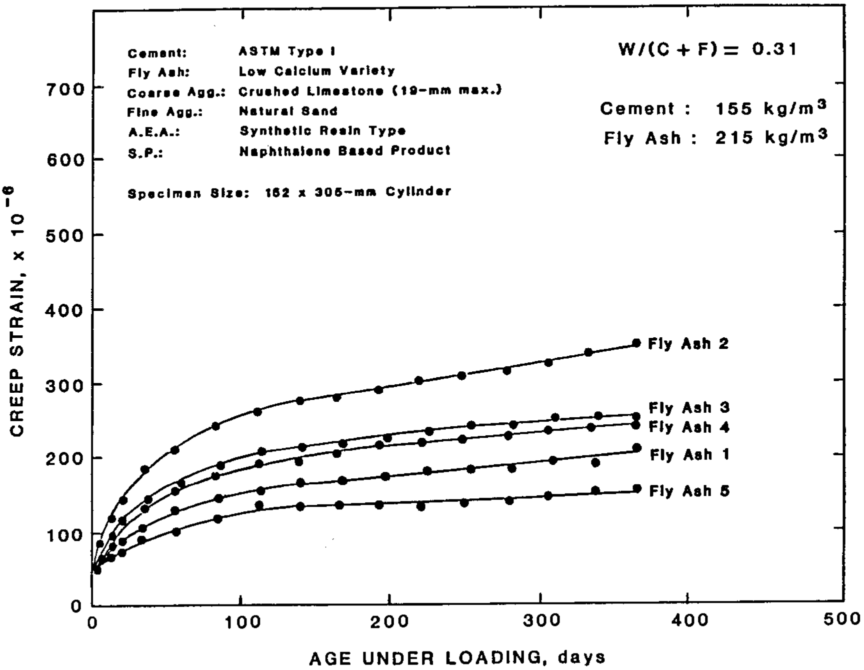

Figure 11. Creep strains for high-volume fly ash concrete.

Drying Shrinkage. The drying shrinkage strains of high-volume fly ash concrete and normal portland cement concrete, determined in accordance with ASTM C 157, are comparable.[11] Figure 12[11] shows such data on drying shrinkage strains on fly ash and control concrete prisms which had been cured in lime-saturated water for either 7 or 91 days and then air dried at 23 ± 1.7° and 50 ± 4 per cent relative humidity for periods up to about 500 days.

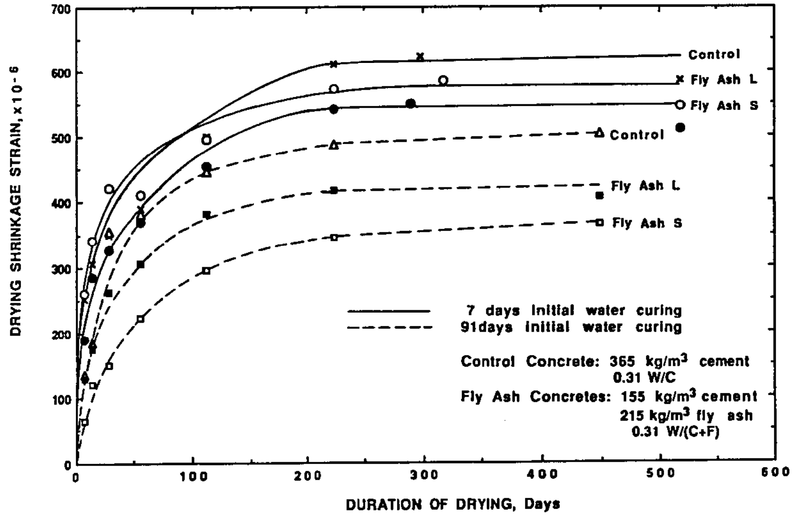

Figure 12. Drying shrinkage of high-volume fly ash and control concrete after 7 and 91 days of initial water-curing.

Water Permeability. Water permeability tests using a uniaxial flow apparatus developed by Bisaillon and Malhotra[20] were performed on the fly ash concrete incorporating 150 kg/m^3 of ASTM Type I cement and 190 kg/m^3 of fly ash. Briefly, the test method consists of measuring the uniaxial water flow through concrete cylinders, 125 mm high with a diameter of 150 mm, under a pressure of 3.5 MPa. The test specimens were maintained in the permeability cells for more than 6 months, and it was found that no water had passed through the specimens during this period. Based upon data previously published, this indicates that the concrete tested has extremely low permeability, although no numerical values can be assigned.[20]

1.6 Durability Aspects of High-Volume Fly Ash Concrete

Freezing and Thawing. A number of investigations have been performed to determine the resistance of high-volume fly ash concrete to repeated cycles of freezing and thawing.[6][10] The test adopted was ASTM C 666, Procedure A, "Rapid Freezing and Thawing in Water." Briefly, this method consists of alternately lowering the temperature of specimens from 4.4 to -17.8°C and raising it from -17.8°C to 4.4°C in 4 hrs, resulting in about six cycles in a 24-hr period. The durability of concrete is determined by measuring the resonant frequency of the test specimens before and after the cycling, and calculating the durability factors. Additional parameters such as weight loss, length change, and changes in pulse velocity caused by the freezing and thawing cycling of the test specimens have also been determined. Following the test, the reference and test prisms are broken in flexure.

The results show that properly air-entrained high-volume fly ash concrete performs satisfactorily in a freezing and thawing environment.[10A] The durability factors after 300 cycles of freezing and thawing range from 90 to 100. The bubble spacing factor and the specific surface of hardened concrete are of the order of 0.20 mm and 20 mm^2/mm^3, respectively. Typical test data are shown in Tables 5 and 6.[8] Similar results have been obtained for the freezing and thawing resistance of high-volume fly ash concrete made with a number of cements and fly ashes from the USA.[10A]

Table 5. Properties of Fresh and Hardened Concrete: Freezing and Thawing Investigation

Mixture Series	Properties of Fresh Concrete			Strength (MPa) 28 days	
	Temperature, °C	Slump, mm	Unit Weight, Kg/m^3	Compressive Strength	Flexural Strength
1	21	205	2400	31.6	4.2
3	23	235	2425	30.5	5.0

Air content: 4.3%

Table 6. Summary of Test Results on Concrete Prisms After 300 Cycles of Freezing and Thawing

Mixture No.	76 x 102 x 390-mm Test Prisms*											
	Weight, kg			Length, mm			Pulse Velocity, m/s			Resonant Frequency, Hz		
	W_0	W_{300}	Change, %	L_0	L_{300}	Change, %	V_0	V_{300}	Change, %	N_0	N_{300}	Change, %
1	7.443	7.333	-2.15	361.03	361.15	+0.033	4914	4627	-5.83	5500	5360	-2.60
3	7.453	7.380	-1.68	360.65	360.71	+0.017	4796	4618	-3.71	5410	5320	-1.64

NOTE: W_0, L_0, V_0 and N_0 represent values of weight, length, pulse velocity, and resonant frequency at the commencement of test;
W_{300}, L_{300}, V_{300} and N_{300} represent test values at the end of 300 cycles of freezing and thawing;
*Each result represents the average of two tests
W/C+F = 0.33; Air Content = 4.4%
Relative Dynamic Modulus and Durability factor 95-97

Penetration of Chloride Ions. Several investigations have indicated that high-volume fly ash concrete has a very high resistance to the penetration of chloride ions.[6][7] The AASHTO T277-83 test method, "Rapid Determination of the Chloride Permeability of Concrete" is one of the most commonly accepted tests in North America, and therefore has been adopted as the preferred technique. Briefly, the above method consists of monitoring the amount of electrical current passed through a 102-mm diameter by 51-mm thick concrete specimen when a potential difference of 60 V dc is maintained across the specimen for a period of six hours. Chloride ions are forced to migrate out of a NaCl solution subjected to a negative charge through the concrete into a NaOH solution maintained at a positive potential.

The conditioning of the concrete disc specimens for the test procedure consists of one hour of air drying, three hours of vacuum (pressure <1 mm Hg), one hour of additional vacuum with specimens under deaerated water, followed by 18 hours of soaking in water. The total charge passed, in coulombs, is used as an indicator of the resistance of the concrete to the passage of chloride ions.

The test results encompassing a number of investigations involving the use of several different fly ashes have indicated that the resistance of high-volume fly ash concrete to the penetration of chloride ions, as measured by the charge in coulombs, is very high. The values of the charge ranged from 150 to 973 coulombs for concretes tested at ages ranging from

28 to 91 days. The general consensus is that for low permeability concretes, the value of the charge in coulombs passed through the specimens should not exceed 1000, and for very low permeability concretes this value should preferably be less than 600. In silica fume concrete incorporating 400 to 500 kg/m^3 of portland cement and 10 per cent silica fume, chloride-ion penetration tests yield a charge in coulombs generally less than 800.

De-Icing Salt Scaling. The scaling resistance of high-volume fly ash concrete to de-icing salts has been carried out by Bilodeau and Malhotra.[21] The concrete was evaluated using the ASTM test method C 672. Briefly, this test method consists of fabricating test specimens with a surface area of at least 0.046 m^2 and a depth of 75 mm. The test specimens are then moist-cured for 14 days, followed by 14 days of drying at a temperature of 23 ± 1.7°C and a relative humidity of 50 ± 5%. At the age of 28 days, the surface of the specimens is covered to a depth of 6 mm with a solution of calcium chloride. The test specimens are then placed in a freezing chamber for 16 to 18 h followed by thawing in laboratory air at 23 ± 1°C and a relative humidity of 50 ± 5% for 6 to 8 h. The procedure is repeated daily; visual examinations are made every five cycles and the test is continued up to 50 cycles.

Instead of the 14 days of curing and 14 days of air drying periods as specified in the ASTM test, the curing and drying periods used were 28 and 42 days, respectively, and 3% sodium chloride solution was used instead of 4% calcium chloride solution. The curing and drying periods were extended to allow more maturity of fly ash concrete, and the sodium chloride solution was used because this is the most commonly used de-icing agent in practice.

In addition to visual examination of the specimens, the weight of the scaled material was also determined. Both visual examination and weight loss determination indicated severe scaling of the surfaces of the test specimens with coarse aggregate visible over the entire surface. According to the ASTM scale of visual rating of 0 to 5, the test specimens were rated 5. Control plain portland cement concrete, made with the same water-to-cementitious materials ratio and the same total cementitious materials content, showed good scaling resistance with a visual rating of 1 which corresponds to slight scaling. The causes leading to scaling and methods to mitigate or eliminate this problem have yet to be solved. Some of the possibilities are: the period of curing prior to exposure to de-icing salts was not adequate, and finishing of this concrete may decrease the air entrainment, bubble spacing, etc.

Carbonation. Limited data on the carbonation tests performed on the broken portions of the cores, drilled after five years from a large block of high volume fly ash concrete, are shown in Table 7.[12] The average carbonation depth as determined by the phenolphthalein test was less than 10 mm after 5 years.

Table 7. Carbonation of High-Volume Fly Ash Concrete

Type of Air-Entrained Concrete Specimen	Curing History	Test Age, Months	Average Carbonation Depth (mm)
76 x 102 x 406-mm prisms*	Moist-cured for 7 days followed by air-cure at 23 ± 1.7°C and 50 ± 5% R.H.	12	3
102 x 203-mm drilled cores**from the 1.6 x 1.6 x 1.6-m block	Moist-cured for 28 days and afterwards left indoors at 23 ± 1.7°C and 50 ± 5% R.H.	31 41 50 57	4 4 7 7

*Mixture Proportions: Water = 115 kg/m^3, ASTM Type I cement = 157 kg/m^3, ASTM Class F fly ash = 216 kg/m^3, coarse aggregate = 1284 kg/m^3, fine aggregate = 627 kg/m^3, super plasticizer = 5.6 kg/m^3, air-entraining admixture = 827 mL/m^3, compressive strength of 152 x 305-mm cylinders at 28 days = 36.4 MPa.

**Mixture Proportions: Water = 95 kg/m^3, ASTM Type II cement = 147 kg/m^3, ASTM Class F fly ash = 187 kg/m^3, coarse aggregate (dry) = 1215 kg/m^3, fine aggregate (dry) = 622 kg/m^3, superplasticizer = 7.0 kg/m^3, air-entraining admixture = 660 mL/m^3, compressive strength of 152 x 305-mm cylinders at 28 days = 41.6 MPa.

Control of Expansion Due to Alkali-Aggregate Reaction. The undesirable expansion of concrete due to reaction between the cement alkalis and certain types of silica in aggregates is a universal problem. Research has shown that alkali-silica reactions in concrete can be controlled by incorporating good quality fly ash as a partial replacement for cement. The generally recommended levels of cement replacement by fly ash are between 25 and 40 per cent.

As described earlier, high-volume fly ash concrete incorporates about 56 per cent of fly ash as a percentage of total binder, together with large dosages of a superplasticizer.

Alasali and Malhotra[13] determined the role of high-volume fly ash concrete in controlling expansion due to alkali-aggregate reaction. Two concrete mixtures were made, one control and one incorporating ASTM

Class F fly ash. The coarse aggregate used was 19-mm crushed limestone; this limestone contains a highly reactive silica phase and has a known history of expansive reaction in concrete.

A number of prisms were subjected to the following seven test regimes to determine the expansion due to the alkali-silica reaction.

Test regime 1: Continuous curing of the prisms in a moist-curing room maintained at 38°C.

Test regime 2, 3: Continuous curing of the prisms in 5% NaCl solution maintained at 38 and 80°C after an initial moist curing for 24 h.

Test regime 4, 5: Continuous curing of prisms in 1 normal NaOH solution maintained at 38 and 80°C after an initial moist curing for 24 h.

Test regime 6, 7: Continuous curing of prisms in 1 normal KOH solution maintained at 38 and 80°C after an initial moist curing for 24 h.

The prisms were exposed to the above regimes for a period of 275 days.

The test results given in Table 8[13] show that, regardless of the test procedure used, the test prisms cast from the high-volume fly ash concrete did not show any expansion in spite of the very reactive coarse aggregate used in the concrete. The above tests confirm the previously published data that fly ash can play an effective role in reducing the expansion due to the alkali-silica reactions in concrete.

Thermal Properties. Thermal properties, i.e., thermal conductivity, thermal diffusivity, and specific heat, of high volume fly ash concrete at various moisture levels has been determined.[22] The transient thermal probe method was used to determine the thermal conductivity[23] and the Shannon and Wells[24] technique was used to determine thermal diffusivity. Tables 9 and 10[22] show some of the test results together with the properties of fresh and hardened concrete.

Limitations. The major limitations in the utilization of high-volume fly ash concrete is the availability of good quality fly ash within economic haulage of the construction site and adequate silo capacity. The other limitations include the compatibility between fly ash, cement and superplasticizers. This needs to be investigated as each source of fly ash is unique. In some instances, the initial and final setting of the high-volume fly ash concrete may be retarded by several hours. This problem can likely be resolved by changing the type and brand of the superplasticizers used.

Table 8. Alkali-Aggregate Expansion of Concrete Prisms (Containing High-Volume Fly Ash) Under Different Storage Conditions

Storage	Type of Mixture	% Expansion at Different Ages							
		7d	14d	28d	56d	84d	112d	168d	275d
1. Plain Water Temp. 38°C	Control*	0.005	0.008	0.003	0.028	0.056	0.063	0.078	0.087
	Fly ash**	-0.006	-0.005	-0.006	-0.001	-0.004	-0.004	-0.007	-0.004
2. 5% NaCl Temp. 38°C	Control	0.003	0.001	0.001	0.014	0.032	0.044	0.064	0.077
	Fly ash	0	-0.006	-0.005	-0.006	-0.001	-0.009	-0.006	-0.004
3. 5% NaCl Temp. 80°C	Control	0	0.018	0.062	0.064	0.083	0.086	0.104	0.130
	Fly ash	-0.011	-0.007	-0.005	-0.005	-0.004	-0.004	0.015	0.025
4. 1 Normal NaOH Temp. 38°C	Control	0	0	0	0.020	0.045	0.061	0.088	0.124
	Fly ash	-0.007	-0.010	-0.012	-0.010	-0.013	-0.010	-0.007	-0.005
5. 1 Normal NaOH Temp. 80°C	Control	0.020	0.059	0.090	0.108	0.158	0.196	0.270	0.347
	Fly ash	-0.011	-0.01	-0.010	0	0	+0.009	0.020	0.038
6. 1 Normal KOH Temp. 38°C	Control	0	0	-0.005	0.020	0.040	0.050	0.071	0.077
	Fly ash	-0.010	-0.010	-0.011	-0.003	-0.007	-0.008	-0.004	-0.003
7. 1 Normal KOH Temp. 80°C	Control	0.020	0.050	0.070	0.090	0.149	0.201	0.266	0.346
	Fly ash	-0.013	-0.016	-0.005	-0.005	-0.005	-0.003	0.014	0.016

*W/C = 0.32, water content = 115 kg/m^3, cement content = 365 kg/m^3, alkali content of cement = 4.12 kg/m^3, Superplasticizer = 9.3 kg/m^3, compressive strength = 47.8 MPa at 28 days, slump = 105 mm

**W/C+F = 0.31, water content = 114 kg/m^3, cement content = 155 kg/m^3 alkali content of cement = 1.75 kg/m^3, Superplasticizer = 6.2 kg/m^3, compressive strength = 36.4, slump = 145 mm

Table 9. Data for Fresh and Hardened Concrete

Mixture Number	Fresh Concrete				Hardened Concrete		
	Temperature, °C	Slump, mm	Unit Weight, kg/m^3	Air Content, %	Unit Weight At One Day, kg/m^3	Compressive Strength, MPa 102 x 203-mm Cylinders	
						7-day	28-day
1	23	75	2415	3.4	2465	--	36.7
2	25	200	2415	4.2	2460	22.0	34.8

Table 10. Thermal Properties of Concrete

Mixture Number	Moisture Content, %												
	0			1		2		3		4		5	
	TC*	TD**	SH***	TC	TD	TC	TD	TC	TD	TC	TD	TC	TD
1	1.56	89	0.171	1.75	95	1.96	101	2.08	105	2.13	98	--	--
2	1.55	89	0.169	1.72	94	1.90	98	2.04	100	2.13	99	2.17	97

*Thermal conductivity in W/°C-m
**Thermal diffusivity in cm^2/sx10^{-4}
***Specific heat in Cal/g.°C
Moisture content is given as a percent of dry weight

The performance of high-volume fly ash concrete, subjected to de-icing salts, is relatively poor and further research is needed before the use of this type of concrete can be recommended for this application involving this kind of exposure.

Applications. High volume fly ash concrete has been used in the field. Examples include concrete block testing for communication satellites, Ottawa, Parklane hotel complex, Halifax, Purdys Wharf Development, Halifax, and shotcrete applications in Nova Scotia and British Columbia.[26]

2.0 HIGH VOLUME SLAG CONCRETE

2.1 Introduction

Over the past twenty years, the Canada Center for Mineral and Energy Technology (CANMET) has been active in research involving the utilization of mineral by-products to enhance the properties and durability characteristics of concrete. In recent years, the research has focused on developing concretes incorporating relatively large amounts of mineral by-products as supplementary cementing materials. The development of high-volume fly ash concrete at CANMET has attracted widespread interest among concrete researchers because of its many excellent properties and durability characteristics. In the case of ferrous slags, the research work so far has been concentrated on normal-strength concretes with large slag replacements, high-strength concretes incorporating slag and silica fume, and activated slag concretes. This chapter deals with slag concretes proportioned in a manner similar to the high-volume fly ash concretes, which contain low quantity of cement and high volumes of fly ash with water content of about 115 kg/m^3. The properties discussed include adiabatic temperature rise, mechanical properties, drying shrinkage, and resistance to chloride-ion penetration of the high-volume slag concretes.[27]

2.2 Mixture Proportions

The physical properties, chemical analysis of cement and ground granulated blast furnace slag and mix proportions are given in Tables 11 and 12.

These slag concretes were proportioned in a manner similar to that of the high-volume fly ash concrete developed at CANMET, in which, the cement, fly ash, and water contents were kept at 155 kg/m^3, 215 kg/m^3, and 115 kg/m^3, respectively. The same principles were followed with the slag concrete proportioning, except that, a range of slag levels were investigated. Also, the cement contents were kept low to accommodate the cementitious properties of slag. The water content of the concretes was kept at a minimum value, at about 115 kg/m^3, and the workability was achieved by means of large dosages of superplasticizers.

2.3 Properties of Fresh Concrete

The properties of fresh concrete, that is, temperature, slump, air content, unit weight, and setting time are shown in Table 13. For the given water content of 115 kg/m^3, the workability of the high-volume slag concretes decreases substantially as the water-to-cementitious materials ratio is reduced below 0.30.

Table 11. Physical Properties and Chemical Analyses of Cement and Ground Granulated Blast-Furnace Slag

	Portland Cement (ASTM Type I)	Blast-Furnace Slag
Physical Tests		
Fineness -passing 45 µm, %	85.3	97
-Blaine, m^2/kg	373	460
Specific Gravity	3.14	2.92
Setting Time, h : min		
- Initial	2:45	--
- Final	4:50	--
Autoclave Expansion, %	0.11	
Compressive Strength of		
51-mm cubes, MPa: -3 day	18.3	
-7 day	24.4	
-28 day	33.3	
Chemical Analysis		
	21.95	38.0
Silicon dioxide (SiO_2), %	4.13	6.63
Aluminum oxide (Al_2O_3), %	2.88	0.40
Ferric oxide (Fe_2O_3), %	61.73	35.7
Calcium oxide (CaO) total, %	0.48	--
Magnesium oxide (MgO), %	3.68	13.6
Sulphur trioxide (SO_3), %	2.81	--
Sodium oxide (Na_2O), %	0.25	0.36
Potassium oxide (K_2O), %	0.44	0.40
Loss on ignition, %	1.47	0.76
Bogue Potential Compounds Composition		
	42.8	--
C_3S	30.7	--
C_2S	6.8	--
C_3A	8.8	--
C_4AF		

Table 12. Mix Proportions

Mixture Series	Batch No.	W/C+S	S/C+S	Quantities, kg/m^3							A.E.A. mL/m^3
				Water	Cement	Slag	C+S	C.A.	F.A.	S.P.	
1	A	0.45	0.60	112	99	149	248	1158	839	5.0	65.3
	B	0.45	0.60	109	97	145	242	1133	821	4.6	70.9
2	A	0.34	0.70	112	98	228	326	1142	762	6.5	288
	B	0.34	0.70	112	98	228	326	1142	762	7.1	403
3	A	0.29	0.75	115	100	301	401	1172	717	7.4	1032
	B	0.29	0.75	115	100	299	399	1166	713	8.3	1143
4	A	0.45	0.50	110	122	122	244	1140	824	5.6	62.6
	B	0.45	0.50	110	122	122	244	1140	824	5.5	65.4
5	A	0.36	0.60	109	121	181	302	1137	757	5.2	113
	B	0.36	0.60	111	123	184	307	1155	770	5.5	181
6	A	0.28	0.70	115	124	288	412	1149	704	9.1	1671
	B	0.28	0.70	114	124	288	412	1150	704	7.6	1382
7	A	0.38	0.50	111	147	147	294	1171	780	4.9	101
	B	0.38	0.50	111	147	147	294	1171	780	5.4	152
8	A	0.30	0.60	111	146	220	366	1139	727	6.0	602
	B	0.30	0.60	112	148	224	372	1158	740	6.7	580
9	A	0.27	0.65	114	148	276	424	1143	700	9.4	2472
	B	0.27	0.65	116	148	275	423	1142	700	9.9	1743
10	Control	0.39	0	114	292	0	292	1140	825	4.7	155
11	Control	0.31	0	114	368	0	368	1242	698	5.3	260
12	Control	0.27	0	116	428	0	428	1211	682	5.9	300

Note: C.A. = Coarse Aggregates; F.A. = Fine Aggregate; S.P. = Superplasticizer; A.E.A. = Air Entraining Admixture;
W/C+S = water-to-cementitious materials ratio; S/C+S = Slag-to-cementitious materials ratio

Table 13. Properties of Fresh Concrete

Mixture Series	Batch No.	W/C+S	S/C+S	Temperature, °C	Slump, mm	Unit Weight kg/m^3	Air Content, %	Setting Time h:min	
								Initial	Final
1	A	0.45	0.60	20	150	2360	4.8		
	B	0.45	0.60	20	150	2310	5.8	7:00	11:20
2	A	0.34	0.70	23	175	2345	5.2	3.20	7:20
	B	0.34	0.70	23	150	2345	5.3		
3	A	0.29	0.75	26	90	2410	4.0	3:20	7:55
	B	0.29	0.75	26	125	2400	4.6		
4	A	0.45	0.50	20	125	2320	5.6	--	--
	B	0.45	0.50	20	115	2320	5.8		
5	A	0.36	0.60	20	200	2305	5.6	7:25	11:50
	B	0.36	0.60	20	175	2345	5.4		
6	A	0.28	0.70	20	225	2385	4.6	4:20	8:40
	B	0.28	0.70	20	200	2385	4.7		
7	A	0.38	0.50	23	175	2360	4.9	5:25	8:40
	B	0.38	0.50	23	165	2360	4.8		
8	A	0.30	0.60	23	225	2345	5.4	4:10	8:00
	B	0.30	0.60	23	90	2385	4.8		
9	A	0.27	0.65	19	215	2385	4.4	5:30	10:55
	B	0.27	0.65	19	225	2385	4.0		
10	Control	0.39	0	25	180	2375	4.6	6:40	8:30
11	Control	0.31	0	24	150	2415	4.4	5:40	7:10
12	Control	0.27	0	25	205	2440	4.1	5:15	6:50

Increasing the slag content at each level of cement resulted in increased water demand, and hence, in increasing superplasticizer dosage. The superplasticizer dosage ranged from 7.5 to 10 kg/m^3 in concretes with the higher slag contents. On the other hand, the superplasticizer dosage of the control concrete with the highest cement content of 428 kg/m^3 was only 5.9 kg/m^3.

Air Content and Dosage of Air-Entraining Admixture (AEA). Figure 13 shows the AEA requirement versus slag content. The required dosage of AEA increased substantially with an increase in the slag content. In comparison, the increase in the AEA dosage with increasing cement content, but at constant slag content, was minimal. The different morphology of the slag particles, as well as their higher fineness and total surface area as compared with that of the cement used, could be a reason for this behavior.

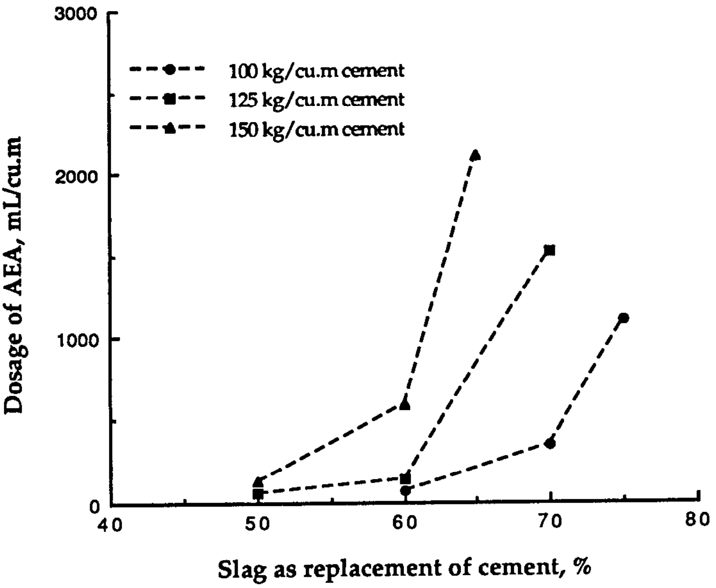

Figure 13. AEA requirement vs slag content in high volume slag concretes.

Time of Setting. The results of time of setting of concrete are shown in Table 13. It appears in general, that there is a reduction in the setting time of concrete with increasing cementitious materials. The setting time of the control concretes were generally close to that of the slag concretes of the same cementitious materials content, however, the time lag between the initial and final set was smaller for the control concretes when compared to that of the slag concretes.

2.4 Properties of Hardened Concrete

Autogenous Temperature Rise. Figure 14 shows the autogenous temperature rise measured using 152 by 305-mm cylinder specimens placed in an autogenous curing chamber. The variation of the autogenous temperature rise with the proportion of slag in concretes is shown in Fig. 15. The placing temperature of the concrete mixtures was about 22 ± 3°C. The maximum temperature rise measured ranged from 5.5°C to 12.3°C, which is considered low. At all three cement levels, the peak temperature reached appeared to decrease with increasing slag content.

Mix No.	1	2	4	5	6	7	8	9
Cement,kg/m³	97	98	122	123	124	147	148	148
Slag, kg/m³	145	228	122	184	288	147	224	275
W/C+S	0.45	0.34	0.45	0.36	0.28	0.38	0.30	0.27

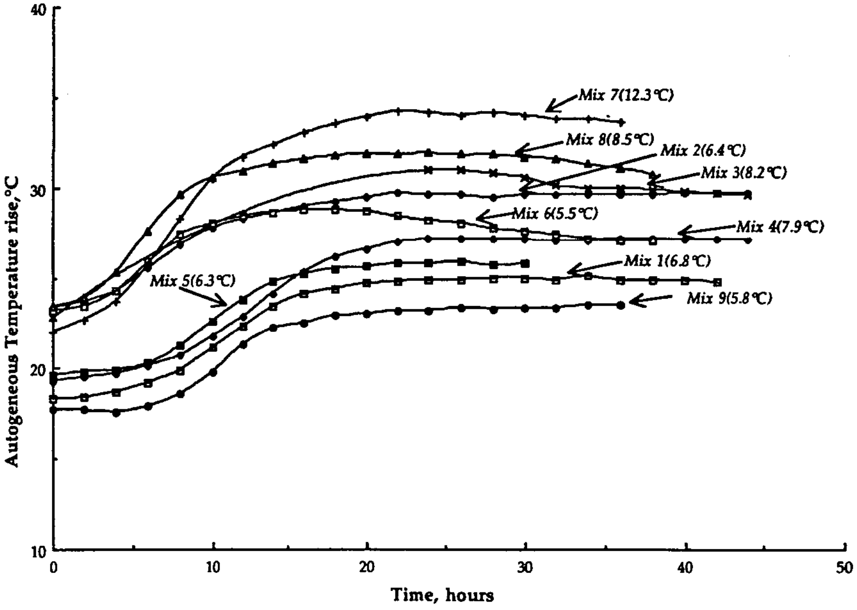

Figure 14. Autogenous temperature rise in 152 x 305 mm concrete cylinders.

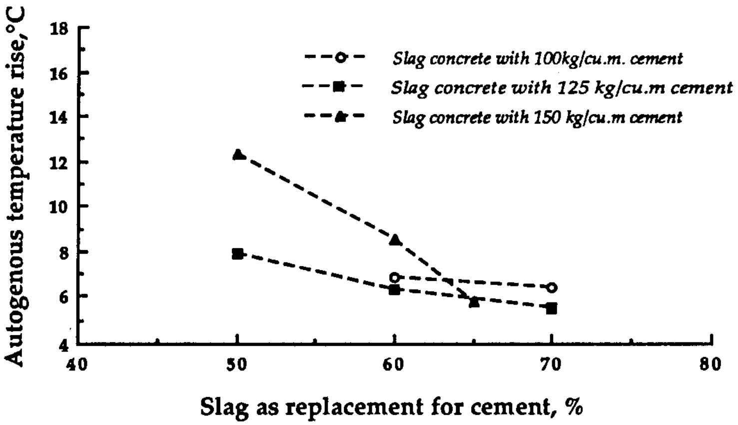

Figure 15. Autogenous temperature rise vs slag content in high volume slag concretes.

Compressive Strength. The compressive strength results of the high-volume slag concretes are given in Table 14 and illustrated in Fig. 16. The relationship of 91-day strength with water-to-cementitious materials ratio is illustrated in Fig. 17. The increase in the 91-day compressive strength with an increase in the total cementitious material is shown in Fig. 18.

The strength development of slag concrete is generally slow at early ages, and this was evident in all the high-volume slag concretes tested. Also, within the testing age of 91 days, the slag concretes seem to reach most of their strength potential by 28 days, when compared to the control concretes. Nevertheless, the strength performance of these concretes was as good as that of the control concretes, and in this system, replacement of a large quantity of cement by slag does not appear to adversely affect the compressive strength development of the concretes from 7 days onwards.

Flexural Strength. The flexural strengths determined at 14 days are given in Table 14. The slag concretes showed better flexural strength than the control concretes at every cementitious material level. The higher flexural strength of the slag concretes has also been observed in previous investigations,[28] and it is believed to be due to the stronger bonds in the cement/slag/aggregate system caused by the shape and surface texture of the slag particles.

Mix No.	1	2	4	5	6	7	8	9	10	11	12
Cement, kg/m³	99	98	122	121	124	147	146	148	292	368	428
Slag, kg/m³	149	228	122	181	288	147	220	276	0	0	0
W/C+S	0.45	0.34	0.45	0.36	0.28	0.38	0.30	0.27	0.39	0.31	0.27

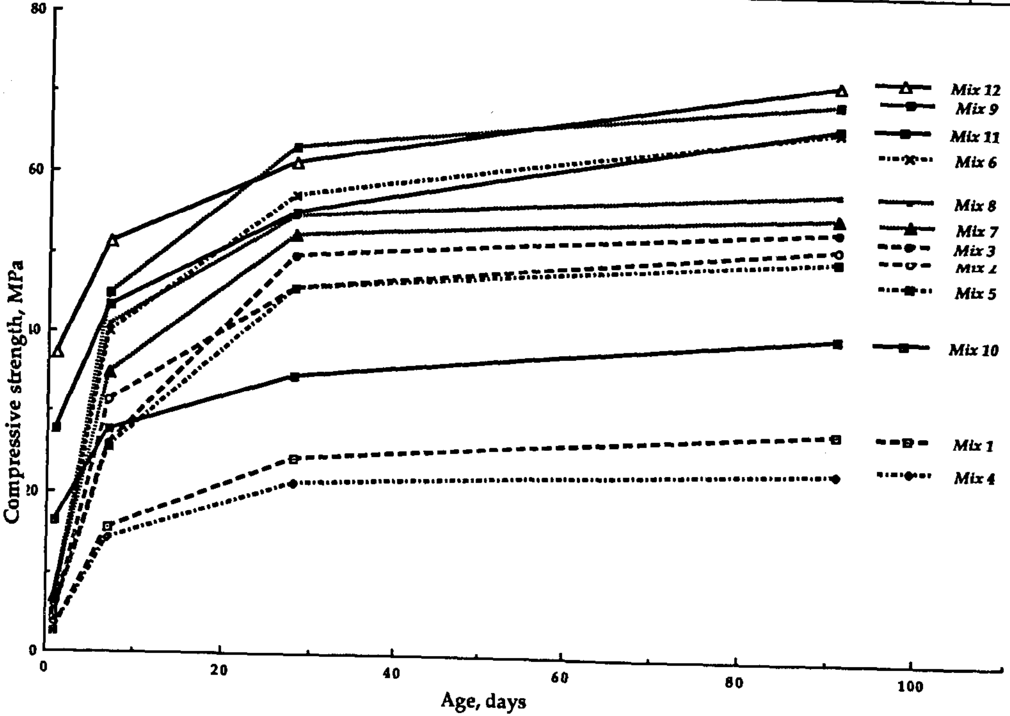

Figure 16. Compressive strength development of high volume slag concretes.

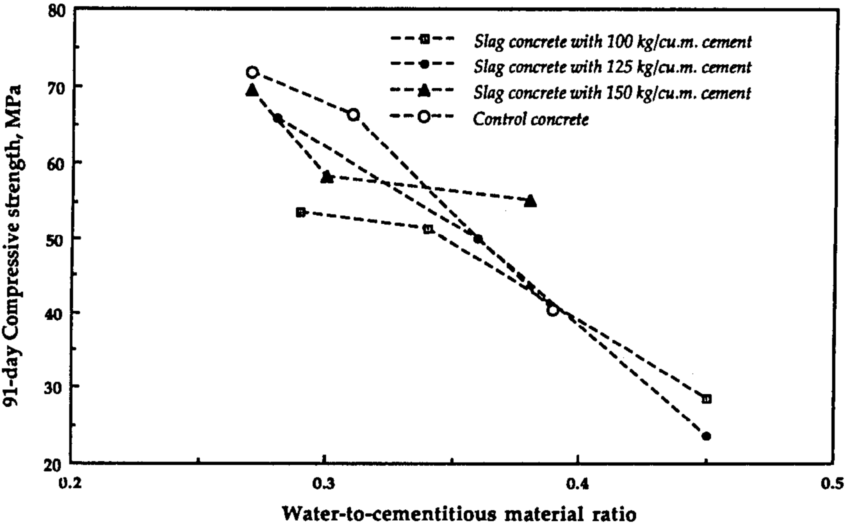

Figure 17. Ninety-one day compressive strength vs water-to-cementitious materials ratio.

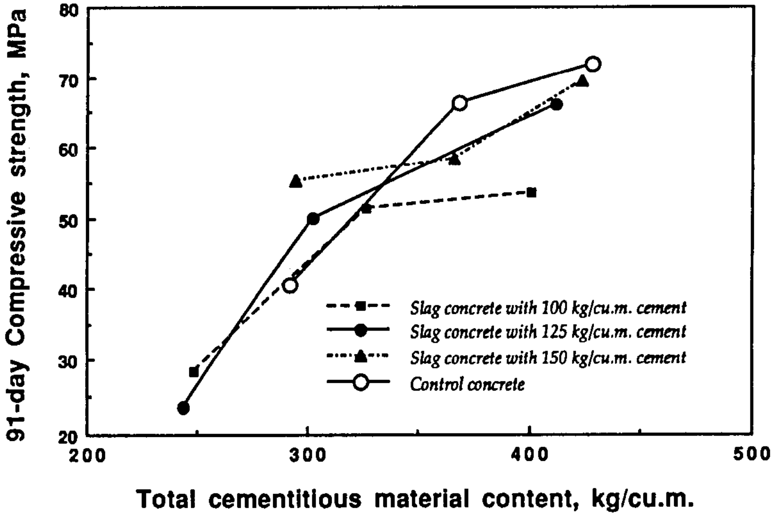

Figure 18. Ninety-one day compressive strength vs total cementitious content.

Table 14. Properties of Hardened Concrete

Mixture Series	Batch No.	W/C+S	S/C+S	Density at 1-day kg/m^3	Compressive Strength[1] MPa				Flexure Strength[2] MPa	Modulus of Elasticity[1] GPa	Chloride Ion Penetration, Coulomb
					1-d	7-d	28-d	91-d	14-d	28-d	28-d
1	A	0.45	0.60	2475	2.5	15.5	24.4	28.4		38.3	
	B	0.45	0.60	2465			19.6		3.9		830
2	A	0.34	0.70	2435	3.8	31.5	45.6	51.4		42.4	
	B	0.34	0.70	2435			43.6		7.8		230
3	A	0.29	0.75	2470	4.5	26.1	49.6	53.6		44.3	
	B	0.29	0.75	2455			37.1		8.3		175
4	A	0.45	0.50	2450	2.5	14.1	21.2	23.5		32.6	
	B	0.45	0.50	2450			19.9		3.4		1160
5	A	0.36	0.60	2435	4.3	25.6	45.6	49.9		42.3	
	B	0.36	0.60	2420			50.8		7.0		325
6	A	0.28	0.70	2460	6.3	40.1	57.3	66.0		45.1	
	B	0.28	0.70	2480			51.2		8.6		215
7	A	0.38	0.50	2455	6.9	34.8	52.3	55.2		44.3	
	B	0.38	0.50	2440			53.6		7.0		385
8	A	0.30	0.60	2430	6.7	40.9	54.6	58.3		42.5	
	B	0.30	0.60	2440			54.4		9.0		275
9	A	0.27	0.65	2445	4.9	44.7	63.2	69.5		43.8	
	B	0.27	0.65	2465			57.4		8.7		320
10	Control	0.39	0	2455	16.4	27.8	34.6	40.3	4.5	40.3*	2985
11	Control	0.31	0	2475	27.8	43.3	55.1	66.4	6.3	45.1*	1285
12	Control	0.27	0	2485	37.2	51.2	61.3	71.8	7.2	46.2*	1305

*Results are at the age of 91 days. [1]Testing carried out on 152x305-mm cylinders. [2]Testing carried out on 76x102x406-mm prisms.

Young's Modulus of Elasticity. The 28-day Young's modulus of elasticity values are shown in Table 14. The values given for the control concretes were measured at 91 days. In general, the modulus of elasticity of the slag concretes increased with increasing slag content and decreasing W/C+S at every cement level. When comparing the 28 days Young's modulus values of the slag concretes with 91 days values of the control concretes, it appears that the high-volume slag concretes developed higher modulus of elasticity than the control concretes. This slight increase in modulus of the slag concretes in relation to the strength has been attributed to a modification in the properties of the slag hydrates compared to those of the control concretes.[29]

Resistance to Chloride-Ion Penetration. The resistance of concretes to chloride-ion penetration, measured according to ASTM C 1202 at the age of 28 days, are given in Table 14. At each cement level, the resistance of the concretes to chloride-ion penetration increases substantially with an increase in the slag content; though there are minor exceptions. The test results show that the incorporation of high volumes of slag in concretes increases the resistance of concretes to chloride-ion penetration significantly. It is to be noted that the 28-day chloride-ion penetration of silica fume concrete with 400 to 500 kg/m^3 portland cement and 10% silica fume is in the range of 300 to 800 coulombs.[30]

Drying Shrinkage Strain. The drying shrinkage strains of the specimens air dried after 7 days of moist curing and the expansion/shrinkage strains of the specimens stored continuously in water are shown in Table 15. In general, the drying shrinkages of the high-volume slag concretes and the control concretes were about the same, ranging from 405 to 493 x 10^{-6} at 112 days. However, at every cement level within the slag concretes, the drying shrinkage seems to decrease slightly at the highest slag level. The drying shrinkage strains of the high-volume slag concretes are of the same order as those of the conventional slag concretes.

Table 15. Shrinkage/Expansion Results

Mixture Series	W/C+S	S/C+S	Drying Shrinkage Strain, x10^{-6} (Specimens air dried)					Expansion/Shrinkage, x10^{-6} (Specimens stored in water)			
			7d	14d	28d	56d	112d	14d	28d	56d	112d
1	0.45	0.60	54	89	213	327	415	+18	+14	+48	+54
2	0.34	0.70	149	188	305	422	493	18	36	+7	+28
3	0.29	0.75	128	185	277	387	472	11	11	+25	+43
4	0.45	0.50	57	121	217	341	405	29	48	7	4
5	0.36	0.60	163	270	319	404	475	4	+4	+18	+43
6	0.28	0.70	121	195	266	334	433	64	46	36	0
7	0.38	0.50	202	255	298	376	--	+18	+57	+61	--
8	0.30	0.60	199	263	316	387	--	0	+29	+36	--
9	0.27	0.65	181	217	277	359	--	+54	+75	+78	--
10	0.39	0	156	241	319	401	419	7	--	--	+50
11	0.31	0	199	270	337	397	451	+7	--	+64	--
12	0.27	0	216	241	319	401	419	+29	--	+93	--

Note:

1. Prior to air-drying, the specimens were stored in lime-saturated water for 7 days.
2. Strains were measured on 76 by 102 by 390-mm prisms.
3. The positive values (+) indicate expansion.
4. The testing is to continue up to 448 days.

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13

Admixtures for Repair and Restoration of Concrete

Noel P. Mailvaganam

1.0 INTRODUCTION

The replacement of defective and spalled concrete to reintroduce a protective and durable environment around reinforcement is of great importance. Therefore, deteriorated reinforced concrete should be repaired with impermeable, highly alkaline cement-based materials, closely matched in properties to the parent concrete. Two or more admixtures are often used to obtain the multifunctional requirements demanded by the manner in which repair products are used. In certain situations specific properties such as high flow, fast setting and rapid strength development, augmenting of the bond to the concrete substrate or corrosion inhibition may be required in a single product!

Repair of deteriorated structures involves conditions that are very different from those encountered in new construction, almost every repair job having unique conditions and special requirements.[1][2] Work on existing structures may require placing of material in poorly accessible areas, performing the repair for rapid turn around time of the structure, and the use of materials with very low toxicity levels. Special procedures not used in new construction, such as shotcrete or preplaced aggregate, may have to be used. Therefore, selection must be based on the knowledge of the physical and chemical properties, and the nature of the environment in which they will be placed and how the materials will interact with the environment in service. Final selection of the material or combination of materials must also take into account the ease of application, cost, available labor skills and equipment.

The role that admixtures play in the formulation of repair products, design of special concrete mixes and the use of certain repair procedures, is best exemplified by a discussion of the use of various admixtures in three areas. *(a)* proprietary repair products *(b)* concrete used to replace defective concrete *(c)* special techniques. This chapter presents information on the use of various admixtures in different repair products and concrete to enable them to comply with in-service conditions and render them suitable to the application procedures of the job. Typical properties of the materials currently used in the repair process are detailed and their advantages and limitations for use in a given set of conditions/environment described.

2.0 PROPRIETARY REPAIR PRODUCTS

2.1 Patching materials

Currently available patching materials are formulated to meet the demands of a repair schedule and aggressive conditions. Requirements of minimum down time for a repair has dictated the development of fast-setting, high strength-developing materials; the necessity to place material under conditions of poor accessibility has led to the development of high flow, self-leveling materials. High early strength development and fast setting is achieved by the use of a range of accelerating admixtures including calcium formate, sodium sulfate, and high alumina cement/portland cement mixes.[3] Corrosion inhibition characteristics can be added to the above mixes by the incorporation of corrosion inhibiting admixtures such as calcium nitrite, sodium nitrite, sodium benzoate or currently marketed proprietary organic inhibitors. Some situations may require longer set times for placing and finishing of the material. Under such conditions, set retarding admixtures such as sodium gluconate or sodium citrate are combined with superplasticizing admixtures and used at dosages which provide set retardation without impairing early strength development.

The success of any patch will depend largely on overcoming the tendency of the concrete/mortar or polymer patching material to shrink after placement, and on securing a bond to the substrate concrete. Admixtures have been used to overcome shrinkage and to promote a better bond. In cementitious systems, shrinkage may be compensated for by the use of expansive admixtures in the mix or the use of superplasticizers to enable the use of very low water contents. Adhesion to the substrate is improved in cementitious systems by the use of bond coats of cementitious slurries or latex/cement slurries.

If unsightly patches are to be avoided, it will be necessary to match their color to that of the concrete substrate. Some experimentation with mixtures of gray and white cement or pigments will be necessary to get the same color after the patch has dried out.

A wide range of patching materials is available and may be conveniently categorized in the following groups: *(i)* portland cements, *(ii)* other chemical-setting cements, *(iii)* latex modified mortar. Some background to these materials is now given.

Most of these products use high early strength (Type III) cement, and contain an expansive admixture that causes the concrete and mortar to expand either in the plastic stage or after it has hardened. The expansion produced in the plastic state establishes intimate contact with the substrate before it hardens, thus completely filling the space and promoting good bond. Expansion is intended to compensate for the anticipated plastic and drying shrinkage and to maintain a tight bond to the substrate. The expansion produced in the mortar or concrete is usually obtained by the use of an expansive agent such as aluminum powder, coke powder, anhydrous calcium sulfoaluminate, or calcium oxide. The properties of available products spans a range of values as shown in Table 1.[3]

In cool or cold weather, the rate of strength gain is too slow. High early strength (Type III) cement with a mixture of superplasticizing and non-chloride accelerating admixtures are used to obtain rapid setting time and rate of strength gain. Commonly used admixtures for this purpose include, naphthalene or melamine formaldehyde sulfonates and nitrates, nitrites, calcium formate, sodium sulfate or carbonate.

Quicksetting Products. Repairs to areas which are heavily trafficked (roads, bridges, airfields and intersection floors) need to be achieved with the least disruption to traffic, or in the case of industrial floors, to production. Also, faster setting and curing materials are required during cooler periods, or in areas which are subjected to continued cold temperatures such as food freezer floors. A number of unique and specialized patching materials have been developed for such special repair applications.

Table 1. Characteristics of Cementitious Patching Mortar and Concretes *(From Pettit, A. R.,* Plant and Engineering, *11:98, 1972. Used with permission.)*

Property	Range
Expansion at 28 days (%)	0.01–010
24-hour compressive strength (psi)	810–3,900
28-day compressive strength (psi)	5,000–11,600
Flexural strength (psi)	920–1,30
Bond strength (psi)	270–500
Resistance to freeze/thaw	
ASTM C 666 Durability factor (%)	69–90
Setting times (mins)	5–45

High Alumina Cement. High alumina cement patching compounds with accelerated set time and strength gain can be obtained by mixing this cement with the appropriate proportion of portland cement (Fig. 1). High alumina cements are 3–4 times as expensive as Type III cement, but it is not unreasonable to consider them for patching work because they produce a faster rate of strength gain than Type III cement, and are also more resistant to sulfate attack.[4] One serious limitation to their use for structural concrete is the conversion reaction which occurs in the hydrated cements. The initially formed hydrates undergo a morphological change to a different crystalline form and this results in a serious strength reduction.[4][5]

Magnesium Phosphate Cements. These are fast-setting, rapid strength developing materials. Both two or one-component proprietary products are available. In the two-component package, the dry magnesia is mixed with the liquid phosphate in small quantities and worked very rapidly. It usually produces a high strength, low permeability patch with a good bond to many surfaces. However, water will affect hardening, even small amounts producing severe strength reduction.[6][7]

Under normal working conditions (i.e., 22°C) the product will harden in 15 minutes and can be opened to traffic within two hours.[7] Magnesia phosphate products are promoted for all weather use, ranging from below freezing temperature to hot weather conditions (90°F). During hot weather a set-control agent like borax is used to obtain extended set times required for mixing, placing and finishing.[7]-[9] The durability of the material, as measured according to ASTM C 666, has mostly shown positive results. However, there have been conflicting results regarding material placed under near freezing conditions on dam substrates. Some evidence indicates that its permeability may be high enough to jeopardize freeze-thaw durability.[10]-[12]

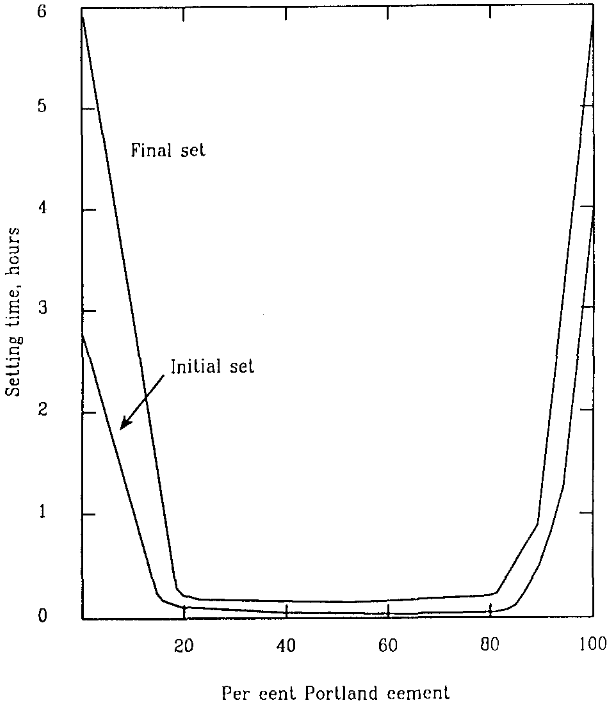

Figure 1. Setting time of mixtures of aluminous and Portland cements. *(From Lea, F. M.,* The Chemistry of Cement and Concrete, *Edward Arnold and Co., London 1970)*

Due to its ability to cure and harden at temperatures at, or below, freezing it appears to be best suited for repair of sliver spalls and popouts, or for emergency work. Typical applications include repairs to bridge decks, commercial freezer rooms, airport runways, industrial floors, highway pavements, truck docks, ramps and stairways. Other features which make it a suitable patching material is the similarity of its coefficient of thermal expansion (7.6 x 10^{-6}/°F) and linear shrinkage value (-0.015%/21 days) to those of portland cement concrete.[5] The use of these materials greatly reduces the duration of interruption of the use of the structure under repair. However, there is a paucity of information about its long term performance in pavement and bridge deck patches and, therefore, this type of material is generally used for temporary repairs.

Calcium Sulfate-Based Materials. Many of the proprietary, rapid setting, patching products are calcium sulfate based. Most contain portland cement in varying amounts; some also contain chlorides. They gain strength very rapidly and can be used in any temperature above freezing. Many have not proved reliable when exposed to moisture and freezing weather.[12][13] These materials can also promote sulfate attack to the surrounding concrete.

Polymer-based materials. Polymer-based materials have found varied use in the restoration of damaged and deteriorated concrete structures. There are two broad classifications of polymer concrete and mortar. The first are materials containing latex emulsions used with hydrating portland cement, and the second are systems without portland cement binder. The latter class of materials do not include cement, they cannot therefore be discussed as admixtures.

Latex-modified mortars include mixtures of portland cement, sand and latex admixtures such as styrene butadiene, polyvinyl acetate, acrylics and epoxy emulsions. The latex is usually used at a level less than 20% by weight of cement in the mixture. Addition of the latex improves the permeability, bond, tensile and flexural strengths. Such mortars can be placed in sections ranging from ½–2" thick in both horizontal and vertical applications such as column and wall repair. The chief advantage of the system is its good workability and ease of application when compared to other similar systems.

Surfaces to be patched with these materials should be thoroughly soaked with water for 12 hours prior to placement of the mortar. All free-standing water should be removed from the surface. Immediately before placing the mortar, the surface should be scrubbed with a 50:50 latex water/cement slurry. Premature skinning of the surface occurs fairly quickly before finishing operations. This may lead to surface tearing during trowelling and subsequent shrinkage crack development.[13][14] Curing and protection of the placed mortar is essential to prevent cracking. The fresh surface should be protected from the sun and left covered for the remainder of the curing time. Full usage of the area can usually be resumed in 72 hours at normal temperatures (20–23°C).

2.2 Grouts

In some instances, specially formulated cement/sand mixtures such as grouts are used for patching. These products usually contain aggregates with a specific gradation, admixtures and other additives to enhance particular properties. Grouts provide flowable consistencies which can be readily pumped into areas that are not readily accessible and where clearances are minimal and where a low likelihood of leaving major voids is needed. Typical applications include void filling, and as a mortar for filling large cracks.

The most important requirement of a grout is that it completely fills the space in which it is placed. Therefore, it must have a negligible shrinkage and remain stable in place, without cracking, delaminating or crumbling.[9] A variety of grouts are in use today which can be classified as follows:[16]-[19]

- Nominal cement-sand mixtures.
- Gas-forming grouts.
- Metallic aggregate grouts.
- Inorganic sulfoaluminate cement or expansive additive-based grouts.
- Fiber reinforced grouts

Gas Forming Grouts. These grouts contain expansion producing ingredients which react with the cement liquor to generate gas bubbles. The gas expands the grout to help compensate for any shrinkage that occurs in the plastic state before the grout has hardened. Vertical and lateral restraints are required to achieve specified strength and volume stability in the hardened stage.[16][19]

Aluminum powder and finely-divided carbon (fluid coke) are used to produce the gas producing reaction.[17] Some of the disadvantages of these products are that they are quite temperature sensitive. Under hot weather conditions the gassing reaction can occur quite rapidly causing the expansion to be dissipated before it can be placed.[15][19] The expansive aluminum flakes and coke particles are susceptible to segregation and flotation if the water content used in the mix is too high.

Sulfoaluminate Grouts. Unlike the gas-forming grouts, most of the expansion produced by sulfoaluminate grouts occurs after the grout has set. Expansion can be produced by a shrinkage-compensating cement (Type K), or an anhydrous sulfoaluminate expansive admixture used with portland cement at a dosage level of 6–10% by weight of cement.[17] The expansion producing reaction occurs when the anhydrous calcium sulfoaluminate (CSA) is converted to the hydrated ettringite. Sulfoaluminate cement-based materials are less prone to strength reduction, due to increased w/c ratios, than the portland cement-based materials. The volume change that occurs with age of the grout is illustrated in Fig. 2, which shows that these types of grouts are sensitive to post-hardened curing; initially achieved expansion could well be lost if there is no moist curing after the grout is placed.

Fiber-Reinforced Grouts. These grouts may have polypropylene, steel or glass fibers dispersed in either a portland cement or shrinkage-compensating mortar. Typical fiber levels can range from 4–6, 2–3, and 2–4% by weight of cement for polypropylene steel and glass fibers, respectively. The fibers impart much improved impact resistance and flexural strengths. Stress required to produce cracking is significantly increased and the integrity of the grout after cracking is preserved, thus preventing a catastrophic type of failure. One of the significant drawbacks of these materials is the segregation of the fibers in the mix when subjected to vibratory compaction; expert handling of the mixes is therefore essential.[6][20]

2.3 Bonding Agents

Bonding agents are natural, compounded or synthetic materials used to join individual members of a structure without mechanical fasteners. These products are often used in different repair applications, such as bonding of new concrete to old concrete, sprayed concrete or sand/cement repair mortar to assist in achieving a reliable bond. Two main types of bonding agents, namely, latex emulsions and epoxies, are frequently used in the building industry. This discussion is limited to latex emulsions. There are a variety of different applications for latex emulsions as bonding agents. Some types have a greater degree of water resistance than others. Table 2 is a comparative chart of the various latex bonding agents used in the industry.

The emulsions generally used in cementitious compositions are of the oil-in-water type, and sometimes contain more than 50% water. Although they are generally stable in the cement/water system, not all emulsions are compatible with cement and the selection of an emulsion for a given application requires an appreciation of the chemistry of the material or alternatively consulting the manufacturer of the product. The following

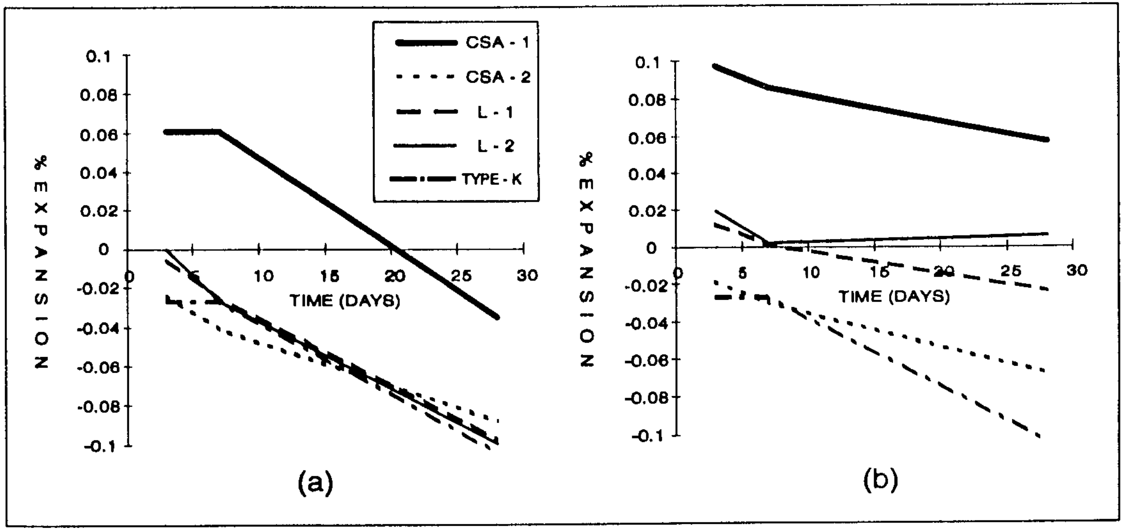

Figure 2. Linear expansion vs time for (a) low dosage and (b) high dosage of expansive admixtures. *(Courtesy Mailvaganam, N., Nunes, S., Bhagrath, R., Effectiveness of Expansive Admixtures in Structural Grout Compositions,* Concrete International, *15(10):38-43, 1993.)*

description of the advantages and limitations of the various types of emulsions used as bonding agents, is intended to serve as a preliminary guide for the user and specifier.

Table 2. Latex Bonding Agents: Comparative Chart *(From Maslow, P., Chemical Materials for Construction, Structures Publishing Co, Farmington, MI, 1974, p. 114.)*

Property/ Test Method	A. Acrylic	B. Polyvinyl-acetate (Non-re-emulsifiable	C. Butadiene-styrene	D.Polyvinylacetate re-emulsifiable
Appearance	Milky white	Milky white	Milky white	Milky white or clear
Solids Content	45.0%	55.0%	48.0%	50.0%
Primary Use	Bonding fresh concrete to old concrete.	Bonding fresh concrete to old concrete Thin layer toppings.	Bonding fresh concrete to old concrete. Concrete admixture. Thin layer toppings.	Bonding to plaster
Application Methods	Brush, broom spray, roller as adhesive; trowel as topping.	Brush, broom spray, roller as adhesive; trowel as topping.	Brush, spray, roller as adhesive; trowel as topping.	Brush, spray, roller
Applications	<—Underlayments, Stucco, grouting-mortar, Terrazzo, Crack Fillers—>			
Cleaning, Surface Preparation	Remove oil, grease; wet surface	Remove oil, grease;	Remove oil, grease;	
Comp. Strength 2" cubes ASTM C109	3200 psi 4100 psi	3400 psi 3600 psi	3300 psi 4000 psi	3200 psi (air) 3000 psi (wet)
Tensile Strength 1" Thick Briquettes ASTM C190	580 psi 615 psi	350 psi 450 psi	450 psi 580 psi	300 psi (air) 410 psi (wet)
Flexural Strength Bar ASTM C-348-61T	950 psi 1,400 psi	1,000 psi 1,250 psi	1,250 psi 1,650 psi	925 psi (air) 750 psi (wet)
Where to Use	Indoor and outdoor exposures; on concrete, steel, wood; guniting; thin section topping. May be used as as plaster bond within 45-60 min.	Indoor and outdoor exposures; on concrete, steel, wood; guniting; thin section topping. May be used as a plaster bond within 45-60 min.	Indoor and outdoor exposures; on concrete, steel, wood; guniting; thin section topping. May be used as a plaster bond within 45-60 min.	Indoor-ceilings primarily. Limited use as concrete bonding agent.
Where Not to Use	Not for extreme chemical exposure. Not for conditions of high hydrostatic pressure.	Not for extreme chemical exposure Not for conditions of high hydrostatic pressure.	Not for extreme accelerators. Not for extreme chemical exposure. Not for constant water.	Do not use as an admixture. Do not use under wet or humidconditions.Do not use at temperatures below 50°C.

Three methods are available by which a latex may be modified to be a useful bonding agent.

(i) Preparing a neat cement slurry utilizing the latex as part of the gauging water.

(ii) The use of a 1:1 water:latex diluted material.

(iii) The use of a re-emulsifiable latex which can be softened and re-tackified upon contact with water.

Method *(ii)* is now discouraged because of the lack of bonding encountered in field applications and laboratory studies which corroborated the field problems. The neat latex produces a failure plane that results from a lack of film formation at the bond interface.[14][21]

Styrene Butadiene Resin (SBR). Styrene butadiene (SBR) latices, which are compatible with cementitious compounds, are copolymers. They show good stability in the presence of multivalent cations such as calcium (Ca^{2+}) and aluminum (Al^{3+}) and are unaffected by the addition of relatively large amounts of electrolytes (e.g., $CaCl_2$). SBR latices may coagulate if subjected to temperature extremes, or severe mechanical action for prolonged periods of time.

Polyvinyl Acetate Latices (PVA). Commercial materials are copolymers manufactured by the emulsion polymerization process. Two main types of PVA's are used in repair: *(a)* non-re-emulsifiable PVA, and *(b)* emulsifiable PVA.

(i) Non-emulsifiable PVA. This PVA forms a film which offers good water resistance, good light stability, and good aging characteristics. Because of its compatibility with cement, it is widely used as bonding agent and a binder for cementitious water-based paints and waterproofing coatings.

(ii) Emulsifiable PVA. These latices produce a film that can be softened and re-tackified with water, permitting application of a film to a surface long before the subsequent application of a water-based overlay. Their use is limited to specific applications where the possible infiltration of moisture to the bond line is precluded.

Acrylic Latices. The resins used are polymers and copolymers of the esters of acrylic and methacrylic acids. They range in physical properties from soft elastomers to hard plastics,[22] and are used in cementitious compounds in much the same manner as SBR latex. They are reported to have better UV stability than SBR latex and, therefore, remain flexible under exterior exposure conditions longer than SBR latex.

Epoxy Latices. Epoxy emulsions are produced from liquid epoxy resin when mixed with the curing agent, which serves additional functions such as an emulsifying and wetting agent and as a surfactant.[18][22] The emulsions are stable and water dilutable from the time of mixing until they gel. Pot life may vary from 1 to 6 hours depending upon the curing agent selected and by adding high amounts of water. Most epoxy emulsions are prepared just immediately prior to use on the job site rather than in the manufacturers plant. This avoids the phase separation that occurs in previously prepared packaged emulsions.

During mixing, equal parts of the epoxy are mixed with equal parts of the curing agent. The mixture is blended for 2 to 5 minutes and allowed to set for 15 minutes for polymerization to begin. Next, water is added slowly while the mixture is mechanically agitated to form the emulsion.

As an alternative to liquid polymer latex, there are now available factory blended powders containing a mixture of cement, spray dried latex powders, sand, and other additives which are simply gauged with water on site and applied to the prepared concrete substrate. The stipple finish obtained provides a good "key" for repair mortar or overlays that are subsequently applied. The grout coat minimizes the loss of water from the overlay to the substrate preventing desiccation of the cement and the resultant poor bond.[18][19] Although the grout coat does provide points of anchorage for bonding, the application of the repair mortar or overlay while this keying coat is still tacky is recommended.[20]

2.4 Resurfacing Materials

Industrial floors in service may be lightly loaded or heavily loaded. While the principles of repairs are similar for both categories, the materials and techniques used may be different . A number of proprietary materials are available for improving wear resistance, or chemical resistance, reduce dusting or improve the appearance of concrete floors. The materials described in this Section are used for the repair and upgrading of industrial floors, where loaded vehicles, such as forklift trucks, traverse the floor surface.

Surface Hardeners. The term *surface hardener* generally refers to a material used to upgrade a floor's wear resistance, reduce dusting and increase chemical resistance. Two main categories are in current use:

sprinkled shake hardeners and liquid hardeners. Shake hardeners produce a special finish that is obtained through the incorporation of selected natural or metallic aggregate into the surface of a newly poured floor.[23][24] Liquid hardeners are materials only applied after the concrete has hardened, they are not considered admixtures and are therefore excluded from this discussion.

The primary objective of this method is to produce a highly finished wearing surface that contains much more aggregate and a considerably less cement paste than a conventional floor. This is accomplished by spreading a mixture of special hard-wearing aggregate and portland cement (called a dry-shake) over the fresh concrete surface at a prescribed rate, after screeding and initial bull floating, and working it with a float machine so that the shake is completely integrated with the surface, or in essence, constitutes the surface. The time of application of the shake to the fresh concrete depends on the material used and the ambient conditions. Shake finishes, require special skills, and should be entrusted only to experienced craftsmen.[23]-[26]

Two types of aggregates are used in shake hardeners, mineral and metallic, the latter being malleable iron obtained from metal borings. The kind of traffic that will operate on the floor should dictate which type of aggregate to use. Metallic floors are generally used in floors where there is continuous steel wheel traffic and point impact. Floors containing mineral aggregate (such as corundum and traprock) tend to be harder, thicker and will not rust.[25] Figure 3 shows a section of a floor incorporating an aluminum oxide (emery) aggregate as the surface hardener. Proprietary products usually contain predetermined mixtures of aggregate/cement in conjunction with conventional or superplasticizing admixtures to aid finishing operations.

Overlays. Concrete overlays may be applied as preventive maintenance on a deck that has been opened to traffic for a short time but was built without a deck protective system, or in the rehabilitation of existing deteriorated floor slabs or decks. Currently available cementitious materials which use admixtures for this method of repair can be categorized as follows:[20][27][28]

1. Superplasticized low slump dense concrete (SLSDC);
2. Latex modified concrete (LMC);
3. High alumina cement concrete and mortar (HAC);
4. Fiber-reinforced concrete incorporating steel or polypropylene fibers;
5. Silica fume concrete.

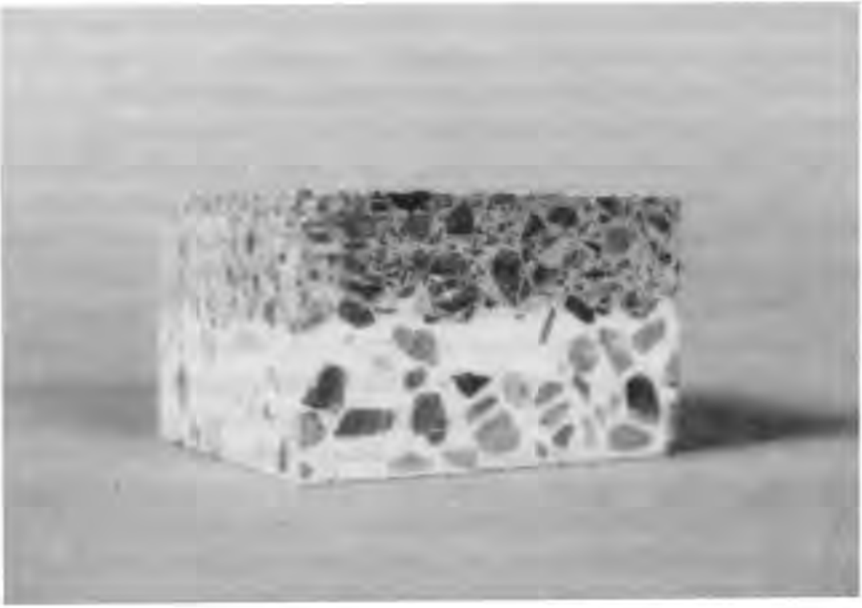

Figure 3. Section of a floor containing Al_2O_3 aggregate as a surface hardener.

Superplasticized Low Slump Concretes and Mortars (SLSDC). Typical overlay mixtures may consist of 1 part portland cement, 1 part fine aggregate, to 1.5–2 parts coarse aggregate by volume. The grading of the aggregate is usually 1/8" to 3/8" and the w/c ratio used ranges from 0.35–0.40. The aggregates for such heavy duty overlays should be selected from clean, hard and irregular or rounded material such as traprock, granite, emery, corundum, or synthetic products like silicon carbide or heat-treated aluminum oxide. A superplasticizer is used to obtain high slump at a low w/c ratio. The higher slump is reported to provide better and more uniform compaction and hydration than the Iowa method.[20][27] Chloride measurements showed that these low slump concrete overlays were effective in reducing chloride ion penetration but were not impervious to them.[24]

Latex-Modified Concrete. Latex modified overlays may be either mortars or concretes. The choice between latex-modified mortar or latex modified concrete is determined by the intended thickness of the overlay. Thicknesses of less than 1" (25 mm) are usually constructed from mortar having 1 part cement to 3.25 parts sand. Aggregate, of maximum size 1/2" (13 mm), is used for overlays greater than 1" (25 mm) thick. Mix proportions of cement:sand:stone are usually 1:2.5:2. The dosage of latex is usually 12–15% polymer solids by weight of cement and the w/c ratio is 0.35 to 0.40. Typical specified slumps are in the range 4–6" (100–150 mm) measured 5 minutes after mixing, and air contents should not exceed 6.5%.[21][27]-[29] The latex should always be maintained at 45°F to 85°F (7–29°C) prior to use.[21]

The water of suspension in the emulsion hydrates the cement, and the polymer enters the structure of the concrete, thereby providing supplementary binding due to the adhesive and cohesive properties of the polymer. In general, this results in concrete having good durability, tensile and flexural strength, properties that are well suited to use in overlays. The structural properties of this type of concrete can vary considerably depending on the type and amount of latex, the type of aggregate, the cement content, and the w/c ratio.[27] As mentioned previously, one of the significant features which distinguishes latex-modified concrete from conventional concrete is the curing procedure. To produce an optimum cure, the initial period of wet curing to hydrate the portland cement must be followed by a drying period in which the latex particles coalesce to form a film.[28][30]-[33] Some of the problems which arise in the use of latex modified concrete are: *(i)* poor finishing characteristics in hot dry weather, and *(ii)* early shrinkage cracking is due to the late application of burlap.[21][26]

Fiber-Reinforced Concrete. Several types of fiber have been investigated but most of the work has focused on the use of steel- and alkali-resistant glass fibers. More recently, polypropylene fibers have been used as a crack-arresting measure in flat slab applications. The addition of steel fiber to concrete results in substantial increase in tensile and flexural strengths. The steel fibers used typically range from 0.010–0.025 inch (0.25–0.65 mm) in diameter, ¾–2" (19–50 mm) in length, and in amounts from 0.3 to 2.0% by volume.[6][20][34][35]

Steel fiber reinforced mixes can be handled and placed using conventional techniques, but mixing problems are encountered when the fibers knot or ball together. The tendency increases as the fiber length , the diameter and the amount are increased. To achieve maximum flexural strength, the mix must be designed to minimize the amount and size of coarse aggregate.[34][35] Chemical admixtures such as superplasticizers provide significant improvement to workability characteristics.

Fibrous concrete has been successfully used for thin overlays on roads and runways and in situations where cavitation or erosion has been a problem, such as on dams, spillways and still basins. Improvements achieved over ordinary concrete include, double the tensile and flexural strength, 1.6 times as much first-crack strength, 9-fold impact strength, and 1.3-times abrasion resistance of normal concrete. However, some studies have shown that fiber reinforced concrete may not provide enduring repairs under conditions where cavitation and erosion occur.[6][20]

Silica Fume Concrete Overlays. Silica fume has been used predominantly as a performance-enhancing admixture in a wide variety of applications where high strength concrete or very durable concrete is required. Recent projects have included high density overlays for parking garage and bridge decks, abrasion resistant concretes for dam spillways and stilling basin, and shotcrete.[36][37] It is a very efficient pozzolan that forms reaction products with lime from hydrated cement and reduces the volume of large pores and capillaries normally found in cement pastes.[38] The second mechanism by which silica fume improves concrete is through the *microfiller effect.* The extreme fineness of silica fume allows it to fill the microscopic voids between cement particles, and the microfiller effect is credited with greatly reduced permeability and improved paste-to-aggregate bond in silica fume concrete compared to conventional concrete.[33][39]

Because of handling difficulties, some admixtures companies in Europe and North America, market silica fumes in a slurry form. Typically, these slurry-admixtures, consisting of 40–60% silica fume by weight, conventional plasticizers, superplasticizers and retarding ingredients, are added to the concrete mix during batching.

The use of silica fume in the dry form normally increases the water demand because of the very high increase in fineness. This effect is counteracted by the addition of a superplasticizer or the silica fume slurry admixtures. Adding 6.5–8% silica fume by weight of cement dramatically reduces the permeability when compared to concrete without silica fume. The improvement makes concretes less vulnerable to attack by chloride and chemicals. Figure 4 presents a comparison of the chloride permeability of silica fume concrete at two levels of silica fume addition with latex modified concrete.

Under average ready mix plant conditions the addition of silica fume to a conventional concrete mix will significantly increase compressive and flexural strengths. Figure 5, for example, shows a concrete mix that normally would give 5,500 psi (38 MPa) in 28 days. Adding 7.5% silica fume by weight of cement and a superplasticizer to maintain a constant water-cement ratio produces a concrete that reaches 9500 psi (65.5 MPa) in 28 days.

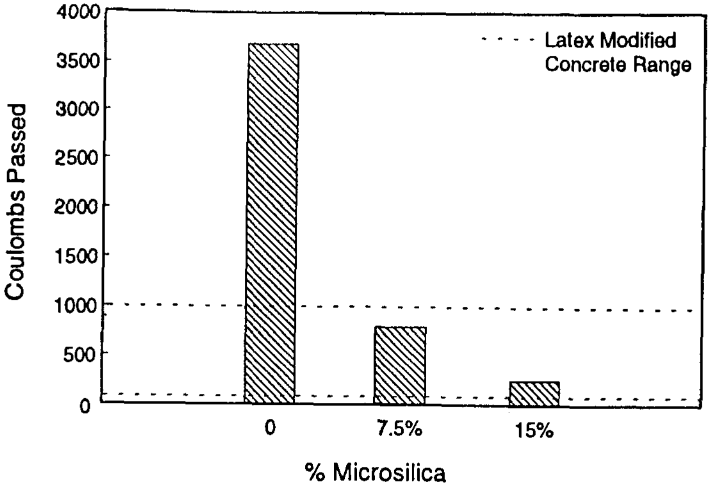

Figure 4. Effect of silica fume on the chloride permeability of concrete. (Type I cement, 550 lbs/yd^3, W/C ratio 0.37.) Test: AASHTO T227-831.

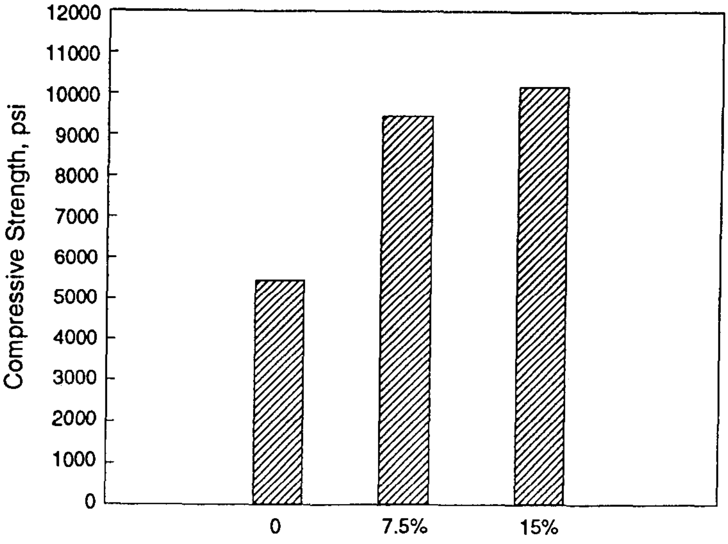

Figure 5. Effect of silica fume addition on the 28 days compressive strength of concrete. (Type I cement, 550 lbs/yd^3, W/C ratio 0.45.) Test: AASHTO T227-831.

Adding silica fume to concrete as a slurry, affects the rheological or flow properties of the mix virtually eliminating bleed water. This requires close monitoring of the surface of the concrete to prevent premature drying which could lead to plastic shrinkage cracks. In most cases, the concrete will need to be treated with a film curing membrane or misted with water to prevent premature drying.[36][37] Therefore, careful attention to curing is essential. Although the mix is more cohesive and sticky than conventional concrete, it is quite moldable and can be placed with a concrete pump at lower pumping pressures.

3.0 CONCRETE INFILL

Concrete is most often used for complete replacement of sections and deep cavities extending beyond the reinforcing bars, while mortar can be used for cavities as small as 1–5".[6][20] Mortar can be placed by hand, gravity or pump, and is generally used in applications where the repairs are too shallow for the coarse aggregate present in concrete and where the fluidity of grout is not required. Special proprietary mixtures are available that are based on portland cement and contain a hard mineral or metallic aggregates to increase the resistance of floors to heavy traffic.

The concrete should have low permeability to moisture, carbon dioxide, chlorides and other depassivating agents. In addition, the concrete should contain the proper air void parameters necessary to resist damage due to freeze/thaw action. Chemical admixtures can play a pivotal role in providing specific modifications to bulk concrete so that proper placing, compaction, and enhanced durability is obtained.

Conventional admixtures are widely used in replacing defective concrete. The main types used to augment durability characteristics in repair work include air entraining agents, retarders, accelerators, and superplasticizers. Other admixtures, such as corrosion inhibitors, integral waterproofers, anti-washout, and freeze-prevention admixtures, are used for specific applications or to offset the limiting conditions (such as cold or hot weather concreting) prevailing during the repair. These applications are discussed under the miscellaneous or special admixtures Sec. 3.3.

3.1 Conventional Admixtures

Air-entraining Admixtures. These are usually salts of wood resins or synthetic surfactants typically used at rates of 0.002–0.6% by weight of the cement content based on the active constituents of the admixture. At these dosages, they produce 5–6% air in concrete with average cement content and 3–4" slumps. Concretes with air contents of 5–8% will achieve the air void parameters (such as bubble spacing, bubble size and specific surface) required to increase the resistance of freeze-thaw action.[40]

Air-entrainment, materially alters the properties of both fresh and hardened concrete. The fresh concrete is more plastic and workable than non-air-entrained concrete. The concrete strength may be reduced somewhat by air entrainment, but the durability of the hardened concrete is improved considerably. A number of factors (such as, mix parameters and ambient temperatures) affect the amount of air-entrained and the air-void parameters. It is, therefore, important to have close control of the quality of the concrete mixes, as well as concreting operations under adverse ambient temperature conditions.

Non-Chloride Admixtures. The use of calcium chloride as an accelerator to offset the effects of cold weather has been widely cited as one of the chief sources of reinforcement corrosion. Its use, is now severely restricted in North America, and banned in the United Kingdom and continental Europe.

Use of accelerators that are not based on chlorides, reduces the serious risk of reinforcement corrosion by maintaining the chloride ion threshold above which corrosion does not occur.[3][17] A number of organic and inorganic salts are currently marketed as non-chloride accelerators. These include: formates, thiosulfates, alkali sulfates, nitrites, nitrates and thiocyanate. Although these admixtures satisfy the requirement of being non-chlorides, some are reported to produce corrosion.[41][42] The use of silica fume (8–10% by weight of cement in the mix) in conjunction with a superplasticizer has shown that strength development can be accelerated to offset the retarding effect of low temperature on strength development.[37][42]

Retarders and Water-Reducing Retarders. The main use of retarders and water-reducing retarders in repair is for the purpose of providing adequate working time for placing and finishing operations, so that tearing of the concrete surface is minimized. They help to eliminate cold joints and other discontinuities when concrete is placed in layers by enabling adjacent layers to be vibrated into each other. Since setting governs the optimum time at which concrete can be re-vibrated, the slower the set the more effectively can concrete be re-vibrated at later ages without loss of strength.[43] Figure 6 illustrates this effect.

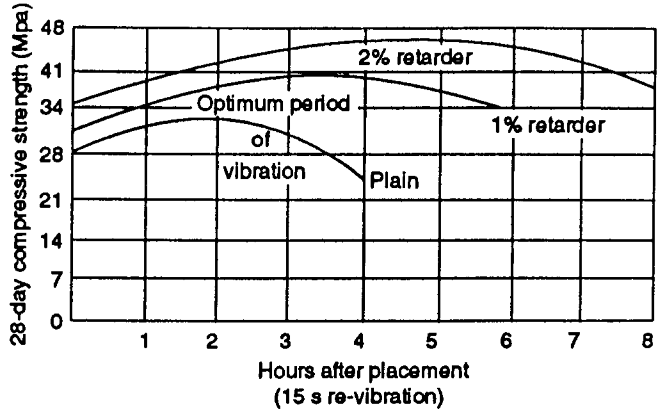

Figure 6. Extension of re-vibration time of concrete using various dosages of a retarding admixture. *(Courtesy R. J. Schutz)*[43]

The placing of large volumes of concrete in successive layers is done in the repair of bridge piers and bridge decks. The repair may involve pours as large as 3000–4000 m^3 of high strength concrete. Consequently, the potential for development of damaging internal stresses in reinforcement or cracks in the structure is increased. Water-reducing and retarding admixtures are used to offset such stresses so that pours of large magnitude can be placed without adverse effects. Although water-reducing retarders themselves will not lower the total heat evolved, the lower cement content, made possible by their use, decreases heat generation and temperature rise. Furthermore, the retardation of hydration that results from the use of these admixtures, delays the liberation of heat and reduces the peak temperature attained during hydration.[44][45]

In the repair of bridge decks, the use of a retarding admixture produces uniformity in the rate of setting and lessens the risk of deflection in the partially hardened concrete that may occur in continuously reinforced structures. The retarded concrete poured over the supports remains plastic until the final pours are placed at mid span.

Repairs to continuous girder bridges is another area where set control plays an important role. The weight of the concrete as it is successively placed on the decks deflects the girders causing the partially hardened concrete to crack. Conventional concreting procedures consists of placing alternate panels so that a positive moment results (Fig. 7). The method is time intensive and costly to the contractor since finishing operations are intermittent and also involve periods of waiting for the concrete to achieve adequate strength. The use of retarded concrete allows deflection to occur while the concrete is still plastic and capable of deforming. Thus, no cracking occurs and finishing operations can follow the pour sequence.

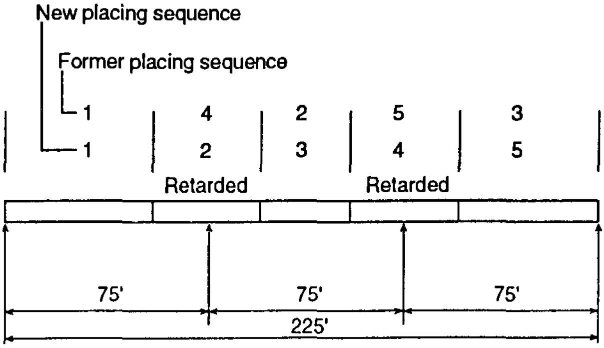

Figure 7. Concreting sequence for continous bridge deck. *(Courtesy R. J. Schutz)*[43]

3.2 Superplasticizers

These are synthetic chemicals (copolymers) which cause the cement particles to be more evenly dispersed, releasing water that otherwise would be trapped within the agglomerates of cement. The dual effect of this action is a marked reduction in the water content required to achieve the desired workability, and more rapid hydration of the cement particles. Superplasticizers can be used to reduce water contents by up to 30%. Consequently, a more dense and impermeable concrete, with a greatly reduced potential for shrinkage and cracking than normal concrete, is obtained. These characteristics of superplasticized concrete ensure that the ingress of damaging moisture, gases and chemicals is greatly retarded, and the protective alkaline environment endures for longer periods.

The admixtures are used at high dosages, for example, the 40% naphthalene formaldehyde-based solution, at a range of 0.6–1.3% by weight of the cement content, and the 20% solids melamine formaldehyde-based materials, at 1.5–3.0%. They are widely used in repair applications where poor access or under water concreting dictates the use of special techniques such as tremie or preplaced aggregate concrete.

3.3 Miscellaneous/Special Admixtures

Corrosion-Inhibiting Admixtures. The protection offered to the reinforcement by the highly alkaline concrete may be increased by the use of corrosion-inhibiting admixtures. A corrosion-inhibiting admixture is a chemical compound which, when added in small concentrations to concrete or mortar, effectively checks or retards corrosion. These admixtures can be grouped into three broad classes, anodic, cathodic, and mixed, depending on whether they interfere with the corrosion reaction preferentially at the anodic or cathodic sites or at both sites.

The most widely used anodic inhibitors are calcium/sodium nitrite, sodium benzoate and sodium chromate. Calcium nitrite and organic-based inhibitors are available in North America as proprietary products. Calcium nitrite is marketed as a non-chloride accelerator, as well as a corrosion inhibitor. For the 25–30% solids in solution, dosage rates range from 2–4% by weight of cement depending on the application.[17] It has been used in bridges, parking and roof decks, marine and other prestressed concrete structures that are exposed to chloride attack. Sodium benzoate has been used in the U.K. in concrete structures exposed to severe corrosion attack and also in combination with sodium nitrite in cement slurries to paint on steel reinforcement before embedment in concrete.[17]

Advantages claimed over sodium nitrites include reduced leaching, efflorescence and potential for reducing alkali/aggregate reaction.[3][17] The corrosion-inhibiting effect produced by calcium nitrite in concrete is shown in Fig. 8. It can be seen that the control of the effects of corrosion is dependent both on the level of chloride ion present at the vicinity of the reinforcement as well as the dosage of the admixture. Sodium nitrite, a fine, free-flowing powder, has been used effectively in the absence of chlorides in both normal and steam-cured concretes at dosages of 1–2% by cement weight. If inadequate quantities are used or if the ratio of the inhibitor to the chloride level is small, corrosion becomes intensely localized and the attack is significant, causing sever pitting. Thus, their use is restricted due to this effect and to the ready leaching which renders the protection a stopgap measure.

Commonly-used cathodic inhibitor materials are bases, such as NaOH, Na_2CO_3, or NH_4OH which increase the pH of the medium and thereby also decrease the solubility of the ferrous ion. Others consisting of aninline and its chloroalkyl- and nitro-substituted forms, as well as the aminoethanol group, are used at 1–2% dosage levels by cement weight in the presence of 1–2% $CaCl_2$.[17] Inorganic salts such as NaOH, Na_2CO_3 and NH_4OH are generally used at a dosage of 2–4%.

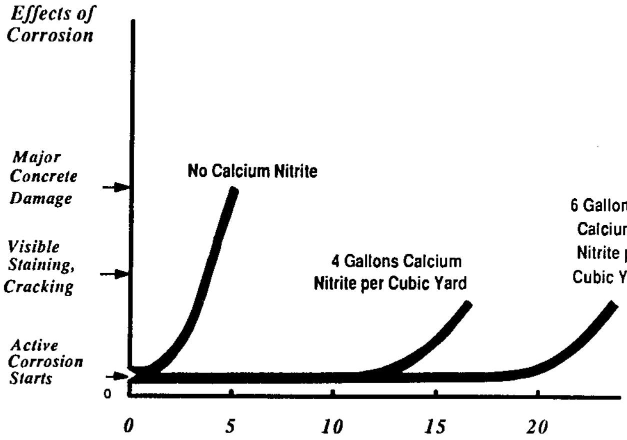

Figure 8. Chloride ion content of concrete at the rebar (pounds of chloride ion per cubic yard).

Mixed inhibitors may simultaneously affect both anodic and cathodic processes. A mixed inhibitor is usually more desirable because its effect is all-encompassing, covering corrosion resulting from chloride attack as well as that due to microcells on the metal surface. Mixed inhibitors, contain molecules in which electron density distribution causes the inhibitor to be attracted to both anodic and cathodic sites. The molecules may have more than one orienting group attached, e.g., NH_4 and SH. Mixed inhibitors are similarly used at 1–2% addition rates.[17]

Admixture formulations containing two or more compounds (multi-component) in which each component plays a specific role or compliments the corrosion resistance capacities of the other are also used. Mixture of calcium nitrite together with calcium formate is used to both accelerate strength and inhibit corrosion during steam curing.

It is important to ensure that when using corrosion inhibitors with other conventional admixtures, they are added separately, at different times of the mix cycle. Corrosion inhibiting admixtures which also accelerate the set of concrete may require the combination of a retarding admixture when ambient and mix temperatures exceed 35°C. In like manner, set-retarding corrosion inhibitors may require the addition of an accelerator to offset the retardation of early strength development (use of sodium nitrite in conjunction with sodium benzoate). Details on corrosion inhibitors are presented in Ch. 14.

Calcium Sulfoaluminate and Lime-Based Expanding Admixtures. Two types of admixtures, calcium sulfoaluminate (CSA) and calcium oxide (lime) based admixtures have provided a means of offsetting volume changes due to hardened shrinkage. Shrinkage compensation is obtained at lower addition rates, while chemical prestressing of the reinforcement is achieved at higher dosages. Although the types of reactions that generate the expansive force and the magnitude of expansion are different in CSA and lime-based admixtures, the effects produced in concrete and mortar, factors affecting the reaction and application are not different.

For use in special fields of construction such as structural grouting and repair of columns, the anhydrous calcium sulfoaluminate is combined with two or more of the admixtures listed below:

- A dispersing admixture.
- A gas liberating agent, e.g., Al powder or fluidized coke particles.
- A powdered acrylic latex to increase bond strengths.
- Mortar density-increasing or decreasing-ingredients such as barytes or bentonite.

The deformation that accompanies expansion as strength increases, introduces compressive stresses into the concrete, which reduce the tensile stresses induced by drying shrinkage. Consequently, both cracking and contraction that occur on drying are reduced. Although, the mechanism of expansion is the same as above for multicomponent admixtures, the rate and extent of expansion is also determined by the resulting modification produced by other components in the admixture. Expansion in the lime-based system is due to crystal growth and the pressure that results when CaO particles hydrate to form $Ca(OH)_2$.

The water requirement for equal slumps is generally higher for concretes containing these admixtures and they show significant reduction in bleeding.[17][46] When used at lower dosages (6–8%), they do not entrain any significant amount of air. However, at increased dosage levels, there is a tendency for foaming. Since concrete mixes containing CSA and lime admixtures show increased cohesion and a reduced bleeding, finishing operations should occur sooner than for portland cement concretes. Due to the lack of bleed water, conditions that promote rapid moisture loss may cause plastic shrinkage. Precautionary procedures detailed in ACI 614-59 should be followed for satisfactory results.

Physical properties such as compressive strength, creep, modulus of elasticity and durability of CSA and lime admixture-containing concretes are comparable to those of corresponding portland cement concretes, especially when dosages are within a range (8–11% CSA and 6–7% lime). When the dosage exceeds the ranges mentioned above, no restraint is provided either internally (by reinforcement) or externally, a point is reached when the expansion will have a disruptive effect on mechanical properties. The admixtures produce most of the expansion at early ages of wet curing. Subsequently, on exposure to lower relative humidity levels as in air curing, a gradual decrease in the amount of expansion occurs with age. Depending on the extent of expansion achieved in the curing period and the rate of shrinkage soon after water curing ceases, significant contraction can occur.[46] Expansion increases with dosage and the effectiveness in controlling shrinkage will be influenced by the degree of restraint present during expansion.

Dampproofing and Waterproofing Admixtures. The ingress and migration of moisture in liquid and vapor can be prevented or retarded to varying degrees. Treating of concrete to retard, not stop the absorption of water or water vapor by concrete or to retard their transmission through concrete is considered to be *dampproofing.*[3][44] Treatment of a surface or a structure to prevent the passage of liquid water under hydrostatic pressure is called *waterproofing.*[3] The positive prevention of the ingress and movement of water under pressure distinguishes waterproofing from dampproofing.

Dampproofing can be achieved in three ways, *(a)* by treatment of the surface, *(b)* by the use of a hydrophobic cement, or *(c)* incorporation of an integral waterproofing admixture in the concrete mix.

Reducing the transmission of water vapor through concrete without stopping it entirely, is a desirable feature. In situations where the concrete contains moisture, a dampproofing treatment, permits the concrete to breathe allowing the water to escape in the form of vapor. Because of its limited effectiveness, dampproofing should be replaced by waterproofing under the following conditions:[3]

- If there is a likelihood that the treated concrete may later develop cracks.
- If the concrete is subjected to a head of water at a later stage.

Integral waterproofing admixtures are often used to restrict or reduce the rate of transport of moisture. An integral waterproofing admixture is a powder, liquid or suspension which, when mixed with fresh concrete, results in *(a)* reduction in the permeability of cured concrete, and/or *(b)* imparts a water-repelling or hydrophobic property to the hardened concrete. The mechanism by which penetration of water is reduced is shown in Fig. 9.

Admixtures that reduce the permeability of concrete (termed *waterproofing)* are effective in reducing the transport of moisture under pressure; whereas materials that impart water repellency *(dampproofing)* may reduce moisture migration by capillary action. Most dampproofing admixtures are ineffective in reducing water passage under a positive hydrostatic head. Dampproofing and waterproofing admixtures may be grouped in accordance with their physical and chemical characteristics as follows.[17][47]

(a) Water-repelling materials including soaps and fatty acids (which react with cement hydrates), and substances like wax emulsions;

(b) Finely divided solids which are inert pore-filling materials;

(c) Chemically reactive, finely-divided solids;

(d) Conventional water-reducing, air-entraining and accelerator admixtures;

(e) Miscellaneous, e.g., methyl siliconates;

(f) Hydrophobic blocking ingredient.

Materials in group *(a)* are dampproofing admixtures, while materials in groups *(b)*, *(c)*, and *(d)* are more effective in reducing the permeability of concrete and are, therefore, designated waterproofing admixtures.[47]

The most widely used water-repelling materials in group *(a)* are the calcium or ammonium salts of fatty acids such as stearates. Finely-divided solids may either be inert or reactive with the cement hydrates. Reactive materials include some silicates, finely ground blast furnace slag, and pozzolanas such as fly ash and diatomaceous earth. Inert materials used are fullers earth, talc, bentonite, and other siliceous powders. Sodium methyl siliconate solutions have been used in limited quantities in the USA for bridge deck resurfacing, but more widely in Russia. Although absorption of water is significantly reduced, this admixture extends setting significantly.[17]

Proprietary products are available both as dry powders and liquids. Usually, a stearate soap is blended with talc or fine silica sand and used at the prescribed dosage per weight or bag of cement. In commercial liquid preparations, the fatty acid salt (soap) content is usually 20% or less, the balance of the solid material is made up of lime or $CaCl_2$. Some proprietary admixtures combine two or more admixtures (e.g., stearates and non-chloride admixtures) and may be regarded as multifunctional. The object of such composite mixtures is to effect a reduction in permeability and impart dampproofing qualities without the strength reduction that occurs at early ages when soap-based materials are used.

More recently, a waterproofing admixture called Hydrophobic Blocking Ingredient (HPI) based on two principal components, reactive aliphatic fatty acids, and an aqueous emulsion of polymers and aromatic globules has been introduced to North America. The system has been widely used in Australia and Asia to combat severe marine and soil sulfate conditions. Both types of admixtures increase the resistance to water penetration, either by acting as pore fillers or by creating a hydrophobic coating within the pores or by combining both effects. A twenty year track record is claimed for the product.[48]

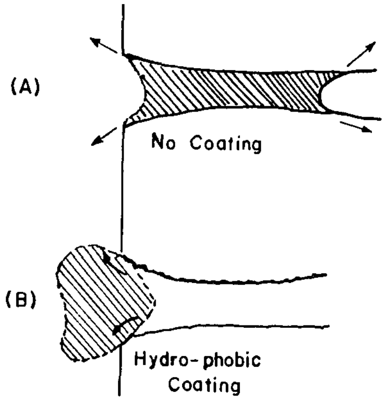

Figure 9. Mechanism by which water penetration into concrete is reduced. (A) concrete with no admixtures, and (B) concrete containing and integral dampproofing admixture.

Alkali-Aggregate Expansion Reducing Admixtures. The possibility of using chemicals to reduce expansion was first suggested in the early 50's. Because of limited laboratory and lack of field data pertaining to the use of these admixtures, no meaningful practice was formulated at that time.[49] However, due to the depletion of good aggregate sources, and the increased incidence of damage to large concrete structures resulting from this reaction, there has been a resurgence of interest in the development of a chemical to reduce the expansion caused by alkali-aggregate reaction. More recently, Japan has used these chemicals in the manufacture of precast elements and in a limited number of structures.

Materials that have been studied include proteinaceous air-entraining agents, aluminum powder, copper sulfate, sodium silicofluoride, alkyl alkoxy silane, lithium carbonate, lithium fluoride, styrene-butadiene rubber latex, lithium hydroxide and water reducing and set retarding agents. The expansion of concrete containing reactive limestone aggregate could be reduced by adding lithium and ferric chloride.[1] Any chemical that is used should not only reduce expansion but also not adversely affect other concrete properties such as setting times, mechanical characteristics and durability.

Treating the reactive aggregate with calcium phosphate prior to its use in concrete has been tried as a method of countering the alkali-silica expansion. This method was less effective for concrete containing reactive carbonate aggregates.[50]

Details of the alkali-aggregate expansion reactions are described in Ch. 14.

4.0 SPECIAL REPAIR TECHNIQUES

In certain situations, repair work may have to be carried out under limiting conditions, such as adverse weather, restricted access to the work area, rapid turn around time, etc. Under these conditions, special repair materials and techniques are used to facilitate repair work not readily performed with normal techniques. In such applications, specific admixtures and combinations of one or more admixtures are used to enhance placing characteristics without seriously affecting structural and durability properties of the placed concrete. Some of the methods used in this category of special techniques are discussed below.

4.1 Underwater Repair

Preplaced Aggregate Concrete (PAC). Preplaced Aggregate Concrete (PAC) is produced by first placing graded coarse aggregate in forms and then filling the voids in the aggregate mass with grout mixture. It differs from ordinary concrete in the manner of manufacture, the proportion of aggregates used in the mix and in cement requirements. Normal compressive strength values range from 2500 to 7000 psi (17–48 MPa) and densities generally are higher than normal concrete, ranging from 142–155 lbs/cu.ft. (2270–2480 kg/m^3).[3]

PAC was originally developed for structural repairs, primarily because of its low setting shrinkage, reduction in drying shrinkage due to point to point contact of the preplaced aggregate particles, and good bond to existing concrete. It has been used in many different applications such as underwater concreting, mass concrete structures, repair of tunnel linings, underpinning foundations, resurfacing of dams, repair of piers, and spillways, and for intruding high density aggregate for radiation shielding.[3] The method lends itself to use in vertical or overhead structures, and can be produced as readily underwater as above ground, in thick or thin sections. It is particularly useful for repair in locations where only a minimum of construction equipment can be used or where placing conditions are difficult, such as underwater concreting and also where a low volume change is required.[50][51] Since this is a specialized type of construction it is important that well qualified personnel, experienced in this method of construction, carry out the work.

The primary function of the grout is to fill voids in the coarse aggregate, to bind them together upon hardening and to consolidate the entire mass. The quality of PAC concrete depends on the use of a grout mixture which is cohesive, workable and develops sufficient strength in the hardened state. Grout mixtures consist of cement, sand (ratio of 1.6 by mass), supplementary cementing materials (fly ash and slag), water and admixtures.[52][53] Fly ash and slag have been used to replace between 30–50% of the cement, and these materials contribute to reduced heat evolution, impermeability, higher ultimate strength and erosion resistance. Chemical admixtures provide air entrainment, delayed setting, increased flowability and homogeneity of the grout, lower water cement ratios, reduction in setting shrinkage and expansion of the grout.

Tremie Concrete. The most widely used method for placing concrete underwater for the repair of bridge piers and dams, is by tremie. A tremie consists of a vertical pipeline, topped by a hopper, which is long enough to reach the lowest point to be concreted from a working platform above the water.

The quality and strength of tremie concrete is greatly dependent on proper mix design and placement. Concrete poured in this manner usually has poor edges and much laitance. Flow problems can be encountered, extending the placing time and causing gravel pockets due to the need to lift the pipe to facilitate concrete flow. Cohesiveness and flow properties are greatly improved by using admixtures.[54][55] Previous work showed that a combination of water-reducing and air-entraining admixtures enhances uniformity of the placed concrete. More recently, the use of superplasticizers in conjunction with cohesion-inducing agents such as antiwashout admixtures and silica fume has superseded the use of conventional admixtures in this application.

Concreting with Antiwashout Admixtures. Dewatering of hydraulic structures for repair is difficult and expensive. Recent advances in cohesion-inducing admixtures have allowed placement of concrete under water without the use of conventional tremies. The concrete is cohesive enough to allow limited exposure to the water, yet has good mobility to move underwater with little loss of cement. Such cohesion inducing admixtures are referred to as antiwashout admixtures (AWA's).

Most AWA's are composed of water soluble cellulose ethers or water soluble acrylic-type polymers as the main component.[56] The action of admixtures is to increase the viscosity of water in the mix. This results in an increased thixotropy of the concrete and an improved resistance to segregation. Dosage of the admixture ranges from 1–1.5% by weight of the water in the mix and it is frequently used in combination with a superplasticiser.[57] The magnitude of the effect produced is dependent on the admixture dosage and the molecular weight of the main component. It is usually discharged into the mixer at the same time as the other materials.

Typical applications of AWA is in the production of non dispersible colloidal underwater concrete. Minimum w/c ratios range from 0.36–0.40. Cement and fine aggregate contents are usually higher than corresponding mixes placed on land. Silica fume may be used in conjunction with a superplasticizer or conventional water reducers to reduce segregation. Often it is difficult to adjust the mixture proportions to achieve desired design parameters for all properties of concrete. Consequently, the properties of colloidal underwater concrete are controlled by the addition of three chemical admixtures. The key to a non-dispersible concrete with self leveling characteristics is the successful optimization of the AWA with the superplasticizer used to increase the slump.

Non-dispersible concrete can be poured into a water filled form without a tremie pipe to produce dense structural repairs. This type of material has particular advantages over conventional concrete both in terms of the quality of the repair produced and the reduction in placement cost.

4.2 Shotcrete

Pneumatically applied concrete containing a maximum coarse aggregate size of 10 mm is usually termed *shotcrete.* It can be applied by either a *dry mix* or *wet mix* process. The dry mix process involves premixing of the cement and sand, and transferring through a hose in a stream of compressed air. The end of the hose is equipped with a suitable nozzle at which point water is injected and mixed with the material as it exits at high velocity. The water content can be adjusted at the nozzle, and is restricted to approximately that required for proper hydration. Set-accelerating admixtures normally in the powder form are introduced into the premix, whereas a liquid accelerator is added to the water at the discharge nozzle or, as a separate injection at the nozzle. Steel and other fibers are usually incorporated in the premix.[58]

The high impact force at which the material is applied compacts it to form a dense concrete possessing very high bond strength. Compressive strength values can range from 35–50 MPa (5075–7250 psi) depending on the degree of rebound, hydration, and the dosage of the accelerator used. In general, strength reduction occurs with an increase in admixture dosage.[17][59] The range of aggregate-cement ratio in the mixes that can be sprayed is limited, and that typically used in repair work is 3.5:1 to 4:1 by weight. Mixes for the dry process are conveniently obtained from bagged premixed cement and aggregate with or without accelerating admixtures. The process is particularly suited to restoration work that requires the replacement of concrete that has been lost or cut away, and to insure against future damage by adding a further layer of concrete.[59] Since low w/c ratios are used, the *no-slump* characteristic affords it to be placed in layers of limited thickness on vertical and overhead surfaces.

In the wet process, a predetermined ratio of cement, aggregate and water is batched, mixed, and transferred to a pump. The concrete is pumped along a flexible hose to a discharge nozzle from whence it is projected at high velocity on to the surface to be coated. A rapid setting admixture like sodium aluminate or metasilicate solutions is commonly added at the nozzle to enable build up of thick layers.[59] Here, the nozzleman controls the placing of the material only, the mix proportions being determined at the batching stage.[59] Wet process shotcrete is probably more suited to the application of large quantities of material, typically in new construction. Because of the tendency to sag, and greater shrinkage potential due to higher water contents, a diminished bond to reinforcement is produced. Accordingly, the wet process is less suited to, and has therefore been seldom used for restoration work.

The advantages of shotcrete include the ease of placing, the excellent bond, and relatively low shrinkage. One of the disadvantages and limitations of the process is that it requires specially-trained workers and is difficult to control. Hence, quality is dependent on the workmanship. The method can be used in a variety of applications except in areas of poor access and is unsuitable for use where congested reinforcement is present.

4.3 Cold and Hot Weather Repairs

For construction purposes, cold weather constitutes a period when the prevalent mean temperature drops below 4.5°C (40°F).[3][60] Hot weather is any combination of temperature in excess of 32°C (90°F), low relative humidity, and wind velocity that tends to impair the quality of the plastic and hardened concrete. Repair materials, placed when cold and hot weather conditions prevail, are subject to damaging temperatures and drying winds that adversely affect set-times, increasing the potential for cold joints; at low temperatures, the rate of strength development is seriously retarded and the potential for frost attack is increased. The adverse effects of both cold and hot weather can be countered and offset by the use of admixtures and the implementation of controls during the repair. RILEM committees on cold and hot weather concreting in recognizing the use of antifreezing and extended set retarders respectively, attest to the usefulness of these materials.

Repairs Under Cold Weather Conditions. Accelerating admixtures offset set extension and slow strength development. Depending on the dosage used, non-chloride admixtures enable concrete and mortar to be placed at subfreezing temperatures (-6.7°/20°F) and reduce protective measures required for cold weather work. In addition, early strength development permits earlier stripping and reuse of forms and, hence, completion of work. Tables 3 and 4 show the set-time modification and strength performance of a non-chloride and freeze-prevention admixture.[60]

When concreting is carried out under more drastic Arctic weather conditions, special admixtures which affect the physical condition of the

Table 3. Setting Time Performance of a Non-chloride Accelerating Admixture *(With permission from* Shotcreting, *American Concrete Institute, SP-14, 1966.)*

Mix	Cement (lb/yd^3)	Time of Set Initial Set (h:min)	Comparison (h:min)
Plain	422	12:35	Ref.
NCAA @ 10 oz/112 lb*	422	10:50	-1:45
Plain	518	10:40	Ref.
NCAA @ 10 oz/112 lb*	520	7:45	-2:55
Plain	603	8:55	Ref.
NCAA @ 10 oz/112 lb*	600	7:05	-1:50

Note: NCAA = Non-chloride, accelerating admixture, concrete temperature = 50°F, ambient temperature = 50°F, slump = 6 1/2 in., air content = 1.5 ± 0.3%.

* 10 oz/112 lb = 296 cc/50.80 kg

Table 4. Setting Time and Strength Performance for New Freeze Protection Admixture

Mix	Plain	Class 4 Admixture
Dosage, oz/cwt	----	60
Cement, Type I lb/yd^3	725	726
Slump, in.	8 1/2	8 1/4
Air Content, %	0.9	1.5
Time of set @ 25°F		
Initial set, h:min	11:55*	5:45
Comparison, h:min	----	-6:10
Compressive Strength, psi		
3 d @ 25°F	490	1340
7 d @ 50°F**	1200	5700
28 d @ 50°F**	2620	7240

Note: Concrete Temperature + 73°F, ambient temperature = 25°F

* Petrographic examination indicated evidence of freezing in the plastic state.

** Strength of specimens cured for 3 d at 25°F, then cured at 50°F until tested.

mix water are used. Antifreezing admixtures are capable of depressing the freezing point of water in concrete considerably, so that their use is of practical significance. Improved cohesiveness, plasticity, minimization of cold joints and sand streaking are some of the advantages. They have been widely used in the former Soviet Union at temperatures as low as -30°C, facilitating earlier stripping and use of forms, earlier completion of construction projects and occupancy. Considerable cost benefits are realized in the fabrication of precast elements, for patching and repairs, foundation work, and slabs on grade for garages.

The mode of action of the antifreezing admixture is two fold:[62]

- To lower the freezing point of water in concrete and act as either a weak accelerator or retarder of setting and hardening. The admixtures that are used for this purpose include sodium nitrite, sodium chloride, weak electrolytes and organic compounds such as high molecular weight alcohols and carbamide; or,
- To accelerate significantly the setting and hardening with good antifreezing action. In this group belong chemicals such as calcium chloride, sodium nitrite, calcium nitrite-calcium nitrate and urea.

Generally, larger dosages of antifreezing admixtures are used compared to chemical admixtures. For example, with 8% sodium nitrite, 50% of water will still be in the liquid state in concrete at a temperature of -15°C. Premixed dry mix mortars with this product can be used at -5°, -15° and -20°C.

Although antifreezing admixtures have been used extensively in the former USSR, much more data has to be generated from their use in Europe and North America before these admixtures can be used on a regular basis. The admixtures are expensive because they are used in higher dosages. The hardening rate is sometimes too slow, the accelerating rates may be affected by plasticizers, compatibility with other normal admixtures as well as their effect on long term durability has to be established for each mix and curing regime.

When concrete is to be placed in cold weather, it is preferable that accelerators or antifreezers be used in combination with air-entraining agents and water-reducing admixtures. This not only reduces the amount of freezable water in the mix, but also generally reduces the quantity of antifreezers and accelerators needed to obtain desired effects compared to the amounts that have to be used when these are used separately. In addition these combinations may be useful in increasing the resistance of concrete to frost action and to corrosive agents. The application of antifreezing admixtures is described in detail in Ch. 11.

Repairs Under Hot Weather Conditions. Retarding admixtures compensate for adverse effects under hot arid weather conditions where temperatures in excess of 35°C prevail. They help overcome the damaging accelerating effects of high temperature. These admixtures lengthen the permissible period for vibration between batching and placing by an extension of vibrational limit of the concrete (Fig. 6).[43] As an operational procedure therefore, it is an advantage in such pours to use retarding admixtures, since the inevitable delays will not necessarily result in the discarding of concrete that is produced by rapid consecutive batching. If a pour is to be halted either by operational problems or by design, the last layer placed before the interruption can be further retarded by the use of larger dosages of the admixture, thus eliminating the need for construction joints.

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14

Alkali-Aggregate Expansion and Corrosion Inhibiting Admixtures

V. S. Ramachandran

1.0 ALKALI AGGREGATE EXPANSION INHIBITING ADMIXTURES

1.1 Introduction

In the 1920's and 1930's, several structures built in California, USA, developed severe cracking within a few years of their construction. In 1940 Stanton demonstrated that the alkali-aggregate expansion reaction was the main cause for such deterioration.[1] It was shown subsequently, that in these concrete structures, a combination of high alkali cement and opaline aggregate was used. The cracking of concrete due to alkali-silica reaction was also recognized in many other countries. In 1957, another deleterious expansive reaction known as alkali-carbonate reaction was reported by Swenson.[2] Since then, several international conferences have been held to discuss concrete failures resulting from alkali-aggregate expansion in many parts of the world.

The alkali-aggregate expansion (AA) involves chemical interaction between alkali hydroxides, usually derived from cement and reactive components in the aggregate particles. In addition to alkali-silica and alkali-carbonate expansion reaction, a third type referred to as alkali-silicate reaction in concrete containing argillite and greywacke has been proposed, and this reaction is generally slow and the mechanism is not completely worked out.

Several publications have appeared describing in detail the possible mechanisms of the alkali-aggregate reactions. In the cement paste the presence of alkalis increases the pH to 13.5–13.9. It has been reported that the hydroxyl concentration of solution of concrete made with a high alkali cement may be 10 times as high as that made with a low alkali cement and 15 times that of a saturated $Ca(OH)_2$. In general terms, the reaction in the first stage proceeds through the hydrolysis of the reactive silica by OH to form alkali-silica gel and a secondary overlapping stage involving the absorption of water by the gel, which will increase in volume as a result. The principal source of alkali is cement but other sources should not be ignored. The mixing water, sea water, and possibly some mineral constituents in the aggregate such as illitic clays, micas, or feldspars, ground waters, de-icing salts, and admixtures are other sources. Some of the natural materials that have been identified as alkali-reactive in concrete include opaline silica, chalcedony, volcanic glass, and siliceous cement/cryptocrystalline quartz. Some admixtures, such as $CaCl_2$-based formulations and superplasticizers, may aggravate alkali-silica reaction.

The alkali-silicate expansion reaction is the result of aggregates containing greywackes (sand stone containing feldspar or clays) and those that exfoliate such as vermiculites. Also phyllosilicates and other minerals are shown to react with alkaline solutions.[3] At high pH, reactions involving silicates, (zeolite and clay mineral) have been reported but the significance of these reactions to alkali-aggregate expansion still remains unknown.[4]

The alkali carbonate reaction differs from the other varieties in that the affected concrete does not contain significant amounts of silica gel and known alkali-expansive silica minerals have not been found in the aggregate. Details of the mechanism are still debated. In one proposal, expansion is attributed to the growth and rearrangement of brucite crystals in the restricted space in which de-dolomitization takes place, as follows.

$$\mathrm{Ca\,Mg(CO_3)_2 + 2Na\,OH \rightarrow Mg(OH)_2 + CaCO_3 + Na_2CO_3}$$

$$\mathrm{Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2NaOH}$$

Another suggestion is that the expansion is due to cryptocrystalline quartz (alkali-reactive silica is not uncommon in limestones).[5] In the earliest explanation, Gillott[6] attributed the expansion to swelling pressure generated by pickup of moisture by fine constituents, particularly dry clay exposed to de-dolomitization reaction.

Regardless of the type of rock or mineral, increases in expansion are influenced by alkali content, water, temperature, and time of exposure. The preventive measures against alkali-aggregate expansion reactions are as follows. Not all aggregates are reactive and such aggregates may be the right choice. However, there are reactive and marginally reactive aggregates which promote good mechanical properties in concrete that may be available in close proximity to the construction activity and may have to be used. Use of low alkali cement and blending with additives may be needed with such aggregates. It is generally acknowledged that below a specific amount of alkali per cubic meter of concrete made with a reactive aggregate, very little expansion takes place. Technically low alkali cement is that containing alkali in amounts below 0.6% Na_2O equivalent (Na_2O equivalent = Na_2O + 0.658 K_2O). Figure 1 shows the expansion of mortar containing cement with different amounts of Na_2O equivalent.[7] Expansion is generally lower as the ratio decreases. Another method is to replace Portland cement partly by fly ash, or blast furnace slag, silica fume or rice husk ash. The effect of lowering w/c ratio in concrete and its consequence on alkali-aggregate expansion has yet to be resolved. Lower w/c ratio enables better strengths, lower porosity, lower permeability, and lower mobility of alkali ions. However, pore alkali concentration will increase. Air entrainment may be able to reduce expansion by accommodating the reaction products. Avoidance of admixtures that contain large amount of alkalis, use of low cement content, sealing concrete after providing adequate time lapse for drying, and coating of aggregate particles with an impermeable material are some of the measures that reduce the alkali-aggregate expansion reactions. Some admixtures especially lithium salts are known to reduce alkali-aggregate reactions. The preventive methods using admixtures are discussed in detail under Secs. 1.3–1.5.

1.2 Test Methods

Several test methods have been proposed in ASTM standards to evaluate the aggregates for their potential to cause the deleterious alkali-aggregate reaction. The C 295.90 deals with the petrographic examination. This methods determines the physical and chemical characteristics of materials, and classifies and estimates the amount of the constituents. The

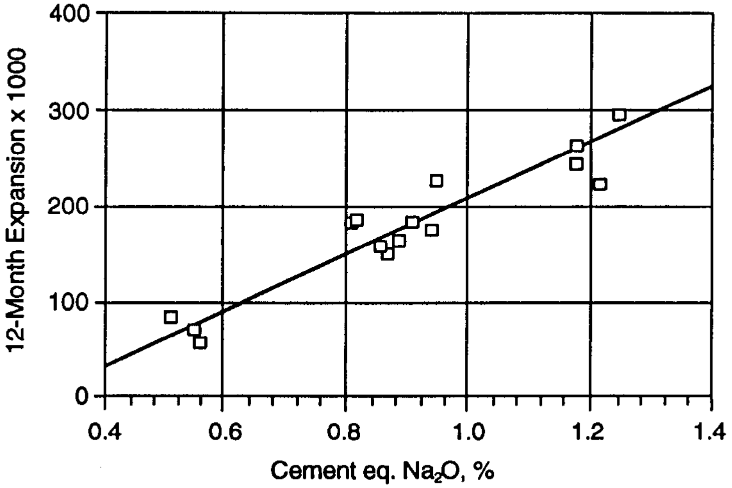


Figure 1. Expansion of mortar containing different amounts of Na_2O. *(Reprinted with permission, The Concrete Society.)*

technique identifies the potential alkali reactive constituents such as opal, cristobalite, tridymite, siliceous and intermediate volcanic glass, argillites, phyllites, metamorphic greywackes, rocks containing highly metamorphic quartz such as greywacke, phyllites, schists, gneisses, gneissic granites, vein quartz, quartzite and sandstone and potential alkali-carbonate reactive rocks calcareous dolomite or dolomitic limestones with clayey insoluble residues. Additional measurements using XRD, DTA, IRA and others may be needed to substantiate petrographic examination.

The behavior of concrete depends on many other factors in addition to the petrographic nature of the aggregate and, hence, prediction of performance often requires length change measurements and other data. In the C 227-90 standard test method for potential alkali reactivity of cement-aggregate combinations, mortar bar is used. The mortar bar is exposed to 37.8 ± 1.7°C for periods ranging for 1 month to 12 months and length changes are measured. It is not easy to differentiate the non-reactive from the reactive aggregate by this test. It is generally considered that the expansion is excessive if the length change exceeds 0.05% at 3 months or 0.1% at 6 month (ASTM C-33). This test should be supplemented by other methods such as the petrographic examination.

The ASTM C 289-87 method tests the reactivity of aggregate with alkali in portland cement concrete as indicated by the amount of reaction during 24 hrs at 80°C between 1N NaOH solution and aggregate that has been crushed and sieved to pass 300 μm and retained on 150 μm sieve. This test has to be used in conjunction with others. Although results are obtained quickly they may not be entirely reliable.

The ASTM C 342-90 for the determination of volume change in cement aggregate combination is primarily intended for research purposes. Mortar is used in the test and the initial temperature and curing additives are similar to those proposed in C 227-90. The mortar is cured for a specific period at 23 ± 1.7°C and 55 ± 1.7°C for 7 days. It is subjected to curing cycles. Length changes are determined after several curing cycles, up to 52 weeks.

There are two ASTM methods to determine the potential alkali reactivity in carbonate aggregates. In ASTM C 586-92, expansion of carbonate rocks while immersed in a solution of NaOH at room temperature is determined. The length changes are followed after 7, 14, 21 and 28 days and at 4 week intervals thereafter. If tests continue after 1 year, measurements are made at 12 week intervals. Expansion in excess 0.1% is indicative of chemical reaction and would warrant further testing such as ASTM C 1105.89. The ASTM C 1105-89 entitled "Length Change of Concrete Due to Alkali-Carbonate Rock," assesses the potential for expansion of concrete caused by alkali-carbonate rock reaction. The specimens are prepared according to ASTM C-157 except that the length changes are measured at 7, 28, 56 days and 3, 6, 9 and 12 months. The aggregate may be considered deleterious if the expansion is equal or greater than 0.015% at 3 months, 0.025% at 6 months and 0.03% at 1 year.

The ASTM standard C 441-89 refers to the effectiveness of mineral admixtures or granulated blast furnace slag in preventing excessive expansion of concrete due to the alkali-silica reaction. In this test, the mortar bar is made with portland cement, mineral admixture or slag and a reactive aggregate consisting of pyrex glass. It is used as a preliminary test to evaluate the effectiveness of these admixtures. The requirements for mineral admixture or slag is specified by C-618 and C-989. The specimens are stored according to the test method C-227.

The Canadian Standards Association (CSA) A 23.2-14A, is entitled "Potential Expansivity of Cement-Aggregate Combinations (Concrete Prism Expansion Method)." There are two versions of the test, one for alkali-carbonate reactive aggregate and another for slow/late-expanding alkali-silicate/silica reactive aggregates. The expansion of alkali-silica/silicate aggregates is determined by storing concrete prisms in sealed containers at 38 ± 2°C and 100% RH. A modified test method is also suggested involving evaluation of changes in the alkali content of cement, the cement content of the mix, the addition of supplementary materials, the use of job mixes or elevated temperature of curing on the expansion of concrete. For the alkali-carbonate reaction test, the prisms are stored at 23 ± 2°C at 100% RH. The alkali content of the cement should be 1 ± 0.2% as Na_2O equivalent. Reagent grade NaOH is added to increase the alkali content of mix to 1.25% Na_2O equivalent based on cement mass. The length change is measured at 7, 14, 28, 56, 84, 112 and 168 days of moist storage and at 6 months intervals thereafter. The CSA test also suggests the maximum allowable expansion values for various test methods. For C and F classifications (CSA), the maximum expansion for alkali-carbonate reactions is 0.01% at 3 months and 0.02% at 1 year for critical areas used for nuclear containment and 0.025% at 1 year for others. For the alkali-silicate/silica reaction the allowable limit is 0.04% at 1 year. The corresponding figures for concrete not exposed to freezing and thawing or to the application of de-icing salts, are raised to 0.04% (at 1 year for alkali-carbonate reactions) and 0.075% at 1 year for alkali-silicate/silica reactions. The CSA also has a test method A 23.2-15 A for petrographic examination of aggregates, CSA A 23.2-19 A for the potential reactivity of aggregates by the chemical method, and CSA, A 23.2-20 A for the alkali-reactivity using mortar bar.

The tests described above require many months to a year or more for evaluation. Accelerated test methods have been suggested using high temperatures, increased alkali concentrations, or autoclaved techniques, and these methods and their limitations have been reviewed in the literature.[8]-[14]

Alasali et al.[15] subjected three types of aggregates that would produce alkali-silica, alkali-silicate and alkali-carbonate expansive reactions, and subjected concretes containing them to room temperature curing, 38°C and 80°C. Most effective expansion occurred at 80°C or during immersion in alkaline or chloride solutions. No one single chemical could be found to produce the largest expansion for all types of aggregates. In severe alkaline environment even low alkali cement in concrete shows expansion. Compared to mortar bars the expansion in concrete was relatively slow.

1.3 Effect of Silica Fume

One of the effective methods of controlling expansive alkali-aggregate reaction is to blend silica fume admixture with the high alkali cement.[16] However, contradictory results have been reported on the effectiveness of silica fume to counteract alkali-aggregate expansion reaction.[17]-[23] Although small amounts of silica fume are found to be effective[22][23] at earlier times, they are somewhat ineffective at longer times.[18]-[21] There has also been concern that at larger dosages of silica fume, silica fume itself may become a source that would react with the alkalis in cement.[24][25] The effectiveness of silica fume depends on a number of parameters such as composition of silica fume (SiO_2 and alkali contents), the percentage of silica fume used, the type of alkali aggregate expansion reaction (alkali-silica or alkali-carbonate) and the type, fineness and alkali contents of cement.

Several publications are available describing the role of silica fume mineral admixture in reducing expansion due to alkali aggregate reaction. Oberholster and Westra,[18] using the Pyrex glass mortar prism test (ASTM C441-69), found that with silica fume as a blend, a "shrinkage" of 0.008% occurred. This was the lowest value of eight mineral admixtures used. In order to verify the effectiveness of the mineral admixtures, a quarry aggregate (reactive) consisting of hornfels and graywackes from the Tygerberg Formation of the Malmesbury Group was selected. Each of the pozzolanic admixtures including silica fume was blended in quantities equal in volume to 5, 10, 15, 20, 25 and 30% by mass of cement (containing 0.97% equiv. Na_2O). The aggregate-cement ratio was 1.5. In order to minimize the dilution effect, this cement (0.97% equiv. Na_2O) was blended with a cement containing 0.16% Na_2O so that cements were obtained containing the same Na_2O equivalent as the balance of the cement after replacement with the pozzolans. The expansion results of mixtures containing mineral admixtures (silica fume and fly ash) are shown in Fig. 2.[18] The top curve shows the effect of dilution with low alkali cement. There is a continual decrease in expansion as equivalent Na_2O decreases from 0.97 to 0.68 at 30% replacement. All admixtures promote a decrease in expansion considerably lower than these values and their effect is not just the result of dilution. Assuming 0.1% expansion as the criterion for allowable expansion, a 10% by volume replacement of silica fume would be required, and silica fume was found to be the most effective of the mineral additions tested.

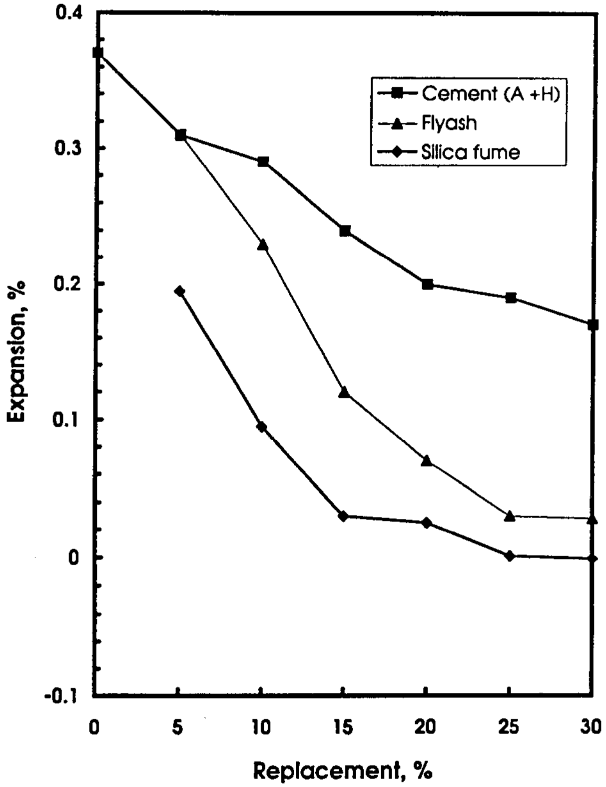


Figure 2. Effect of cement H (0.97% sodium oxide) with increasing amounts of cement A (0.16% sodium oxide) on the linear expansion of mortar prisms.

Olafson,[26] applying a version of ASTM C 227 (modified version of Brotschi and Mehta), used crushed Pyrex as the aggregate and showed that when the pozzolan was of a high surface area type such as silica fume, lower quantities of addition were needed to contain the reaction. The results in Fig. 3[26] show expansion as a function of the total CaO/SiO_2 for the three unhydrated cements with added silica fume. Thus, it can be seen that a CaO/SiO_2 of 1.9 to 2.3 is needed in order to keep expansions under 0.1%, depending on the type of cement. To attain this ratio, 10 to 13% of silica fume should be added; the more the amount of silica fume, the lower would be the ratio. The results of a longer term expansion measurement using an Icelandic sand and a cement with 1.39% equiv. Na_2O alkali is shown in Fig 4.[26] At both 7½% and 10% silica fume, the expansion after 3 years is about 0.06%.

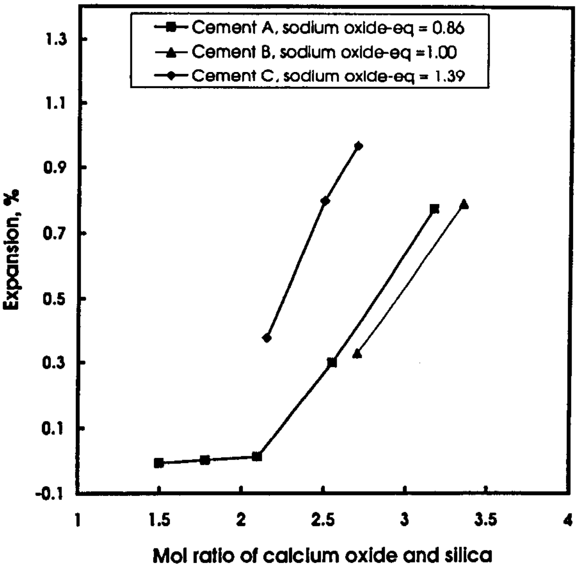


Figure 3. Effect of calcium oxide/silica ratio of cement on linear expansion due to alkali-aggregate reaction.

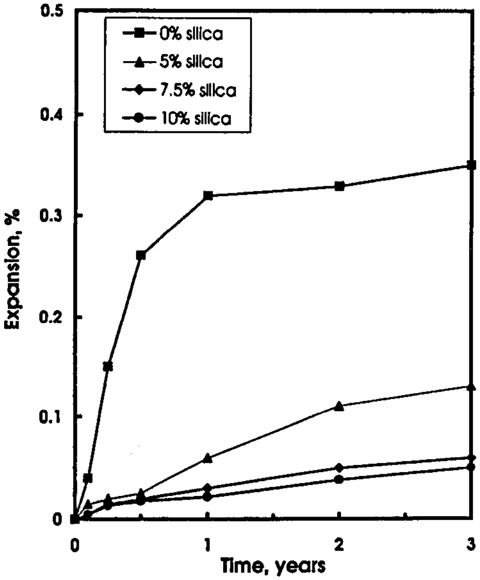


Figure 4. Effect of silica fume replacement on linear expansion of mortar bars containing iceland sand and cement containing 1.39% sodium oxide.

Perry and Gillott[21] have also shown the effectiveness of silica fume to control alkali silica reactions by using Pyrex as the reactive aggregate suggested in ASTM methods C227 and C441. In addition, they tested a very reactive opal from Nevada according to ASTM C227, except the temperatures of 25° and 50°C were used in addition to the standard 38°C. The amounts of cement replaced by the silica fume ranged from 0 to 40% by weight.

Results of experiments performed at 50°C are shown in Fig. 5.[16] Replacement of cement by silica fume significantly reduced expansion, but it appeared that 20% replacement might be required so that the reaction of the opal could be controlled. Evidence presented in this work indicated, however, that superplasticizer addition at 15% replacement level of silica fume may influence expansion in a negative manner.

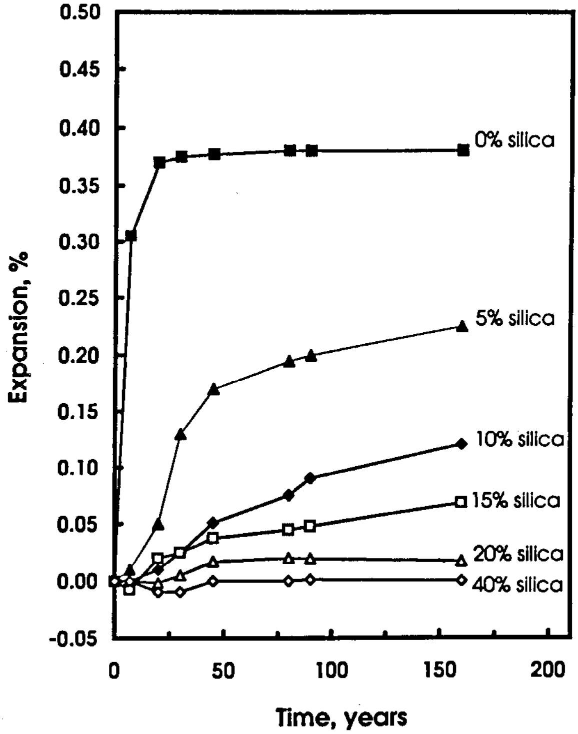


Figure 5. Effect of silica fume replacement on the linear expansion of mortar bars containing 4% reactive opal.

In the work of Durand et al.,[27] the effectiveness of fly ash, slag and silica fume to counter the alkali-aggregate expansion was compared. Addition of silica fume at dosages of 5, 10, and 15% decreased the expansion by 4, 68, and 83% with respect to the reference mortar containing argillite. In concrete containing dolomitic limestone, the corresponding values were[40][48] and 54%. Soles et al.[28] found that, in mortars using meta-argillite (containing slowly reacting species), the effectiveness of silica fume occurred above 10% level. Silica fume had practically no effect in concrete containing dolstone aggregate even at 15% cement replacement.

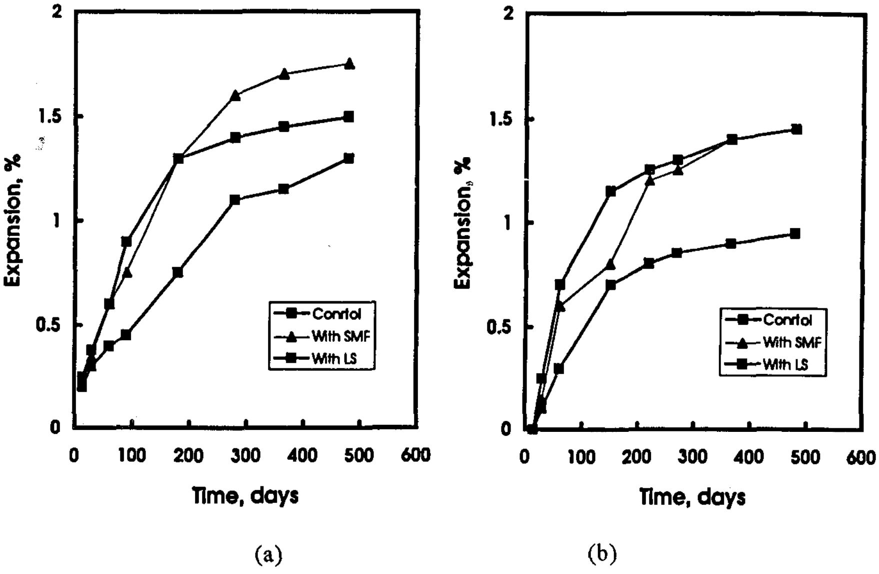
In order to simulate realistic conditions Swamy[29] tested silica fume concrete under a hot-wet and hot-dry exposure regime. The concrete contained cement with 1% Na_2O equivalent, 15% fused silica as a replacement for sand and 10% microsilica. The addition of microsilica decreased the expansion of the reference concrete from 0.732% to 0.273% at 40 days. Crack patterns appearing in the specimens were also studied. They were identified with microsilica as very fine cracks at 0.159% (27 days) expansion and more visible cracks at an expansion of 0.260%. They were largely surface cracks. In the control specimens, at an expansion of 0.046% (7 days), visible cracks appeared. It was concluded that to evaluate the effectiveness of mineral admixtures in controlling alkali silica expansion, criteria that should be considered are: control of expansive strain, control of cracking, preservation of concrete strength, and modulus and control of structural deformation.

Air entrainment in concrete reduces the expansion due to alkali-aggregate reaction. Jensen[30] found that with 4% air voids, the expansion could be reduced by 40% and this was attributed to the accommodation of alkali-silica gel in the air void system. The effectiveness of a combination of silica fume and air-entrainment was studied by Wang and Gillott.[31] Both silica fume and air entrainment individually reduced the expansion but the combination reduced the expansion by the maximum amount. Table 1[31] compares the expansion values in mortar bars containing silica fume and an air entraining agent .

The possibility of increased alkali-silica reactivity in the presence of superplasticizers has been discussed by Wang and Gillott.[32] Mortar bars made with opal, 0, 6, and 12% silica fume and superplasticizer showed greater early reactivity and ultimate magnitude of expansion than the corresponding bars containing no superplasticizer (Figs. 6A and 6B).[32] At 12% silica fume addition, the expansion was delayed for about 2 months. At 24% silica fume replacement, no expansion occurred. In contact with the superplasticizer, increased disorder coefficient and corroded appearance on the surface of opal became evident.

Table 1. Comparison of Expansion of Mortars Containing Silica Fume and an Air Entraining Agent

Silica Fume	Expansion %	
%	No Air Entrainment	With Air Entrainment
0	1.05	0.48
6	0.85	0.45
12	0.62	0.28



(a)

(b)

Figure 6. Effect of silica fume and superplasticizer on expansion: (a) without silica fume, and (b) with 6% silica fume. *(Reprinted with permission, The Concrete Society.)*

Hypotheses concerning the mechanism by which pozzolans provide resistance to alkali-aggregate reactions are generally centered on the type of C-S-H formed during the hydration of cement. When the CaO/SiO_2 ratio of the C-S-H formed is approximately 1.2 or lower, this product is suggested to have an increased capacity for accommodating Na_2O and K_2O in its structure, thereby reducing the hydroxyl ion concentration.[33] During normal hydration without the mineral admixture this ratio is about 1.5.

Direct measurements of pore solutions using a high-pressure press technique have demonstrated that as low as 5% silica fume reduced the hydroxyl ion concentration to levels below 0.3 mol/L.[34] Although this should be sufficient to contain most alkali-silica reactions, longer term studies are needed for confirmation. There is some evidence from results obtained after 200 days, suggesting that the alkali-carbonate reaction may not be controlled by as much as 25% silica fume addition.

The pH and (OH) concentrations have been determined in cement pastes containing 10 and 20% silica fume.[35] The pH and (OH) concentrations decreased in the presence of silica fume. The OH ion contents in the pore solution ranged from a maximum of 735 mM/L for the reference cement (12% alkali) to a low value of 69 mM/L for that containing 20% silica fume. The pH value for the reference was 13.79 which decreased to 12.83 with 20% silica fume. There is a broad correlation between the hydroxyl ion concentration and the alkali-aggregate expansion. There are factors to be considered including the formation of refined pore structure and higher density of the matrix formed in the presence of silica fume that control the expansion reactions.

Based on morphological studies of cement pastes containing silica fume Tenoutasse and Marion[36] concluded that silica fume forms microcrystalline hydrosilicates containing alkalis similar to alkali-silica gels. The expansion property of this product is related to its potassium content. This product does not produce expansion because it occupies the available space in the paste and forms when cement is still plastic.

The long term effectiveness of silica fume has been questioned by a number of investigators.[37]-[39] Berube and Duchesne[39] incorporated two types of silica fume to concrete. One silica fume sample contained 94% SiO_2 and 0.8% Na_2O equivalent (A) and the other, 75% SiO_2 and 3.6% Na_2O equivalent (B). The expansion of concrete containing these silica fumes was monitored for more than 2.5 years (Fig. 7). HAL refers to the high alkali cement and LAL, to the low alkali cement. The results show that both high and low alkali silica fumes produce large expansions. The addition of 10% B is insufficient in the long term to control the expansion. The greater the amount of silica fume, the larger the delay before expansion. The rate of expansion of silica fume concrete increased significantly in the longer run while that of the control leveled off. The proposed explanation for this observation includes the recycling of alkalis which are entrapped initially in the low CaO/SiO_2 ratio, and the existence of high alkali pozzolanic C-S-H.

Although there is clear evidence that the addition of silica fume effectively decreases the alkali-silica expansion in concrete, there is need for long term field data to determine all the parameters that influence the effectiveness of silica fume.

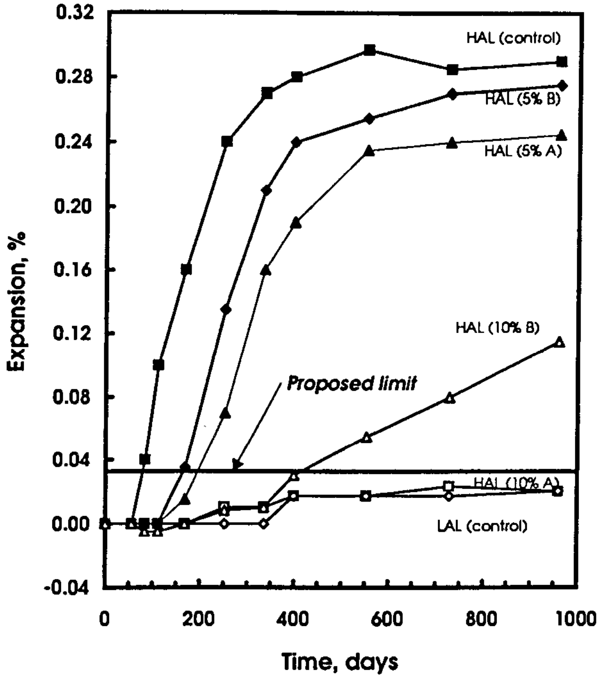


Figure 7. Effect of silica fume on high alkali cements.

1.4 Chemical Admixtures

Lithium-Based Compounds. Chemical admixtures in small amounts are capable of influencing workability, air-entrainment, hydration rate, corrosion, bleeding and strength development. There are other applications of chemical admixtures. There has been an increased activity in recent years to develop chemical and other admixtures to counteract the alkali-aggregate expansivity in concretes. It is also imperative that such admixtures should not affect other physical and chemical properties of concrete. Although substantial work has been carried out on the effect of the chemicals on the expansion reactions, relatively less attention has been directed to their effect on other properties of concrete and long term effects.

McCoy and Caldwell[40] were the first to investigate the effect of various chemicals on the expansion in mortars containing a high alkali cement and a highly reactive pyrex glass. In Table 2, data on the effect of some salts on expansion due to alkali-aggregate reaction are given. The effect of some organic compounds on the alkali-aggregate expansion was also carried out and the results are given in Table 3. The most effective compounds are methyl cellulose and hydrolyzed protein.

It was concluded from extensive earlier work that lithium salts, copper sulfate, aluminum powder, some proteins, and air-entraining agents were capable of reducing the expansion significantly. Following earlier work several others have recently investigated the effect of lithium compounds and some other chemicals on the alkali-silica reaction.

Table 2. Effect of Salts on the Reduction in Expansion of Mortars

Material	Percent Addition	Percent reduction in Expansion (8 weeks)
Aluminum powder	0.25	75
Ba carbonate	1.00	3
Ca carbonate	10.00	-6
Cr phosphate	1.00	9
Cu chloride	1.00	29
Cu sulfate	1.00	46
Li chloride	0.50	34
Li chloride	1.00	88
Li carbonate	0.50	62
Li carbonate	1.00	91
Li fluoride	0.50	82
Li nitrate	1.00	20
Li sulfate	1.00	48
Na chloride	1.00	15
Na carbonate	1.00	44
NH_4 carbonate	1.00	38
Zn carbonate	0.50	34

Table 3. Effect of Some Organic Compounds on the Reduction in Alkali-Aggregate Expansion

Organic Compound	% Addition	Percent Reduction in Expansion
Lactic Acid	1.0	-59.0
Linolic Acid	1.0	37.0
Soybean Oil	1.0	26.0
Acetone	1.0	16.0
Ethyl Acetate	1.0	31.0
Glyceryl Monostearate	1.0	20.0
Methyl Cellulose	1.0	52.0
Methyl Cellulose	2.0	60.0
Sacccharin	0.5	19.0
Hydrolyzed Protein	1.0	56.0-76.0

Lithium hydroxide is an effective additive that reduces the expansion caused by the alkali-silica reaction. Ramachandran[41] prepared seven mixes (Table 4) containing LiOH, opal and different amounts of alkali and studied their expansion characteristics after exposure to 25°C, 38°C or 130°C (in an autoclave). The samples exposed to 25° or 38°C showed the following behavior. Mix 5 exhibited the maximum expansion as it contained 1.2% Na_2O equivalent and 5% opal. Mix 6 with 0.5% LiOH had reduced expansion (Fig. 8). However, after 30 days there was a tendency of the mortar to gradually expand. Mix 7 containing 1.0% LiOH showed decreased expansion up to 50 days. Long term measurements have to be carried out to determine if this dosage is adequate to inhibit expansion.

Table 4. The Composition of Mortar Mixes (Cement:Sand = 1:2.25)

Sample No.	Na_2O Equivalent	LiOH	Opal
1	0.44	0.00	0.00
2	1.20	0.00	0.00
3	1.20	0.50	0.00
4	1.20	1.00	0.00
5	1.20	0.00	5.00
6	1.20	0.50	5.00
7	1.20	1.00	5.00

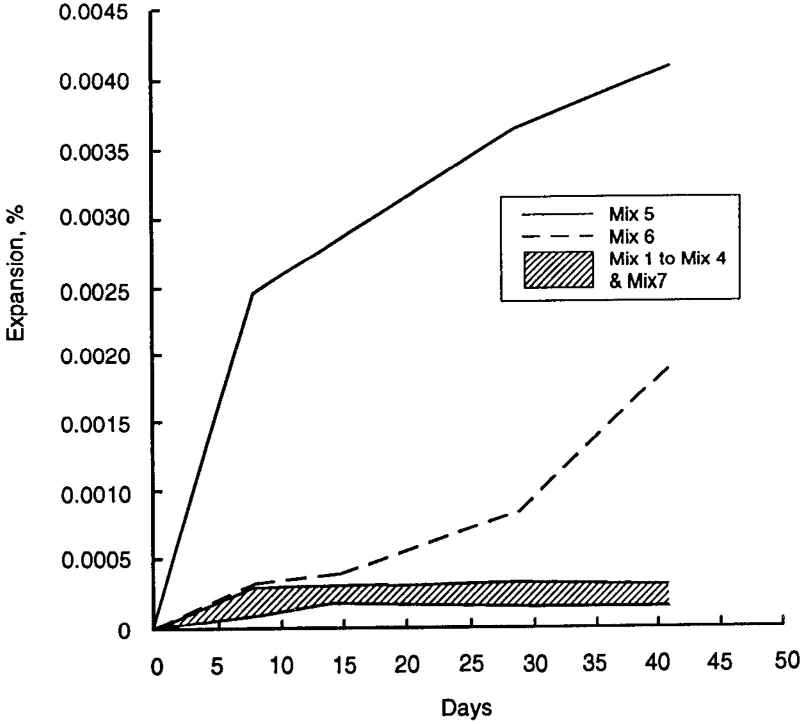


Figure 8. Expansion of mortars containing LiOH.

One of the methods of studying the role of admixtures in countering the alkali-silica expansion is to expose the mortars to an autoclave treatment. The samples mentioned in Table 4 were subjected to a temperature of 130°C for 5 hrs. Although samples 1 to 4 showed almost no expansion, 5–7 exhibited substantial expansion values. The sample 7 exposed to 25 or 38°C had low expansion values, implying that 1% LiOH inhibits expansion. However, the autoclave treatment suggested that 1% LiOH is not sufficient to inhibit the expansion. It is possible that LiOH changes the microstructure and weakens the bond forming characteristics of the mortar under the autoclave treatment. Caution should, therefore, be exercised when applying the accelerated test methods for evaluating the alkali-aggregate expansion characteristics of mortars.

A systematic investigation on the effect of lithium fluoride and lithium carbonate on the expansion of mortars (with 1% Na_2O equivalent) was carried out by Stark et al., and the results are shown in Table 5.[42]

Table 5. Expansion of Mortars Containing Different Amounts of LiF or Li_2CO_3. *(Adapted with permission from Table 4.1,* Eliminating or Minimizing Alkali-Silica, *Stock, et al., 1993)*

		% Expansion, months				
Sample	Dosage, %	6	12	18	24	36
Reference	0.00	0.54	0.62	0.62	0.63	0.63
Ref+LiF	0.25	0.43	0.59	0.64	0.68	0.71
	0.50	0.04	0.06	0.06	0.06	0.06
	1.00	0.02	0.02	0.02	0.02	0.02
Ref+Li_2CO_3	0.25	0.46	0.61	0.62	0.62	0.63
	0.50	0.30	0.50	0.54	0.55	0.58
	1.00	0.03	0.04	0.04	0.04	0.05

Although less soluble than LiOH, both LiF and Li_2CO_3 are capable of reducing the alkali silica expansion. They seem to be converted to LiOH in pore solution. It is also obvious that, in order to obtain good inhibition of expansion, at least 0.5% LiF and 1.0% Li_2CO_3 would be required.

The mechanism of the inhibitive action of LiOH has been proposed by Stark et al.[42] In the presence of KOH and NaOH the gel product incorporates Li ions. The amount of Li in this gel increases with its concentration. The threshold level of Na:Li is 1:0.67 to 1:1 molar ratio at which expansion due to alkali-silica reaction is reduced to safe levels. Diamond and Ong[43] found that when LiOH is added to mortar, much more lithium is taken up by the cement hydration products than Na or K. This would indicate that small amounts of lithium are not very effective. In the absence of other alkalis the product formed with Li is non-expansive. It was thus concluded that a critical amount of lithium is needed to overcome the combined concentrations of KOH and NaOH to eliminate the expansive effect.

In another study involving LiOH, $LiNO_2$ and Li_2CO_3 it was found that all these compounds were able to decrease the expansion due to alkali aggregate reaction.[44] Of these compounds, Li_2CO_3 was found to be more effective than the others. The relative inhibiting effect was considered to depend on the Li/Na ratio.

Ohama[45] also investigated the relative effects of carbonate, hydroxide and fluoride salts of Li. In dosages of 0.5, 0.7 and 1.0%, these compounds decreased the expansion. However, the effectiveness decreased when LiF and $LiOH•H_2O$ were added in amounts greater than 0.7%, although the compressive strengths of mortars were of same value at different dosages.

It appears from the work carried out so far, that not all lithium salts are effective in diminishing the alkali-aggregate expansion reaction.[46] The long term effects have to be evaluated and the optimum dosage requirements have to be determined. Much more work employing reliable predictive tests has to be carried out before the relative effects of various lithium compounds such as hydroxide, carbonate, nitrate, fluoride, perchlorate, chloride, etc, can be substantiated.

Non-Lithium Compounds. Attempts are continuously made to find alternative materials to lithium compounds to counter the alkali-aggregate expansion. A few studies have been made of binary admixture systems. Hudec[47] tested several chemicals including phosphates, nitrates and borates of various cations and found that phosphates have good potential for countering the expansion, especially the alkali-silica type.

Several reports have suggested that the air-entraining admixture in concretes protects them against alkali-aggregate expansion. It is possible that the microbubbles that are entrained can accommodate the reaction products and thus lower the stress development in concrete.[30][40][48] An air-entrainment of 3.6% can cause a 60% reduction in expansion.[49] In Fig. 9 the influence of different amounts of air entrainment on the expansion in concrete is shown. The results suggest that as the amount of air entrainment increases the expansion decreases.

It can be expected that porous aggregate incorporation in concrete should also be able to diminish this expansion.[50] Some work carried out by Berube et al.[51] would suggest that normal air entrainment in concrete may not have significant effect on alkali aggregate expansion. There is concern that the freeze thaw resistance of concrete may be affected if the gel products fill the pores.

The inclusion of retarders and an air entraining agent may result in larger decrease in expansion than when these admixtures are used individually. Fig. 10 gives the expansion values produced by a combination of an air entraining agent with three types of retarders: a commercial retarder (CR), citric acid (CI) and sucrose (SU). The data demonstrate that the expansion in the presence of both admixtures is substantially lower than when only the air entrainment is used.[52] The action of the retarder involves the change in the availability of lime and alkali, production of lower C/S ratio phase and delay in the formation of a rigid structure in the paste. Reduced expansion with air entraining agent-water reducer mixtures has also been substantiated.[53][54]

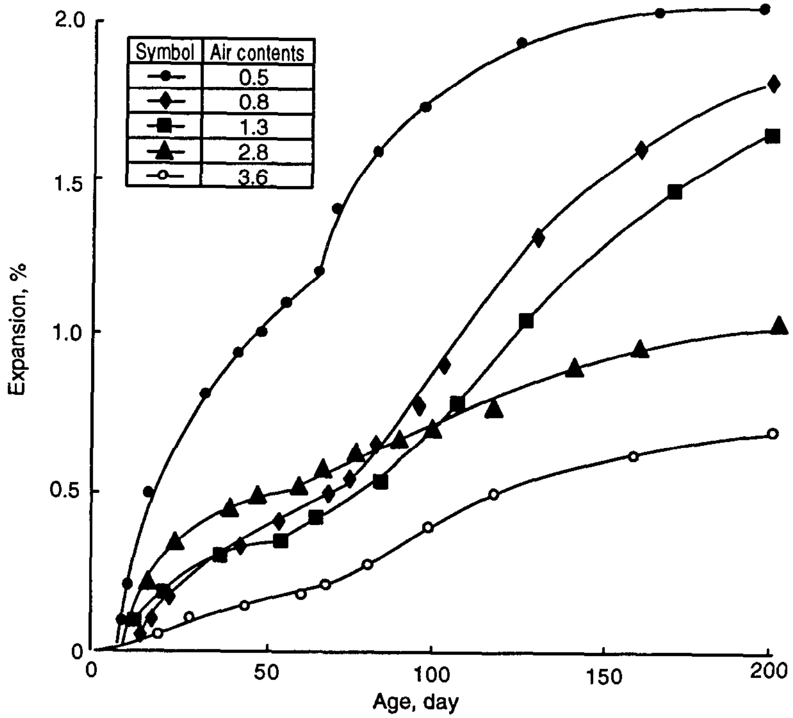


Figure 9. Influence of air entrainment on expansion due to alkali-aggregate reaction.

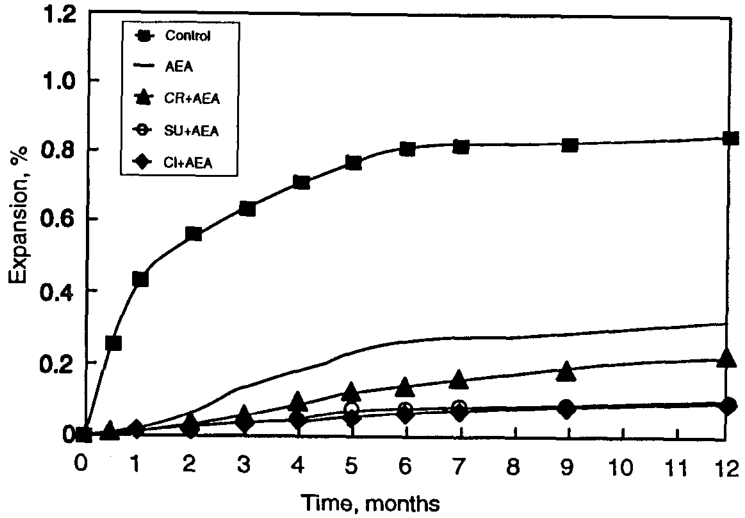


Figure 10. Influence of dual admixtures on alkali-aggregate expansion.

The effect of various chemical admixtures on the alkali-silica reaction has been studied and following conclusions have been drawn.[55] Calcium chloride increases expansion, rate of hydration and a rapid formation of the paste structure. Sucrose dramatically decreases the expansion. Other admixtures such as lactic acid, EDTA and oxalic acid have no effect. The addition to concrete of barium salts containing chloride, hydroxide, acetate, nitrate, and chromate, affects the expansion to different extents. The acetate and nitrate seem to be more effective than the others.[56][57] Similarly, the sulfates, chlorides, and carbonates of Na and K are ineffective, whereas the nitrates of Na and K have been found to be much more effective in reducing the expansion.

Ohama et al.[58] have found that alkyl alkoxy silanes are capable of reducing alkali aggregate expansion considerably. The effect of five types of silanes on alkali-aggregate expansion is evident from the results in Fig. 11. All the silanes decrease the expansion. AAS-2 to AAS-4 seem to be more effective than the others. AAS-1, 2, 3, 4, and 5 are respectively methyl trimethoxy silane, hexyl trimethyl siloxane, octyl trimethyl silane, decyl trimethoxyl silane and hexadecyl trimethoxy silane. The mechanism of their action involves water repellency and air entrainment.

The possibility of using chelating agents to fix K ions was assessed by Hasni and Salomon.[59] Some reduction in expansion was obtained with crown ethers.

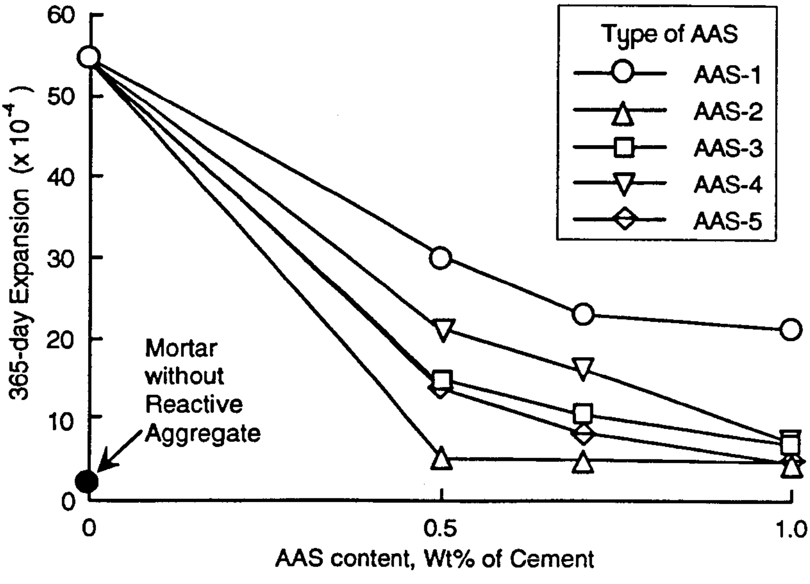


Figure 11. The effect of silanes on alkali aggregate expansion. *(Reprinted with permission, The Concrete Society.)*

1.5 Mineral and Related Admixtures

Introduction. The use of mineral admixtures in concrete results in several beneficial effects such as lower permeability, resistance to thermal cracking, and decreased alkali-aggregate and sulfate expansion. Broadly, mineral admixtures comprise natural mineral substances and by-products from industries. They are added either at the time of mixing or premixed with dry cement powder. The mineral admixture acts as a pozzolan by reacting with lime to form a hardened material, or, by itself, may possess hydraulic properties.

The Canadian Standard (A.23.5-1986) describes mineral admixtures. Class N is a raw or calcined natural pozzolan such as volcanic ash, diatomaceous earth, schist, and opaline hornfel. Fly ash consists of class F, produced normally from burning anthracite or bituminous coal, and class C, normally produced by burning lignite or subbituminous coal and generally shows hydraulic properties. Class G or H are granulated blast furnace slags and class U is condensed silica fume produced from silicon or ferrosilicon industries and contains at least 85% SiO_2. Rice husk ash with pure silica in a noncrystalline form is also treated as a mineral admixture. Burnt clays and shales possessing pozzolanic properties, although not economical alternatives to slag or fly ash, may also be considered mineral admixtures. The detailed classification, properties and action of the mineral admixtures are discussed under Ch. 10.

Fly Ash. Majority of fly ashes have a chemical composition in the range, 42–50% SiO_2, 16–30% Al_2O_3, 5–10% FeO and Fe_2O_3 , 2–4% CaO and 5% alkalis.[7] The average particle size range of fly ash is 0.5–200 μm, specific gravity being 2–3, and a Blaine surface area of 250–325 m^2/kg for Class F and 300–400 m^2/kg for Class C. The pozzolanic activity of fly ash depends on its fineness and glassy content.

Fly ash in concrete is capable of reducing the alkali silica and alkali silicate/silica expansion. Figure 12 provides data on the effect of 0–30% fly ash on alkali-aggregate expansion in mortars.[7] It is obvious that the effectiveness of fly ash depends on its amount in the mortar. The degree to which expansion is controlled by fly ash depends on its physical and chemical nature. Pepper and Mather[129] estimated for four fly ashes, the minimum replacement (by volume) of cement by fly ash needed to reduce the expansion by 75% (Table 6).[129]

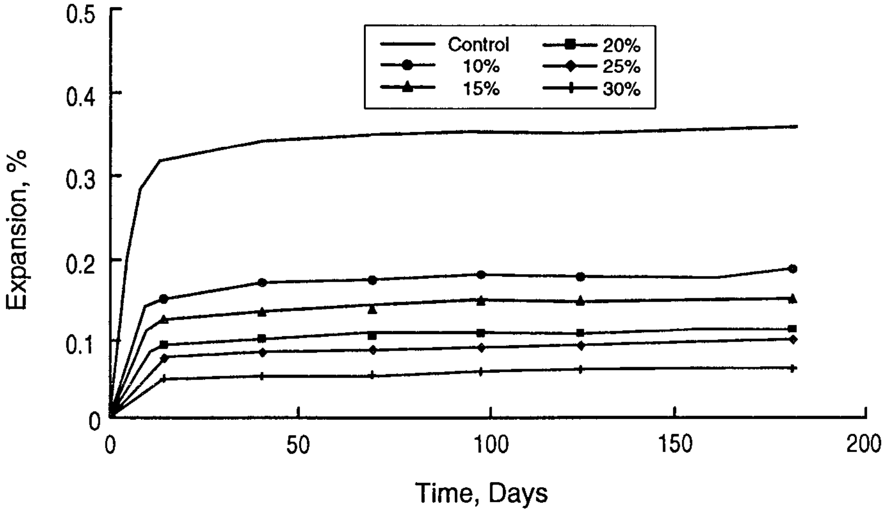


Figure 12. The effect of different amounts of fly ash on expansion.

Table 6. Minimum Replacement Levels of Fly Ash for Reducing Expansion

Material	Minimum % replacement		
	14 days	6 months	average
Fly Ash I	46	36	41
Fly Ash II	48	36	42
Fly Ash III	52	36	44
Fly Ash IV	45	34	40

The effectiveness of fly ash depends on, among other factors, the alkali concentration in it.[61] Three fly ashes, A, B, and C, containing 2.34, 3.07, and 8.55% alkalis (as Na_2O), were mixed with concrete to evaluate the amount required to cause < 0.04% expansion. The results are plotted in Fig. 13.[61] Even 40% PFA-C is not sufficient to meet the performance criteria. PFA-B, containing much more Ca and Si, than the others is the most efficient in countering the expansion although it has more alkali than PFA-A. While 18–19% PFA-B is sufficient, 22–24% PFA-A is needed for controlling the expansion. The results do not imply that the Ca content is critical. It is generally believed that with high Ca fly ash, higher replacement levels may be needed to reduce expansion. Possibly, as these fly ashes contain larger amounts of alkali sulfate, they tend to increase the amount of soluble water soluble alkalis in concrete.[62] The amorphous or glass content in fly ash is also a critical factor dictating its effect on alkali silica reaction.

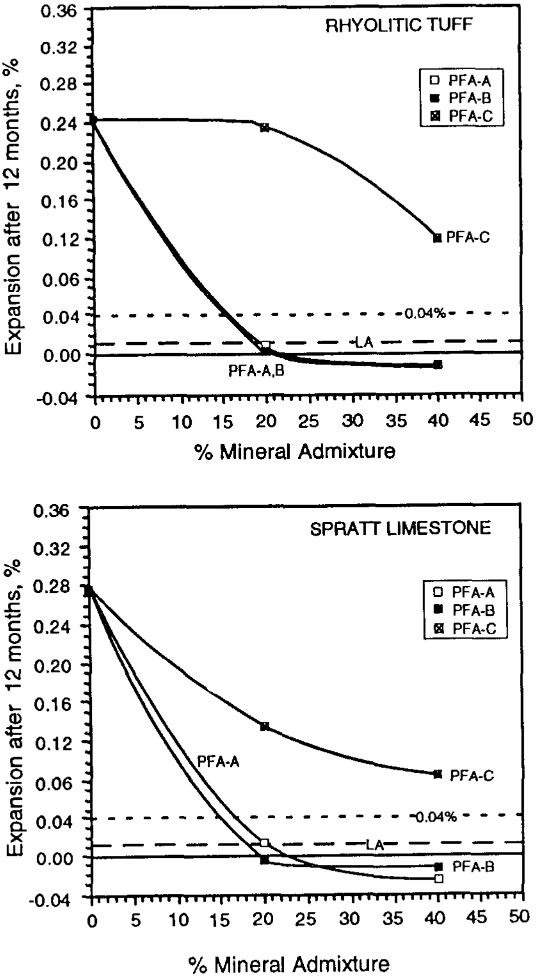


Figure 13. Expansion at 1 year as a function of fly ash content.

The factors that are to be considered for assessing the role of fly ash as an inhibitor for the alkali-aggregate expansion are the following. The R_2O content in fly ash tends to accelerate the alkali-aggregate reaction, quartz and mullite in fly ash decrease the expansion, and the quantity of alkali in cement determines the effective amount of fly ash needed in the mix. An empirical formula has been suggested by Kobayashi and co-workers to assess the effectiveness of fly ash in alkali-attack prone concrete:[63]

$$\Sigma CA + 0.83\Sigma FA - 0.046\Sigma F \leq 4.2 \text{ kg/m}^3$$

where ΣCA , ΣFA and ΣF represent total alkali content in cement, fly ash, and the total amount of fly ash, respectively. By applying the equation for 14 fly ashes it is seen that fly ash with an alkali content > 5.5% is not a desirable amount of addition. From the equation it can be deduced that if the cement has 1.2% alkali and fly ash with as high as 4% alkali, the expansion can be controlled with 20% fly ash. In practice, however, a safety factor should always be included.

The role of fly ash and slag to control the expansion due to alkali-carbonate reaction has been reported by Soles and Malhotra.[64] The two year study indicated that slags are more effective in reducing the alkali carbonate than alkali-silica reaction. In contrast, the condensed silica fume and natural pozzolans were much less effective in suppressing alkali-carbonate reaction than alkali-silica/silicate reaction. It has been reported that high volume fly ash concrete (cement:fly ash = 155:212 kg/m^3), irrespective of the methods used for evaluation, is highly effective in inhibiting expansion due to alkali-aggregate reaction.[65]

Slag. Slag consists of silicates, aluminosilicates of calcium and other bases. The granulated slag is a glassy material that is obtained when molten slag is rapidly chilled. The chemical composition of slag depends on the type of pig iron produced and on the type of iron ore. The mean composition of slag is 30–40% SiO_2, 8–18% Al_2O_3, 40–50% CaO, 0–8% MgO, 0–1% FeO, 0–2% Mn_2O_3 and 0–2% S. Because of its hydraulic properties slag can be used in higher amounts than fly ash.

The ability of slag to control alkali-aggregate expansion was first reported by Cox in 1950. Many subsequent studies have confirmed the effectiveness of slags.[66] Important references to work on slags can be found in international conferences organized by the American Concrete Institute and in other reference books.[7][17] There is some disagreement on the effect of slag on alkali-carbonate reaction. Several hypotheses have been put forward to explain the action of slag. They include dilution effect, pozzolanic action, entrapment of alkalis in the CSH phase, changes in the C/S ratio of the CSH phase, changed role of calcium hydroxide and decreased permeability of slag cement concrete.

The relative effectiveness of different amounts of slags on the expansion of mortar with a high alkali (1.19% Na_2O) cement, has been tested adopting the ASTM C-441 (Table 7).[67] The expansion is reduced in the presence of slag. There is a considerable expansion reduction at 60% addition. If the criterion that the expansion should be less than 0.1% at 1 year is applied, it would be appear that at least 60% slag is required to control expansion.

Table 7. The Effect of Different Amounts of Slag on Alkali-Silica Expansion in Mortars

Age, days	Average Expansion,% (Slag Content)				
	0%	30%	40%	60%	75%
28	0.47	0.15	0.09	0.02	0.01
56	0.51	0.17	0.10	0.02	0.01
180	0.51	0.17	0.11	0.03	0.02
270	0.51	0.16	0.11	0.03	0.02

The contribution of alkalis in slag to the alkali-silica reaction determines the total expansion. According to Hobbs, slags contribute one half of their total alkali content to the reaction.[68] Alasali's more recent work would suggest that the alkali contribution could be between 0 and 100%.[69] In Table 8 are given the expansion data for concrete containing four slag concrete mixes with various amounts of alkalis.[69]

Table 8. The Effect of Alkali Content on Expansion in Portland Cement/ Slag Concrete

Mix No.	Cement	Alkali(kg/m^3)		% Expansion in 1 year
		Addition	Total	
C-1	1.5	0	1.5	0.126
C-2	1.5	1.5	3.0	0.382
C-3	1.5	2.5	4.0	0.553
C-4	1.5	4.5	6.0	0.657

In the above table the cement was replaced by 50% slag containing 0.65% Na_2O equivalent. Mix C-1 contained 1.5 kg/m^3 alkali. In mixes C-2, C-3, and C-4, the alkali content was increased to 3, 4, and 6 kg/m^3, respectively. The specimens were cured at 38°C. The results in Table 8 were compared with those obtained in concrete containing no slag. The expansion of these mixes in terms of alkali contents showed the following: expansion in C-1 to C-3 mixes containing slag was greater than that containing no slag, indicating that in concrete with cement replaced by 50% slag, and deleterious expansion occurs at a lower level than would be expected if only portland cement and/or added alkali contributed to alkali reaction. The results suggest that slag was effectively contributing nearly 1 kg/m^3 of alkali to mix C-1 (assuming alkali content is the only cause for expansion). In conclusion, the data indicated that slag had contributed all of its alkalis *to mix C-1, only ⅔ to mix C-2, ⅓ to mix C-3, and none to mix C-4*.

Although slag is very efficient in decreasing expansion due to alkali-silica reaction, its influence on alkali-carbonate expansion reaction has yet to be resolved. Durand and Chen obtained reduced expansions[27][70] as evident from the results in Fig. 14.[70] Work of Williams and Rogers shows that, at a 25–50% slag levels, expansion occurs after exposure of concrete for 5 years.

In summary, it can be concluded that inclusion of large amounts of slag (both air-cooled and granulated types) are effective in reducing the alkali-silica reaction and, in some instances, alkali-carbonate reaction. The mechanism of this action is determined by the dilution effect, fundamental properties inherent to the slag, and the amount of alkalis in the slag.

Other Siliceous Additives. In addition to silica fume, fly ash, and slag, there are other natural or processed siliceous materials that can be used to suppress the expansion caused by the alkali-silica reaction. By the addition of these materials, the OH concentration in the pore solution is readily decreased. Diatomite has been used to control the alkali-aggregate expansion. Mehta tested the efficiency of a highly active pozzolan obtained by incinerating rice hulls. The surface area of these ashes was about 50–60 m^2/g.[71] Table 9 shows how, by adding 15% of this active material, the expansion can be reduced by about 95%.[71]

Natural pozzolans have also been used to control expansions in alkali-prone concrete systems. Santorin Earth, a volcanic ash has been found to decrease expansions caused by alkali-silica reaction. In an accelerated test the expansion could be reduced from 0.7% for the reference, to about 0.15% with 30% Santorin Earth.[72]

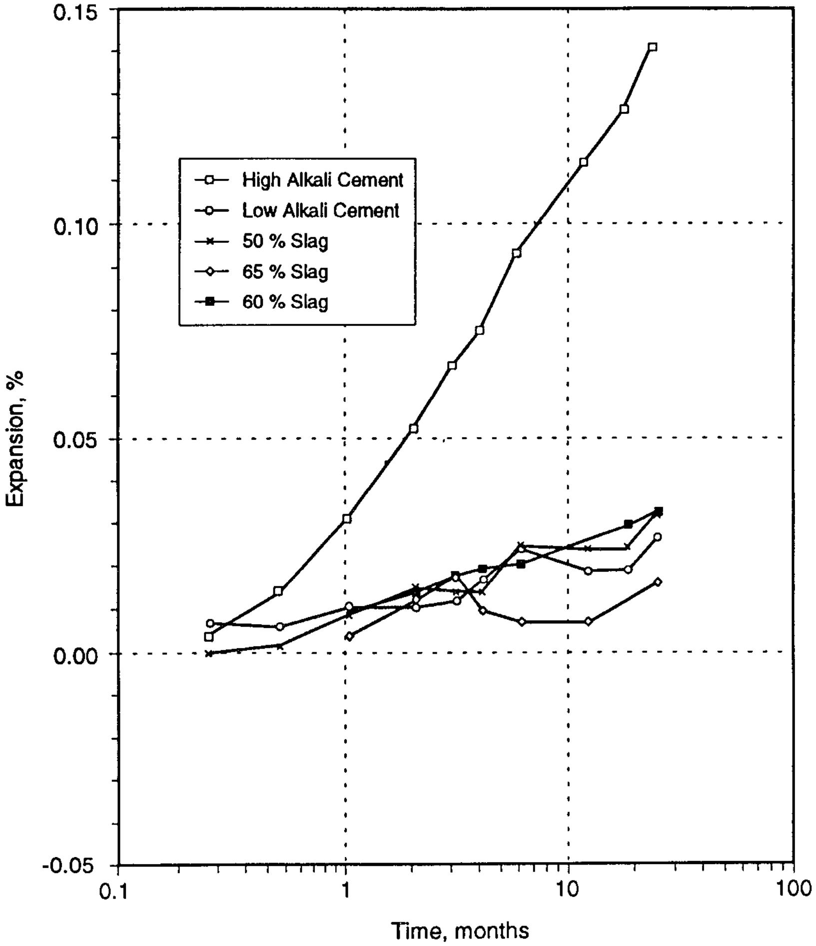


Figure 14. The effect of slags on the expansion in concrete containing dolomitic limestone.

Table 9: Effect of Rice Hull Ash on Expansion of Mortar

Rice Hull Ash (%)	Reduction in Expansion, % of Control		
	14 days	3 months	6 months
5	52.2	50.2	49.3
10	90.4	87.8	86.6
15	97.4	95.0	94.0
20	98.6	96.9	95.8

Zeolitic materials have also been investigated for countering the expansions. In one study the incorporation of this admixture in an amount of 24% was found to be unacceptable. It could however, be used in concretes exhibiting marginal expansions.[73]

Calcined clays have pozzolanic properties and some work has indicated that they are capable of reducing the alkali-silica expansion substantially. In a study by Andriolo and Sgaraboza,[74] it was found that, at addition levels of 15% calcined clay, the expansion was reduced from about 0.18 to 0.02%. Metakaolin, obtained by calcination of china clay, has been tested for its ability to decrease the alkali-silica expansion.[75] Metakaolin was added in amounts of 0, 5, 10,15, 20 and 25% (cement replacement). Expansion was monitored over a period of 18 months. The results are shown in Table 10. The concrete without metakaolin expanded by 0.45% in 6–9 months. Expansion is reduced to less than 0.01% with 10–15% by weight of metakaolin. The presence of metakaolin in concrete did not result in a decrease in the compressive strength.

Table 10. Effect of Metakaolin on Expansion of Concrete

% Metakaolin	Expansion (%, in months)			
	1	6	12	18
0	0.037	0.425	0.449	0.457
5	0.021	0.191	0.249	0.312
10	0.016	0.013	0.011	0.012
20	0.015	0.008	0.006	0.007
25	0.022	0.020	0.008	0.013

2.0 CORROSION INHIBITING ADMIXTURES

2.1 Introduction

In North America, and in many other countries, vast populated areas are exposed to severe winter conditions and heavy snow fall. These conditions have necessitated removal of snow and ice from pavements. Large quantities of salts, especially sodium chloride and calcium chloride have been used to melt ice. The amount of salt consumed for highway de-icing in the USA has increased dramatically from the 50's and now stands at 10 million tons per annum (Fig. 15).[76] In the year 1990, 25% of all salt produced in the USA was used for de-icing purposes, whereas the figure was only 2% in 1940.

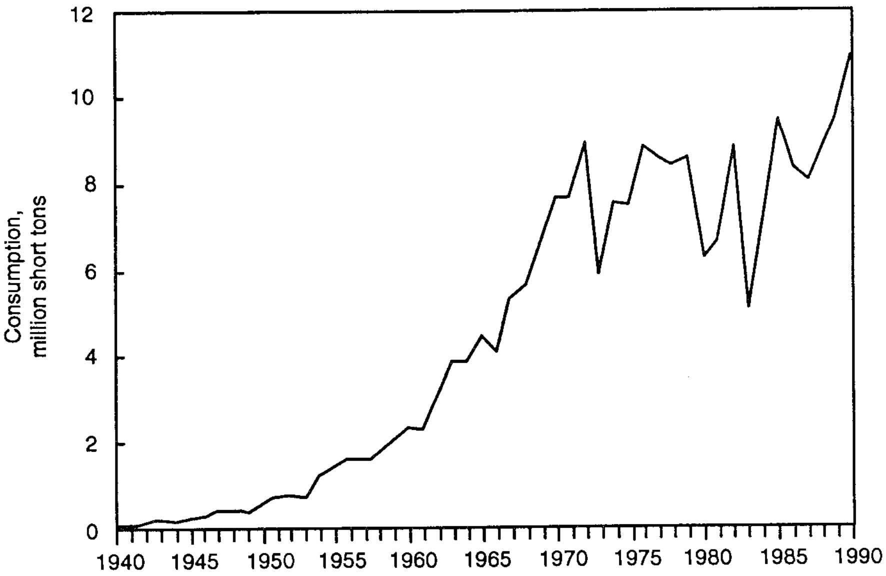


Figure 15. The consumption of salt in the USA in the years 1940–1990.

In order for a salt to be useful as a de-icer, it must effectively melt the ice, be economically attractive and ecologically acceptable. Several alternatives to sodium chloride have been suggested but it seems, considering all the factors, sodium chloride is still the most popular salt for use on pavements. The eutectic temperatures of some chemicals are shown in Table 11. Lithium chloride, calcium chloride and aluminum chloride are some of the salts that have very low eutectic temperatures.

There are problems associated with the use of de-icing salts on reinforced concrete members. Many thousands of bridges with cast-in-place concrete and reinforced steel have developed cracks allowing corrosive chemicals to reach the steel. As the steel corrodes, the resultant rust produces pressure on concrete, causing crack development. Additional damage occurs due to the ingress of moisture and chloride that aggravate processes related to freeze-thaw, vibrations, and impacts. Salts also damage reinforced pavements, pavement joints, highway drainage systems and parking garages. A study has estimated that it would need 3 trillion dollars during the next decade simply to halt the rate of deterioration of bridges in the US.[77]

Table 11. Eutectic Temperatures of Some Chemicals

Chemical	Eutectic Temp. (°C)	Concentration at the Eutectic
Aluminum chloride	-55	25.3
Ammonium Sulfate	-19	38.3
Calcium chloride	-55	29.8
Calcium nitrate	-18.5	35.0
Lithium chloride	-80	25.3
Potassium chloride	-10.6	19.8
Sodium chloride	-21.1	23.3
Sodium nitrite	-19.6	28.0
Urea	-8.4	31.0

2.2 Corrosion of Steel

Processes and Measurements. Corrosion of steel in concrete is an electrochemical process. The electrical flow is generated internally within the system. Electrical cells called galvanic cells are formed and the flow of electricity is provided by water containing dissolved chemicals. Electric potentials are generated as a result of the existence of two dissimilar metals, different concentrations of electrolytes, moisture, oxygen, etc. The cell electrodes are anode and cathode. In corrosion of steel, a reaction occurs at the anode involving the formation of Fe ions and electrons, as follows:

$$\underset{\text{(iron)}}{Fe} \rightarrow \underset{\text{(iron ions)}}{Fe^{+}} + \underset{\text{(electrons)}}{2e^{-}}$$

The principal chemical reaction at the cathode is as follows:

$$\tfrac{1}{2}O_2 + H_2O + 2e \rightarrow 2(OH)^-$$

Ferrous and hydroxyl ions react to form ferrous hydroxide according to the reaction as below:

$$Fe^{++} + 2\,(OH)^- \rightarrow Fe(OH)_2\ \text{(rust)}$$

Sometimes further reaction occurs to form ferric hydroxide (another type of rust). If conditions exist that do not allow these reactions to proceed, then the cell is not operative and corrosion does not occur. Numerous studies have been carried out to determine the composition of the rust, and the formation of different oxide phases of Fe have been reported.[78] They include $Fe(OH)_2$, $Fe(OH)_3$, α-FeOOH, β-FeOOH, γ-FeOOH, δ-FeOOH, α-Fe_2O_3, γ-Fe_2O_3 and Fe_3O_4. Also, the crystallinity, stoichiometry, particle size and morphology of the oxide components may vary widely.

In normal concrete, the water in the pores is highly alkaline because of the presence of Na , K and Ca hydroxides. The pH of the solution may be 12.5 or higher. Under this condition of high alkalinity, a protective film of Fe_2O_3 forms on the surface of steel. The steel is further protected by the physical shield offered by the concrete cover. In spite of these factors, steel can corrode because of the severity of the exposure conditions such as salts in a marine environment, de-icing chemicals on bridge decks, highways and parking garages, carbonation from the atmosphere, geographical conditions of temperature and humidity, salts from ground waters, and other forms of attack resulting in the ingress of moisture, salts, carbon dioxide, etc.

Chlorides, if present in solutions and in contact with the steel, can break down the passive Fe hydroxide layer and promote corrosion. Chlorides may be present in the admixtures, aggregates or may diffuse into concrete on exposure to marine environments or from the application of de-icing salts. The chemically bound chloride with the calcium aluminate phase is not available in solution to cause corrosion, unless it is destabilized by ions such as sulfate. The action of chloride is to form an iron chloride complex which may be a form of $FeCl_2$, $FeCl^+$ or $FeCl_3^-$ ion. It is also possible that the iron chloride complex reacts with hydroxyl ions to form ferrous hydroxide and chloride ions. The effect of chloride compounds depends on the cation associated with the chloride, calcium chloride being much more deleterious than sodium or potassium. The breakdown of the passive layer is thought to be related to the ratio of Cl^-/OH^- in concrete pore water.

Several methods have been suggested to measure corrosion of steel in concrete. Some of the common techniques include potential measurements, weight loss determination, cyclic voltammetry, linear polarization and electrochemical impedance spectroscopy. The potential measurement involves determination of potential over a period of time. In this method, the potential of the steel versus reference electrode (e.g., standard calomel electrode) is measured using a high resistance dc voltmeter. The measurement of potential over a period provides information on the stability of the corrosion process. This method, however, does not measure the rate or extent of corrosion. The weight loss due to corrosion is determined by exposing the sample to the required environmental conditions. The difference in weight before and after exposure in a predetermined period can be used to determine the corrosion rate. This method is not used in the field because it is destructive in nature. The cyclic voltammetry is based on polarizing the test specimen anodically from the corrosion potential and recording the current required for this polarization. The method involves cyclic sweep of potential till a steady state is reached. This technique is useful for deriving mechanistic information and is not used for obtaining the corrosion rate. Cyclic polarization is similar to cyclic voltammetry and gives information on the pitting potential and breakdown potential. In the linear polarization technique, a small voltage is applied both anodically and cathodically using a potentiostat and counter electrode. The current required for this perturbation is plotted as a function of current[79] In conductive electrolytes the slope of the curve is known as the *polarization resistance*. Using the information on the corroded area, the rate of corrosion can be determined. This technique measures instantaneous corrosion. The application of impedance techniques for measuring corrosion rates of steel in concrete has been described by Berke et al.[80] In the electrochemical impedance spectroscopy, voltage is applied over a range of frequencies and the current that is needed to cause the voltage perturbation is measured. This method gives information on the characterization of the corroding surface from which corrosion rate and overall corrosion behavior can be predicted.

There are several methods of controlling or preventing corrosion in new as well as in existing structures. Reinforced concrete can be coated with epoxy polymer, usually in the factory by fusion bonding. In most instances the coated bars have shown good behavior.[81] Waterproofing membranes are applied on to the concrete to prevent the ingress of chloride ions. They should be properly applied so that they are free from breaks or cracks. They should also be protected from mechanical abrasion of vehicles. Another method is to have several inches of cover on slabs that are subjected to heavy chloride exposure. Materials such as latex, slag and silica fume-based materials are used for this purpose. They are capable of reducing the permeability of concrete. Removal and replacement of delaminated concrete, impregnation of concrete, removal of chloride ions and cathodic protection are some of the other methods adopted to control corrosion in existing structures. Corrosion inhibitors are chemicals that may be added to the concrete mix to prevent corrosion of embedded steel.

2.3 Impermeability and Corrosion Inhibition

Some of the important factors that control the corrosion of steel in concrete are permeability, resistivity and carbonation. Permeability of concrete determines the rate of ingress of carbon dioxide, chloride ions, oxygen and moisture flow. Extensive tests have emphasized the importance of adequate concrete cover over steel to mitigate or eliminate corrosion of steel. Low permeability covering material can be fabricated by using superplasticized concrete. Concrete containing mineral admixtures and polymers are capable of reducing the permeability of chloride ions considerably. Incorporation of such admixtures is expected to strengthen the transition zone, thus decreasing or eliminating cracks and enhancing the impermeability characteristics of concrete. Although these admixtures are not classified as corrosion inhibitors, they are very effective in preventing corrosion of steel. One of the popular methods of determining the permeability of chloride is the rapid test prescribed by ASTM C1202-91 and AASHTO T 277. It takes the current measurements up to 6 hrs. Recent work by Feldman and coworkers has suggested that this test induces changes in the pore structure and resistivity of the concrete specimens. They found that the determination of the instantaneous current provides reliable data on chloride permeation.[82]

Fly Ash. The resistance of fly ash concrete to chloride ions has been studied by many workers. In a study of fly ash concrete with cement contents 124–182 kg/m^3 and fly ash contents in the range 170–251 kg/m^3 (samples 1 to 9 in Table 12) at a constant fly ash-cement ratio of 1.37–1.38, it was found that the resistance to chloride penetration was enhanced significantly in the presence of fly ash.[83]

The permeability characteristics of concretes to chloride ions may be assessed in terms of coulombs. This is based on a rapid chloride permeability test specified in AASHTO standard T 277-83. In Table 12, mixes 10 to 12 refer to the reference concrete containing no fly ash. The coulomb values at 91 days range between 320 and 2313. Fly ash concretes outperform the reference concrete in having very low coulomb values. Comparing the values at equal water-solid ratios, the reference concretes show much higher values than those containing fly ash.

Table 12. Resistance of Fly Ash Concrete to Chloride Ion Penetration

Mix No.	W/C+FA*	Charge Passed (Coulombs)	
		28 days	91 days
1	0.38	2231	491
2	0.31	1841	470
3	0.27	1160	373
4	0.39	918	325
5	0.31	794	320
6	0.27	471	278
7	0.39	3737	1078
8	0.31	2018	636
9	0.27	1144	535
10	0.39	2984	2313
11	0.31	1283	1005
12	0.27	1305	1003

* W= Water ; C= Cement ; FA= Fly Ash

The influence of carbonation on fly ash mortar and concrete in the presence of sodium chloride has also been examined. Carbonation depth and corrosion were reduced in fly ash concrete when prepared without the reduction in cement, but carbonation was accelerated when fly ash was used to replace cement.[84]

The relative performances of Class F and class C fly ash cement pastes have been studied by Roy et al.[85] It was found that in class F fly ash systems the resistance to chloride penetration was increased at all levels of replacement. However, class C fly ash provided high resistance to chloride ions only at a high replacement levels. It was also observed that increasing the curing temperature was very beneficial in decreasing the chloride ion penetration because of the advanced degree of reaction of fly ash and higher proportions of the C-S-H phase.

The reaction of fly ash and calcium hydroxide (formed from the hydration of the silicate phases in cement paste) reduces the amount of lime that is normally formed in cement pastes. Concern has been expressed on the possibility of reduced pH values in fly ash concrete promoting corrosion of steel. Almoudi et al. monitored the corrosion behavior of reinforced fly ash concrete for 4 years.[86] Generally, it was found that the fly ash concrete had a significantly higher resistance to corrosion than the reference concrete. The fly ash concrete had a pH value higher than 12.5 even after most of the lime had reacted with fly ash. In addition to factors already described to explain the increased resistance of fly ash concrete to corrosion, other possibilities such as the ability of fly ash concrete to bind more chloride and the possibility of unreacted fly ash blocking the pores or disrupting the continuity of the pores should be taken into account[87]

Silica Fume. A large amount of work has been carried out to demonstrate that the silica fume concrete exhibits a very low permeability to chloride ions. A comparison of the permeability of silica fume concrete with that of latex modified concrete or low w/c concrete shows that the silica fume concrete has the lowest permeability of the three mixes studied (Fig. 16).[88][21]

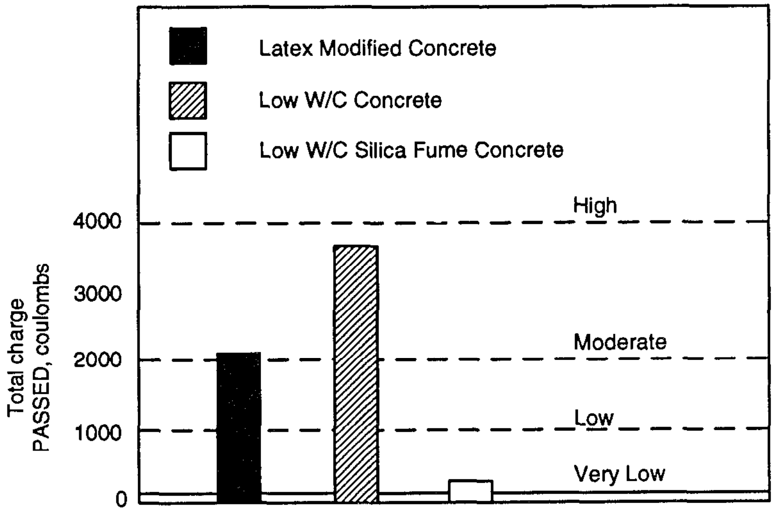


Figure 16. The chloride permeability in some concretes.

The effect of the amount of silica fume on the permeability of chloride at different depths in concrete has been determined by Marusin (Table 13).[89] The chloride content in the top layer, up to 12 mm, is similar for all concretes. The best performance in terms of low Cl^- ion penetration is shown by concrete containing 10% silica fume. It indicates that in concrete with high amounts of silica fume, increased amounts of silica fume exist in an uncombined form.

Table 13. Soluble Chloride Ion Content at Different Depths in Silica Fume Concrete

Mix No.	Silica Fume (%)	Cl^-(% wt. Concrete) at different depths (mm)			
		0-12	12-25	25-37	37-50
1	0	0.384	0.134	0.037	0.031
2	5	0.363	0.056	0.023	0.019
3	10	0.338	0.033	0.020	0.019
4	15	0.348	0.035	0.027	0.020
5	30	0.365	0.039	0.027	0.020

The effect of pH on the permeability of chloride ions has been examined for silica fume cement paste. The cement paste containing 6% silica fume was exposed to Cl^- solutions (3% NaCl) at a pH of 13 and 11.5. Even after 12 months of exposure to NaCl, Cl^- penetration was minimal at pH 13. At pH 11.5 some penetration of Cl^- occurred because of the leaching of Ca ions.[90]

Slags. Blast furnace slag concrete is very effective in withstanding sulfate attack. Its behavior towards the permeation of chloride solutions has been studied extensively. A systematic investigation was carried out on chloride permeability through slag concrete containing 50% slag replacement. The effects at different water-solid ratios were also compared.[91] The Cl^- permeability of slag concrete was compared with that containing silica fume (8%) or fly ash (25%). All were made at a W/C+SCM (SCM: supplementary cementing material; C: cement and W: water) ratio of 0.55 (Fig 17). At 28 days of curing slag concrete with a value of 935 coulombs, was less permeable than silica fume, fly ash and reference concretes, which had values of 1177, 3537, and 4685 respectively. In another study of antiwashout underwater concrete containing slag, it was found that Cl^- ion diffusion was considerably reduced from 1.5 cm^2/day to about 0.3 cm^2/day at a slag replacement level of 50%.[92]

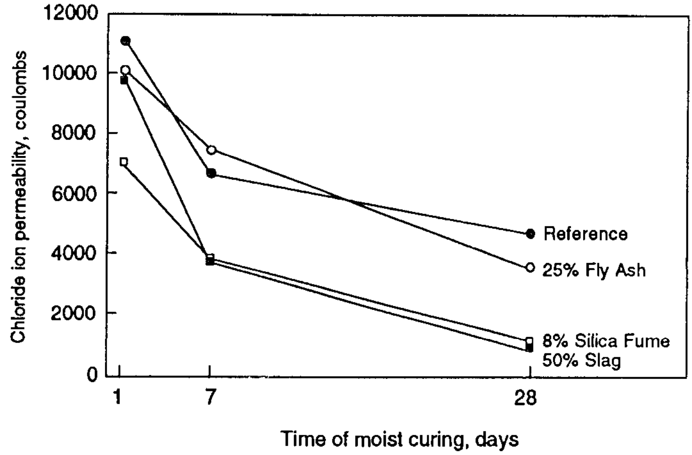


Figure 17. Chloride permeability in concrete containing mineral admixtures.

Polymer-Modified Mortars. Polymer-modified mortars are used for various purposes because of their adhesive and waterproofing qualities. Ohama et al.[93][94] have carried out extensive investigations on the properties of polymer mortars. The mortar mixes containing polymers such as styrene-butadiene, ethyl vinyl acetate, and polyacrylic esters in amounts of 0–20% with respect to cement were subjected to accelerated corrosion tests. They were also exposed to pressurized carbon dioxide for 72 hrs. The corroded area of steel was compared.

Figure 18 compares the corrosion inhibiting rates of the three polymer-modified mortars. The SBR mortar at 20%, provides the maximum inhibiting effect. PAE at 20%, exhibits the lowest resistance to corrosion. It was also observed that the chloride penetration was very much lower in SBR and EVA mortars. Marusin compared the chloride penetrated at various depths in concrete treated with sealers, coatings, and admixtures such as superplasticizers, polymer emulsions and silica fume.[95] The latex concrete and superplasticized concrete reduced the amount of chloride penetration, mainly due to their ability to reduce water requirement. For the reference concrete without the addition, the superplasticized concrete, acrylic latex, SB latex and epoxy modifier, at a w/c ratio of 0.44, 0.29, 0.29, 0.34, and 0.26, the acid soluble ion content (% by weight at a depth of 12–25 mm) was respectively 0.121, 0.021, 0.032, 0.028, and 0.115, suggesting that all admixtures-containing concretes were more impermeable to Cl^- than the reference concrete.

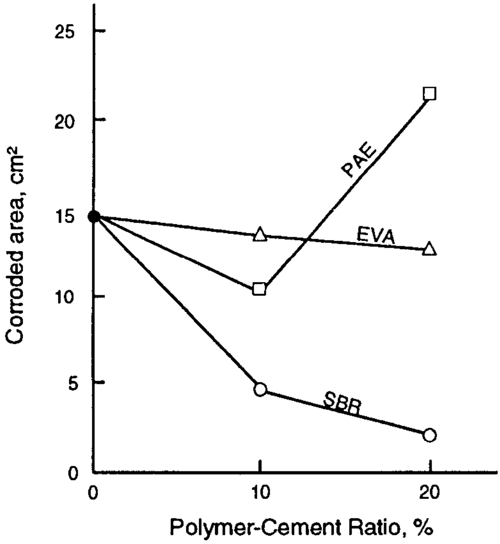


Figure 18. Corrosion inhibiting properties of polymer-modified mortars.

2.4 Chemicals as Corrosion Inhibitors

Introduction. Corrosion inhibitor is a chemical that is usually added in small amounts, as opposed to mineral admixtures which are added in larger amounts to reduce the permeability of concrete. Some chemicals used as corrosion inhibitors are capable of reducing or even inhibiting corrosion of reinforced steel. As already explained, one of the prime causes of steel corrosion is the ingress of chloride ions into concrete that depassivate steel. The loss of the protective oxide film exposes iron to corrosion. It is very essential that an effective inhibitor should not adversely affect the concrete properties and durability.

The practice of using corrosion inhibitors was pioneered in the Soviet Union. Because of the cold climatic conditions prevailing there, the antifreezing admixtures were advocated for winter concreting practices.

The antifreezing formulations contained large amounts of chloride compounds, and to counteract their adverse influence on corrosion, addition of corrosion inhibiting chemicals became necessary.[96] Several important reviews have been published on corrosion inhibitors in the last 20 years.[97]-[102] The types of inhibitors that have been studied include calcium and sodium nitrites, sodium benzoate, sodium/potassium chromate, sodium salts of silicates and phosphates, stannous chloride, hydrazine hydrate, sodium fluorophosphate, permanganate, aniline and related compounds, alkalis, azides, ferrocyanide, EDTA and many chelating compounds. In terms of practical experience and research data, nitrite-based compounds occupy a dominant position.

Corrosion inhibitors belong to three classes, depending on the mode of their action. Anodic inhibitors are passivators or strong oxidizing chemicals such as nitrites, chromates and molybdates. They strengthen the protective oxide layer over the steel which otherwise would breakdown in the presence of chloride ions. The mechanism involves redox reaction in which the inhibitor is reduced and steel becomes oxidized to iron oxide as follows:

$$2Fe^{++} + 2OH^- + 2NO^-_2 \rightarrow 2NO + Fe_2O_3 + H_2O$$

The chloride and nitrite ions engage in competing reactions. The cathodic corrosion inhibitor reduces the corrosion rate indirectly by retarding the cathodic process which is related to anodic dissolution. In this process, access to the reducible species such as protons to electroactive site on the steel is restricted. Reaction products of cathodic inhibitors may not be bonded to the metal surface as strongly as those used as anodic inhibitors. The cathodic inhibitor materials are bases such as NaOH, Na_2CO_3 or NaOH which increase the pH of the medium and thereby decrease the solubility of Fe. Most work has been carried out on aniline and its chloro-, alkyl-, and nitro-substituted forms and mercaptobenzothiazole.[103] The effectiveness of the cathodic inhibitor is related to its molecular structure. Increased overall electron density and spatial distribution of the branch groups determine the extent of chemisorption on the metal and hence its effectiveness. The mixed inhibitor influences both the cathodic and anodic processes. Because of the microcell corrosion processes occurring in reinforced concrete, a mixed inhibitor is ideally suited for application. They are aromatics or olefins with at least one proton and electron acceptor functional groups such as NH_2 or SH as in aminobenzene thiol.

It is essential that any of the inhibitors, to have practical applicability, should have certain requirements. The compounds should have strong electron acceptor or donor properties or both. The inhibitor should have good solubility characteristics and rapidly saturate the corroding surface and not leach out. The major amount of the added admixture should not be strongly adsorbed by the cement paste and making it unavailable to inhibit corrosion. It should induce polarization of the respective electrons at relatively low current values. It should be compatible with other admixtures that are used in concrete. It should be effective at pH and temperature of the environment in which it is used. The physical and durability of concrete should not be adversely affected. It should not be toxic and pose hazards.

Calcium Nitrite/Sodium Nitrite. Although a substantial amount of work has been carried out on different types of corrosion inhibitors, no other inhibitor has received as much attention as calcium nitrite. A good review on inhibitors, with special reference to calcium nitrite, has been published recently.[104] The process of manufacture of calcium nitrite became available in Japan after which an extensive research on calcium nitrite as an inhibitor was initiated in the USA. Nitrite has been used in the USA for more than 12 years and for nearly 35 years in Europe. In addition to other advantages Ca nitrite has a reasonably high solubility in water (40%). In the passivation of iron, in the presence of Ca nitrite, the reaction between iron and NO_2 produces NO. There was concern about the production of NO gas in concrete and also nitrite ions influencing the size of the anode and the dangerous cathodic reaction. It has been found that if produced, NO gas converts to NO^-_3 in the presence of O_2 only after corrosion has taken place with the destruction of concrete. It was also shown that the nitrite did not influence the reactions involved in producing anode but reacted with the resulting products of anode. Also, the reaction of NO^-_2 with hydrogen to produce NH_3 is not of concern because it can proceed only in an acidic environment.[105]

Calcium nitrite meets the requirements of the ASTM C 494. It accelerates the setting times and also rate of development of strength. In Table 14 the relative setting times and strength development in concrete containing Ca-nitrite are compared with those of the reference.[106]

The setting time is accelerated and compressive strength is increased as the amount of Ca nitrite is increased. At a dosage of 5% the percentage increase in strength at 1 day is 47% and at 7 days the value is 25%. Thus, Ca nitrite is both an accelerator and a corrosion inhibitor. In concrete systems it has little effect on air content and slump.

Table 14. Influence of Calcium Nitrite on Concrete Properties

Mix No.	% Accelerator (cement basis)	% Acceleration (Initial Set)	Compressive strength (MPa)		
			1d	3d	7d
1	0	-	10.4	21.2	29.0
2	1.69	24	14.1	22.5	29.9
3	3.39	30	14.9	23.8	32.9
4	5.06	38	15.3	24.3	36.4

Extensive work has been carried out by Berke on the effectiveness of Ca nitrite to control corrosion. In one study extending over a period of 4 years, 1200 samples were prepared including 15 mix designs and 4 dosages of nitrite at 0, 3 and 6 gals/yd^3. The concentration of calcium nitrite in water was 30%.[107] In these tests the specimens were partly submerged in 3% NaCl with 1.3" concrete cover. Corrosion was measured by polarization resistance technique, electrochemical impedance and visual inspection by periodic removal of the specimen. Total corrosion was expressed in terms of m mho/cm^2 months. The results of corrosion with reference to time are shown for concrete containing different amounts of $Ca(NO_2)_2$ in Fig. 19.[105] The study demonstrates that Ca nitrite delays the onset of corrosion and when it begins, the rate remains lower than that of the unprotected members. The corrosion resistance is better in a lower w/c ratio concrete.

Some studies have been carried out both in the laboratory and on minibridge decks and it has been concluded that Ca nitrite provides more than an order of magnitude reduction in the corrosion rate.[108][109] For example Gaidis and Rosenberg[110] subjected large concrete slabs, simulating a bridge deck, to daily salt application. Potentials developed by Cu/$CuSO_4$ were determined. Potentials more -ve than -350 mV were considered noncorroding and were not taken into account. Potentials between -350 and 400 mV were given weight of 1%, between -400 and 450 mV were valued at 2, and those between -450 and 500 mV at 4 and so on, geometrically. The weighted corrosion rate was computed by taking into account the number of squares involved in corrosion and it was plotted against time up to 5 years (Fig. 20). The results demonstrate the effectiveness of Ca nitrite. It was also determined that Ca nitrite conferred protection against corrosion if the chloride to nitrite ratio weight ratio (Cl^-/NO^-_2) did not exceed 1.5.

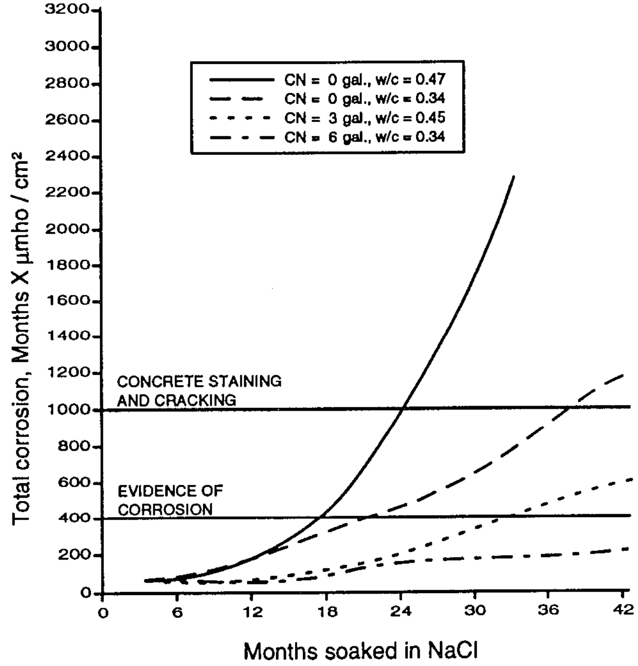


Figure 19. Corrosion vs time in 3% NaCl as a function of w/c ratio and calcium nitrite content. *(© NACE International. All rights reserved by NACE; reprinted with permission.)*

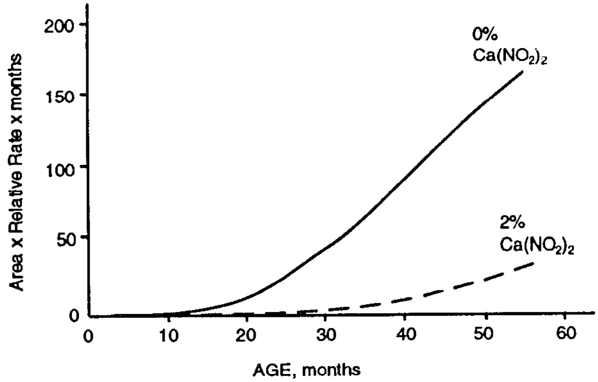


Figure 20. Weighted total corrosion of concrete with 2% calcium nitrite. *(Reprinted with permission.)*

The role of calcium nitrite in controlling chloride diffusion in concrete has been studied using a silica fume concrete. The results showed that Ca nitrite inclusion increases the coulombs according to AASHTO T 277.[111] However, in the presence of nitrite the diffusion coefficient for chloride is either lower or has no effect (Table 15). Other studies have indicated that the nitrite is compatible with fly ash concrete.

Table 15. Chloride Diffusion Coefficients and AASHTO T 277 Coulomb Values for Silica Fume-Calcium Nitrite Concretes *(Reprinted with permission.)*

Mix No.	Silica, %	Ca Nitrite L/m^3	AASH T 277 Coulombs	Diffusion Coeff. 10^{-8} cm^2/s
1	0	0	3663	11.0
2	0	20	4220	6.0
3	15	0	198	0.7
4	15	20	253	0.5
5	7.5	10	380	0.8
6	0	0	3485	2.0
7	0	20	1838	2.0
8	15	0	75	0.3
9	15	20	119	0.3

It is important to know what dosages of the inhibitor are to be added in order to counteract the corrosion of steel. The dosage required is related to the amount of chloride in concrete. A large amount of work has been carried out to determine the chloride-nitrite ratios that will control corrosion. Berke and Rosenberg,[105] basing data from various studies, have determined the chloride-nitrite ratios at which corrosion occurs, using a 30% nitrite solution. Based on these results, some guidelines were developed for the dosage requirements of calcium nitrite. These values are given in Table 16.

Table 16. Calcium Nitrite Dosage Requirements at Different Chloride Levels *(Reprinted with permission.)*

Calcium Nitrite (Gallons/yd^3)	Chloride (Pounds/yd^3)
2	6.0
3	9.9
4	13.0
5	15.0
6	16.0

In the above examples calcium nitrite was added as an admixture to the concrete mix. Some work has been carried out to test the possibility of repairing concrete by impregnating it with the nitrite.[112] Of the methods, the one of soaking the concrete, drying it by heating above the boiling point with subsequent soaking with aqueous nitrite solution, appeared to be the best. The test revealed that the treated area outperformed the adjacent untreated area. Table 17 shows the extent of nitrite penetration at different levels in a concrete deck at three locations. Chloride amounts at different depths are also given. Typically 20 l/m^3 of 30% Ca nitrite solution can protect steel in the presence of 7.7 kg/m^3 of chloride (105). The average Ca-nitrite content at a depth of 51–64 mm is about 26 l/m^3 of a 30% solution.

Table 17. Chloride and Nitrite Levels in Three Cores.* *(Reprinted with permission.)*

Depth(mm)	South West		Center		North East	
	Chloride	Nitrite	Chloride	Nitrite	Chloride	Nitrite
0-12	3.6	29.6	1.3	46.4	2.1	36.1
25-38	2.1	30.6	0.95	51.9	0.25	62.2
51-64	1.8	10.4	0.90	32.6	0.55	39.5
75-89	1.55	4.5	0.65	19.3	0.45	47.4
102-114	o.75	1.5	0.45	10.9	0.55	11.4

* Chloride=kg/m^3, Nitrite= L/m^3 of 30% solution
0.27 kg Ca Nitrite is present in a liter of 30% solution

Although molybdate compounds have been advocated for corrosion inhibition purposes, they have not been used as inhibitors in concrete practice. Hope and Ip examined the synergistic effect of Ca Nitrite-sodium molybdate combination on corrosion of steel in concrete.[113] The inhibitor mixture contained 4.5 parts of Ca nitrite to 1 part of molybdate. The test solution contained the inhibitors and sodium chloride solution. The concentration of the inhibitor was 0.12% by mass of lime water. The amount of NaCl was increased from 0 to 2% by mass of lime water. Corrosion was determined by visual inspection, ac impedance and half cell potential measurements. Steel potential became less negative and was about -70 mV SCE nine weeks after contact with the chloride solution,indicating a low probability of corrosion. Experiments showed that the inhibitor-to-chloride ratio of 1:11 protected steel from corrosion and that the combined admixture was more effective than when Ca nitrite was used alone. No data were given on the behavior of this formulation in reinforced concrete. The other properties such as setting time, strength, and durability aspects have to be determined if this formulation has to be used in practice.

Studies carried out on the effect of sodium nitrite on corrosion have generally concluded that it reduces corrosion considerably. The relative effectiveness depends on the dosage and the amount of chloride present in concrete. Gouda and Monfore found that 1–2% $NaNO_2$ by mass of cement reduced corrosion of steel in the presence of 2% admixed calcium chloride.[114] In the presence of 0.5% nitrite, passivation occurred initially but active corrosion proceeded afterwards. Several other investigators have confirmed the effectiveness of sodium nitrite in inhibiting or retarding corrosion.[98][99][115]-[117] The relative corrosion effects of sodium nitrite admixed with different amounts of calcium chloride are shown in Table 18.[98] In the presence of calcium chloride, 20–40% of the surface corroded. However, when sodium nitrite is present with calcium chloride, there was practically no corrosion effect. Andrade et al.,[118] applying galvanostatic and potentiodynamic polarization curves, determined polarization resistance which provided instantaneous corrosion rate. The results for three mortar mixes containing 1 or 2% calcium chloride and 2% calcium chloride + 2% sodium nitrite are shown in Fig. 21. Just after mixing, the corrosion rate with chloride+nitrite was lower than that with chloride alone. Ratios of $Cl^-/NO^-_2 = 1/1$ are not effective as the resistivity of the concrete is low. According to their study, for inhibition of corrosion, Cl^-/NO^-_2 > or = 1/1.5. One of the problems associated with the use of $NaNO_2$ is its detrimental effect on concrete strength. Curves for strength of mortar cubes containing 0, 2, and 4% chloride to which 0, 2, 4, and 6% $NaNO_2$ are added, are compared in Fig. 22.[98] The mortars containing only sodium nitrite have low strengths compared to the reference specimens. Even in the presence of calcium chloride there is a general decrease in strengths. The splitting strengths are also decreased considerably. There is also concern that the addition of sodium nitrite to concrete containing alkali-prone aggregates may enhance the alkali aggregate expansion.

Table 18. The Effect Sodium Nitrite on the Corrosion of Steel. *(Reprinted with permission.)*

Calcium Chloride(%)	Sodium Nitrite (%)	Surface Corroded (%)		
		0	20	40
0	——	*	—	—
2	——	—	*	—
4	——	—	—	*
0	2	*	—	—
0	4	*	—	—
2	2	*	—	—
2	4	*	—	—

* Indicates the incidence of corrosion

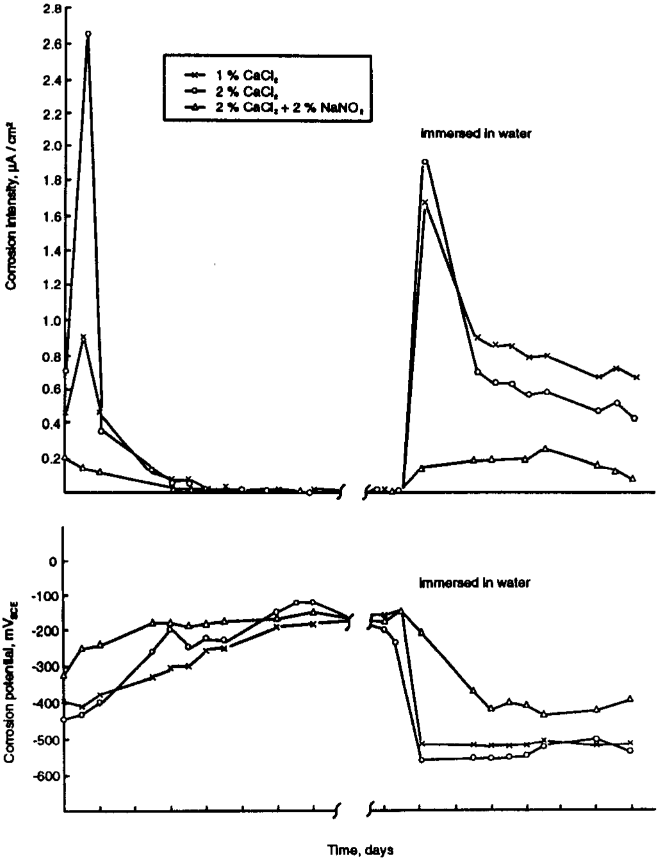


Figure 21. Corrosion intensity and corrosion potentials of concrete containing sodium nitrite and calcium chloride.

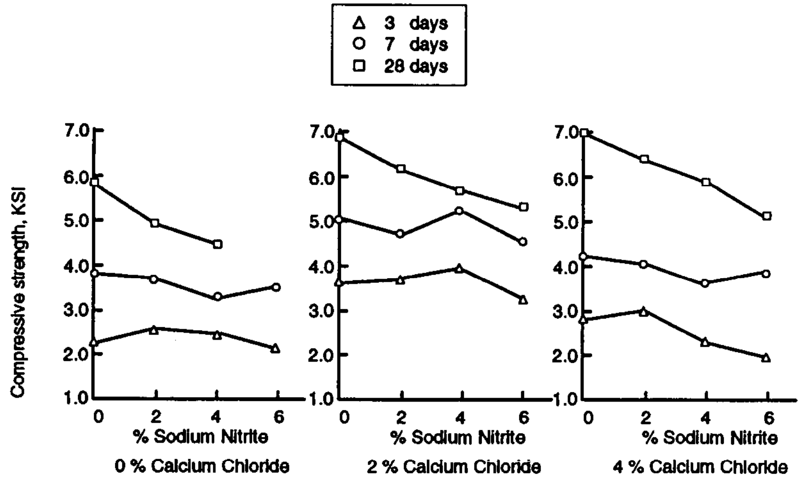


Figure 22. Effect of sodium nitrite and calcium chloride on compressive strengths of mortar cubes. *(Reprinted with permission.)*

As already stated the strength of concrete is decreased in the presence of sodium nitrite. In this regard, the effect is similar to that of sodium carbonate and sodium silicate which accelerate set but decrease strengths. In spite of low strengths, the concrete containing sodium nitrite shows the same permeability to chloride ions as the reference specimens having higher strengths. This would indicate that the pore structure is modified by sodium nitrite. According to Collepardi et al.,[119] a cracked concrete containing sodium nitrite when exposed to sea water, exhibits severe corrosion. Based on this work, it has been concluded that even in uncracked specimens with sodium nitrite, corrosion may take place after some time.

Other Corrosion Inhibitors. The work of Arber and Vivian[120] on stannous chloride has indicated that stannous chloride is a corrosion inhibitor. In a short period of testing and without the presence of chlorides, it does appear to decrease corrosion as measured by the tensile strengths and appearance of steel. Table 19 compares the tensile strength values in mortars containing different amounts of calcium chloride and stannous chloride.[120] The addition of calcium chloride has some positive effect on strengths at earlier ages but at 90 days there is a drastic reduction in strength. The addition of stannous chloride not only increases the strengths but they are maintained for longer periods. All the specimens were initially cured for 6 hrs in steam and subsequently moist-cured. The corrosion inhibition character was attributed to the stannous ion. In the work of Hope and Ip,[121] concern was expressed about the solubility of stannous chloride in water. Small white particles were formed after stannous chloride was mixed with lime water. Based on the behavior dosages up to 0.3% stannous chloride, they concluded that stannous chloride was not a promising corrosion inhibitor.

Table 19. The Tensile Strengths of Mortar Containing Different Amounts of Chlorides

Admixture (%)	Admixture	Tensile Strength (MPa)		
		7 days	28 days	90 days
Nil	Nil	2.00	2.79	3.16
2	Calcium Chloride	2.07	2.12	0.34
4	Calcium Chloride	2.23	1.17	0.46
2	Stannous Chloride	2.52	2.96	3.57
4	Stannous Chloride	2.92	2.93	3.12

Sodium benzoate has also been suggested as a potential corrosion inhibitor. Lewis et al. have described the application of benzoate as an inhibitor.[130] In this patent, the inhibitor could be applied as a mortar coating on steel at a dosage of 2–10% or incorporated integrally in concrete. Lewis et al. determined the physical properties of concrete to which 2% benzoate was added.[123] The setting times were not affected but the compressive strengths decreased. A comparison of the compressive strength of concrete containing 2–5% Na benzoate with that of the reference shows that at 28 days, the compressive strength of admixed concrete is decreased by about 40%.[122] The corrosion inhibiting property of benzoate needs further study. Lewis et al.[123] have concluded that sodium benzoate has a more persistent inhibitory effect than calcium nitrite. Gouda[114][115][124] found that to realize an inhibitory effect equal to that of sodium nitrite, the dosage of benzoate has to be increased six-fold.

The potential corrosion inhibitive properties of the compound Na_2PO_3F, has been tested by Andrade et al., either by incorporating it in a mortar or as a penetrant.[96] This compound acted as an anodic inhibitor, possibly with some cathodic action. The minimum required ratio of phosphate to Cl was suggested as 1. Impregnation of this chemical into concrete was also efficient in reducing corrosion.

Many other organic and inorganic compounds have been studied for their effect on corrosion. Potassium chromate is an anodic corrosion inhibitor. With the chromate, in order to obtain the same inhibitive effect as that using sodium nitrite, the dosage has to be doubled. It promotes the inhibitive action in the absence of chloride. When chloride is present, as for example, at 2% calcium chloride, no passivity was observed.[98] The physical properties of concrete are affected by the addition of chromate. The strength may decrease by about 30%. The action of several inhibitors was studied by Gouda and Halaka.[115] The critical concentration of these inhibitors required to prevent corrosion of steel in the presence of 2% NaCl is shown in Table 20.[115] Generally higher amounts are needed when blast furnace slag is used. The most effective inhibitors are sodium nitrite and potassium chromate.

Table 20. The Critical Concentration Requirements of Some Inhibitors. *(Reprinted with permission, The Institute of Materials.)*

Inhibitor	Critical concentration requirement (%)	
	Portland cement concrete	Blastfurnace slag concrete
Sodium Nitrite	0.75	1.5
Potassium Chromate	3.00	3.5
Sodium Benzoate	5.50	6.0
Disodium phosphate	5.50	6.0
Ammonium stearate	5.00	6.0

Other compounds that have been tested for their inhibiting action include carboxylic acids, hydrazine hydrate, chelating compounds, aniline and related compounds and petrolactam-based compounds.

Yau and Hartt investigated the influence of various chelating agents such as TEA, EDTA, DPTA, HEDTA and Chel-138 on their ability to control corrosion.[125] All the chemicals reduced the compressive strength of concrete. The strengths were particularly low in the presence of TEA and EDTA, the values being 3.6 and 4.6 MPa at 28 days compared to a value of 6 MPa for the reference. In the presence of 0.1 NaCl solution at pH 10 and 12, both HEDTA and Chel-138 decreased the critical potential for pitting. This decrease was proportional to the concentration of these additives. Hydrazine hydrate behaves as a normal anodic inhibitor.[126] The function of hydrazine hydrate is to block the anodic sites and, thus, enhance the anodic polarization above a critical concentration depending on the hydrazine-aggressive ion ratio. Higher concentrations of hydrazine cause instantaneous passivation of steel. Water soluble carboxylic acids such as malonic acid and a dicarboxylic acid have been shown to function as good corrosion inhibitors even in the presence of 2.5% chloride.[127] However, they cannot be recommended for use in concrete because they unduly retard the setting of concrete.

In spite of a large amount of published information, many unresolved questions still remain.[128] They include: the mechanism of passivation and depassivation of steel in the presence of chloride, the amount of chloride necessary for depassivation, the relative roles of mixed chloride and that applied externally on corrosion, the amount of corrosion product that is needed to cause destructive corrosion, the range of half cell potential that represents corrosion activity, and the best method of analysis of corrosive chloride.

Commercial Products. There are not many corrosion inhibitors in the market. The one produced by Master Builders is called Rheocrete 222. It is a water-based organic material. It has no significant effect on slump and rate of hardening of concrete. It is claimed to delay corrosion of steel both in cracked and uncracked members. In one experiment, it was found that the steel in the reference concrete showed corrosion in about 8 weeks, whereas that containing Rheocrete took 36 weeks to corrode. The recommended dosage for optimum corrosion protection is one gallon per cubic yard (5 liters per cubic meter). This admixture would need an increase in the amount of air entraining agent to obtain a specific amount of air. Protection would be needed to prevent the admixture from freezing and it is recommended that it be stored above 1.7°C and not exceeding 52°C. It is supplied in 55 US gallon drums.

W. R. Grace produces two types of corrosion inhibitors, DCI and DCI-S types. DCI-S does not have the same accelerating action as DCI. The DCI inhibitor increases the early strength development in concrete. This effect increases with the dosage. Both admixtures are compatible with all types of portland cements and other admixtures. Both may moderately reduce the amount of entrained air. Both freeze at about -15°C but the corrosion inhibiting properties are restored by thawing and thorough agitation. Mix water adjustment is necessary when using these admixtures. The adjustment factor is 0.635 kg of water per liter.

The Axim Concrete Technologies produces an inhibitor known as Catexol 1000CI. The action of this admixture is to stabilize the passive layer of iron oxide on the steel and also increase the density of concrete, thus decreasing the permeability of chloride ions. This inhibitor is particularly effective in concrete containing pozzolanic additives. In leaner mixes some retardation occurs. Good distribution of the admixture is promoted by addition during batching. It is compatible with other admixtures, but each admixture should be added separately.

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15

Miscellaneous Admixtures

Noel P. Mailvaganam

1.0 INTRODUCTION

Miscellaneous admixtures include a group of materials that are used to produce special modifications in concrete and mortar. They are widely used in a variety of proprietary building products, either as the sole ingredient to achieve a specific property in the concrete or mortar such as color, or in combination with one or more different admixtures to obtain multifunctional characteristics as in self-leveling flooring compositions.

The following materials are listed under the category of miscellaneous admixtures.

- Expansion producing
- Bonding
- Pumping aids
- Pigments
- Flocculating
- Dampproofing and permeability reducing
- Alkali/aggregate inhibiting
- Corrosion inhibiting
- Fungicidal, germicidal, and insecticidal
- Shotcreting

Information presented covers the mode of action of the admixture, its effect on the plastic and hardened properties of concrete and mortar, the factors affecting the modifications it produces, and the test methods used to evaluate its performance and quality. It emphasizes the more practical aspects related to its use in building products such as structural grouts and flooring compositions. During the last decade, corrosion inhibiting and alkali aggregate reaction inhibiting admixtures have been used more widely in concrete, particularly in North America and Europe for the former, and in Japan for the latter. Their inclusion in concrete mixes to ensure the durability of the structure has thus become a relatively common practice. A more comprehensive treatment of their use in concrete was therefore required. Accordingly, these admixtures are described in greater detail in Ch. 14.

Latex emulsions are often used in different repair applications such as bonding of new concrete to old concrete, sprayed concrete, or sand/cement repair mortar to assist in achieving a reliable bond. The chemistry, effects on the properties of plastic and hardened concrete, and the relevant standards that govern their use are discussed in detail in Ch. 9.

2.0 EXPANSION PRODUCING ADMIXTURES

In this chapter, admixtures that produce expansion are classed under a single general group: *expansion-producing admixtures.* This group is subdivided as follows:

(a) Admixtures which control settlement and provide expansion in the plastic stage. These are gas generating materials.

(b) Admixtures which control plastic settlement and hardened shrinkage by providing expansion in both the plastic and hardened state. These are composed of calcium sulfoaluminate and lime-based materials.

(c) Admixtures which do not control settlement, but provide expansion only in the hardened state. They consist of granulated iron filings and chemicals that promote oxidation of iron in the presence of moisture and air.

Due to the rigorous control of materials, conditions and procedures that promote corrosion in concrete, the use of expansive agents based on the rusting of iron particles has been severely restricted to situations where the application is only of a temporary nature, e.g., in quick setting compounds used to seal cracks where there is a flow of water.

2.1 Gas Forming Admixtures

Background and Definitions. These admixtures can be grouped into two classes:

(i) Single component admixtures, consisting chiefly of a gas producing agent and other minor ingredients for bubble stability and acceleration of the gassing reaction.

(ii) Multicomponent admixtures, which contain other chemical ingredients for water reduction and strength increase.

Chemical Composition. A variety of metals and other materials are used as single component admixtures: metallic Al, Mg or Zn which release hydrogen,[1] H_2O_2 which liberates oxygen,[2] nitrogen and ammonia compounds which liberate nitrogen,[3] and certain forms of activated carbon or fluidized coke which liberate air.[4][5] Of these, Al powder is more extensively used than others.

For producing hydrogen, both the unpolished granular and polished leaf Al powder are used. The standard 100 mesh varnish leafing grade used in the paint industry is suitable. The granular material which shows less luster than the leafing grade may contain a passive oxide coating which is less readily attacked by moist air. Therefore, it is more stable on storage and, since it is slower reacting than the leaf grade, it produces expansion over a longer period in the plastic state.

Calcium hypochlorite is utilized in conjunction with H_2O_2 to produce oxygen. The ratio of hypochlorite (70% active chlorine) to hydrogen peroxide (30% active solution) may be 1.5 or higher.[2]

Materials which liberate nitrogen consist of a suitable nitrogen gas delivery agent which can be organic or inorganic compounds (preferably azo, hydrazine, or azide type) with an activator.[6] An important prerequisite for the nitrogen delivery agent is the presence of at least one NN bond in the molecule. Aluminate and copper salts have been used as activators.

The release of air in the cement water system occurs when fluidized coke or certain forms of activated carbon passing the 30 mesh sieve are used. A moisture content of 3% is required for the fluidized coke to function properly.

Multicomponent admixtures are generally used in structural grouting of machine baseplates and cementing of porous formation of oil wells. Commonly available commercial products combine two or more of the following type of admixtures : *(a)* gas forming; *(b)* workability aids (water reducers and plasticizers); *(c)* retarders; *(d)* accelerators; *(e)* gel stabilization admixtures (water retainers, cohesion inducing thixotropic or flocculating admixtures); *(f)* pozzolanic or supplementary cementing materials such as slag and other fillers like calcium carbonate. Although this type of proprietary admixture is available on the market, in many instances preblended, factory made grouts containing cement, sand and admixtures are used.

Oil well cementing admixtures consist of an array of compositions designed for a wide range of temperatures and pressures depending on the depth at which grouting is carried out. In addition to air entraining agents and retarders, Al powder may be combined with three special types of admixtures peculiar to the oil well cementing application. These are water retainers, densifiers, and density reducers. Al powder is also coated with a water soluble resin (abietic acid) to produce the following properties which increase the effectiveness of the gassing reaction:

- Delay the expansion until the grout or cement slurry reaches its final location
- Reduce the effects of high temperature and pressure on the gassing reaction so that the efficacy of the of the expansion produced is realized at the required depth
- Stabilize the gas bubble and prevent coalescence as the height of the grout lift is increased

Three types of retarders are used: *(1)* starches or cellulose products; *(2)* sugars; and *(3)* acids or salts of acids containing one or more hydroxy groups, which are usually chosen for their efficacy at high temperatures. The water retainers are generally gels clays, latex emulsions or cellulose ethers. Air entraining agents such as vinsol resin stabilize the gas bubbles while iron, barytes, and bentonite are used to increase or reduce the density of the grout. The admixtures are normally preblended with a suitable cement at a dosage rate which is dependent on the placing conditions.[7]

Mode of Action. The requirement of all gas generating admixtures can be rationalized as a process wherein a known quantity of the gassing agent reacts with chemicals added or present in the cementitious mix, to generate a known volume of gas with a predetermined amount of expansion.

Hydrogen gas is produced by the reaction of the alkaline reaction products of freshly mixed cement with aluminum powder. Minute bubbles are produced throughout the mass causing it to expand. The duration of the reaction is usually 1–1½ hrs, gas evolution normally ceasing prior to the setting time. Although the mechanisms by which expansion occurs in both grouts and cellular concrete containing Al powder are essentially the same, the process for the latter requires a more precise control of the reaction. Sodium hydroxide is generally added to the mix to ensure that all Al powder is consumed.

In the oxygen liberating systems the reaction between calcium hypochlorite (bleaching powder) and hydrogen peroxide occurs with the production of calcium chloride that accelerates the reaction.[8]

Reaction in the nitrogen gas producing system takes place by the decomposing action of the activator (Cu salts) on the N-N of the nitrogen containing molecule.

Fluidized coke particles liberate air as water or the cement liquor displaces air contained in the pore spaces of the particle. The reaction intensity is reported to be affected by the moisture content of the particle prior to the addition of the water to the mix. A moisture content of 3% has been found to be optimal.[4]

The gassing reactions occurring in grouting admixtures, pre-blended proprietary grouts, and oil well cementing compositions are essentially similar to those occurring in single component admixtures. However, the other components of the admixture exert secondary effects that modify the rate of the reaction. Vinsol resin coated on the Al powder can significantly delay and reduce the rate of gas evolution.

Factors Affecting the Gassing Generating Reaction. The rate, duration and extent of gas generation is determined by the following factors:

(a) Type and quantity of the admixture
(b) Composition and fineness of the cement
(c) Ambient and mix temperature conditions
(d) Water content and consistency of the mix
(e) Mix proportions
(f) Presence of other admixtures in the mix.

(a) *Type and quantity of gassing admixture:* Unpolished aluminum powder reacts faster than the polished variety or that which is precoated. Precoated material, producing a more gradual reaction, allows the maximum expansion potential to be obtained. The fineness and moisture content of the fluidized coke particle influences its gas generation capability. In the nitrogen gas generating system, the type of nitrogen releasing agent used produces different reaction intensities. The extent and intensity of the reaction is also proportional to the quantity of admixture used, different dosages producing varying amounts of expansion and densities.

(b) *Composition and fineness of cement:* Cements with higher values of alkali contents and fineness accelerate the gas evolution in concrete and mortar containing aluminum powder. The reaction in the nitrogen- and oxygen-releasing systems are initiated and controlled by activators incorporated into the mix and, hence, the rate and duration of such reactions are independent of the cement composition and fineness.

(c) *Mix proportions:* Characteristics of mix ingredients and their proportions affect the quantity of gassing admixture required to generate a desired expansion, e.g., mixes with poor cohesion tend to use higher dosages.

(d) *Consistency of the mix:* Amount of mixing water and consistency of the mix influence the rate and duration of the hydrogen producing reaction. The intensity of the reaction is initially increased at higher water contents. The trend, however, is reversed after a certain water content and consistency are reached. An optimum amount of water is required to obtain the maximum expansion and it depends on the type cement and aggregates. Table 1 shows the effect of this factor on the expansion reaction in portland cement grouts.[9] Although mix consistency does not directly affect the nitrogen- or oxygen-producing reaction (since released alkalis are not necessary for this reaction), very high consistencies may affect the magnitude of expansion if a significant amount of gas escapes from the fluid mix prior to the setting of the cement.

(e) *Temperature:* The expansion reaction produced by aluminum powder is affected significantly by temperature. At 30°C the reaction may be completed within 20 minutes, while at 5°C the reaction may not be completed for several hours. Approximately twice the quantity of the admixture is required at 5°C to produce the same amount of expansion as that obtained at 20°C. Table 2 shows the effect of ambient temperature on the expansion produced prior to setting. Temperatures exceeding 30°C accelerate the reaction to such an extent that the expansion is practically completed before the concrete or mortar is poured in place.

The reactions of the nitrogen- and oxygen-producing systems are not directly affected by temperature. The air-releasing coke particle system behaves in a manner contrary to that observed in the aluminum powder systems (lower temperatures, such as 10°C, produce more expansion than higher temperatures). This effect cannot be readily explained.

(f) *Influence of other chemical admixtures:* Sodium hydroxide added to the mix during the manufacture of cellular concrete accelerates the reaction and ensures that all the added aluminum powder is consumed in the reaction. In the hydrogen peroxide/hypochlorite reaction, calcium chloride is produced in sufficient quantities to cause a rapid set of the mix. Materials such as saponin and neutralized vinsol resin are used in cellular concrete to stabilize the cell structure and prevent the escape of gas from the mix before hardening occurs. Stability of the gas cell improves homogeneity of the void structure and minimizes drastic strength variations.

(g) *Mixing criteria:* Mixing speed, duration of mixing period, and type of mixer used may affect the quantity of gassing agent required to obtain a given amount of expansion. Prolonged mixing will result in a loss of evolved gas, causing a decrease in volume.

In cellular concretes, the sequence of addition of hydrogen peroxide and hypochlorite to the mix affects the rate of gas generation. A more gradual expansion occurs when the hydrogen peroxide is added prior to the hypochlorite.

Table 1. Influence of the Water Content on the Expansion of Aluminum Powder Containing Cementitious Grouts[9]

Quantity of Mixing Water (% dry mass of dry mix)	Consistency of Grout to 24 hrs After Casting	% Volumetric Expansion
16	thixotropic, pourable	0.66
16.5	pourable	0.70
17	pourable	0.76
17.5	fluid	0.50
18	very fluid	0.34

Table 2. Effect of Ambient Temperature Variation on the Rate of Expansion in an Aluminum Powder-Containing Structural Grout*

Ambient Temperature (°C)	Free Expansion at 1 hr (%)	Expansion at Initial Set (%)
10	0.43	0.60
20	1.12	3.40
30	2.30	2.80
40	0.50	0.50

*Courtesy Sternson Ltd.

Effects on the Plastic Properties of Concrete and Mortar.

(a) *Water reduction:* Single component admixtures containing the gassing agent as the sole active ingredient will not produce any water reduction in the mix. The use of water reducers, superplasticizers, retarders and an air entraining agent in conjunction with the gassing agent as a product will result in water reduction. The degree of water reduction will depend on the amount and type of admixture used.

(b) *Workability:* Single component admixtures have little effect on workability of concrete and mortar, at normal dosages. Multicomponent admixtures containing water reducing retarders, when used in grouts and oil well cementing compositions, impart high workability that is maintained for long periods. Synergistic effects are often produced giving very cohesive yet workable mixes. In lean and harsh concrete mixes, the use of high levels of gassing admixture yields a "buttery" consistency.

(c) *Bleeding and settlement:* These admixtures, when used in normal weight concrete and mortar, offset plastic shrinkage. The expansion compensates for the vertical contraction due to sedimentation. In applications where the height of the structure is many times larger than the width (as in post tensioned vertically oriented tendons), there is a tendency for water exudation and the accumulation of large quantities of water in the tendon sheath. This is offset by the use of water retaining admixtures with the gassing agent.

(d) *Setting characteristics:* Normal initial and final set times of normal weight concrete and mortar are altered by the use of gassing admixtures. However, when accelerators, water reducers, retarders, or thickening agents are used in conjunction with the gassing agent, setting time is accelerated or retarded, depending on the type of admixture added. Strong retarders normally used with oil well cementing compositions extend the setting times. In the manufacture of cellular concrete, sodium hydroxide or sodium phosphate are added with Al powder, and these and calcium chloride formed in the gas generating reaction promote a rapid set.

Effects on the Hardened Properties of Concrete and Mortar. The bubbles generated by the gassing reaction are distributed homogeneously in the hardened concrete. Depending on a number of factors affecting the reaction, concrete or mortar varying in composition and physical properties can be obtained. For a given application, the amount of expansion, and the time intervals during which it takes place, are important factors to be considered.

(a) *Volume changes:* Although the expansion produced in the plastic state offsets plastic shrinkage, once the grout or concrete has set, the expansion produced has little effect on the subsequent shrinkage caused by drying or carbonation (Fig. 1). Mortar and cellular concrete containing gassing agents produce higher drying shrinkage than ordinary concrete and mortar.[2] In proprietary grouts which contain water reducing admixtures,

the restrained volume after hardening has been found to be larger than that of reference mixes.[10]

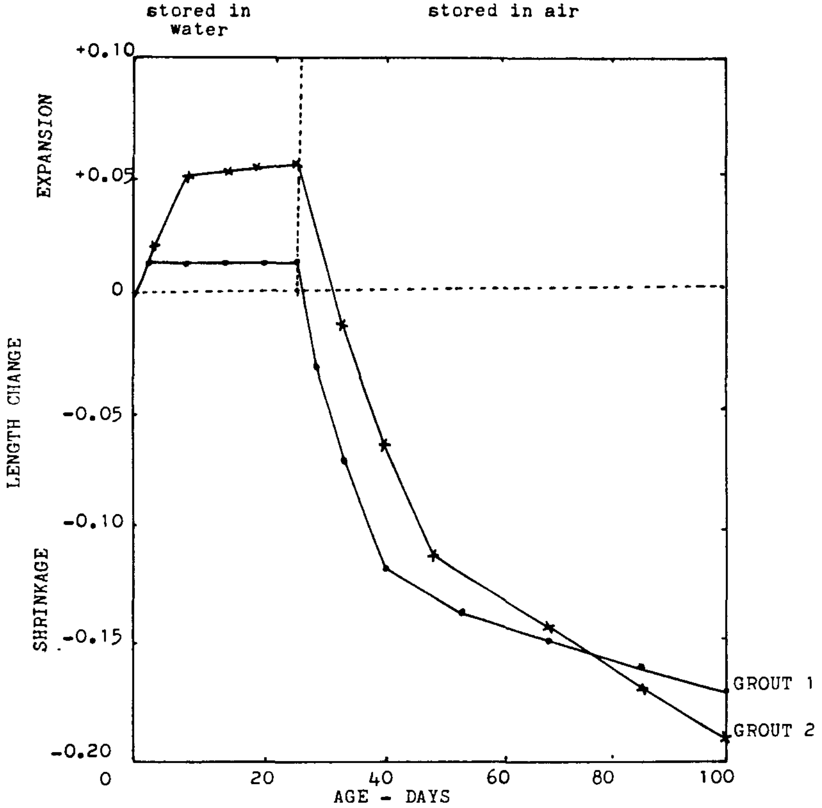

Figure 1. Drying-shrinkage of two gas-producing grouts by ASTM C-157 procedure. *(Courtesy G. K. Gunnyon and D. R. Morgan)*[10]

(b) Strength: When expansion of the concrete or mortars is restrained by external pressure, little or no strength reduction results from the use of the gassing systems. Under unrestrained conditions, however, the gas bubbles tend to rise to the surface and may not be uniformly distributed throughout the mortar. Additionally, numerous horizontal cracks may form, resulting in significant strength reduction (Fig. 2). The effect increases with dosage of the admixture.

Other admixtures in multicomponent materials modify the strength values obtained. Water reduction and water retention, due to the use of water-reducing and viscosity-increasing admixtures, decrease porosity. Thus, increased strength values are obtained. Accelerators or retarders present in the mortar compositions influence the rate of strength development at early ages.

In cellular concrete (hydrogen and oxygen producing systems), strength values are governed by the density of the concrete. Materials weighing 10–20 lbs/ft^3 (160–320 kg/m^3) have little strength while those with densities of 35–100 lbs/ft^3 (560–1600 kg/m^3) have load bearing capacity. The densities can be predetermined by using a specified amount of the gassing agent.

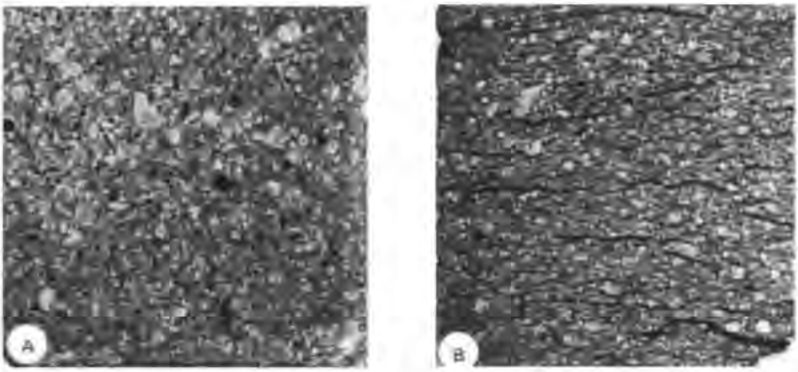

Figure 2. Photographs of cross-sections of hardened aluminum powder containing grout specimens under (A) restrained conditions and (B) unrestrained conditions. *(Courtesy Sternson Ltd.)*

(c) Density: The formation of void framework due to the generation of minute bubbles from the gassing reaction, results in lower concrete and mortar densities than corresponding mixes which do not contain the admixture. Density depends on the dosage of the admixture, degree of restraint, mix proportions, consistency of the mix and bubble stability. A reduction in the density due to the void framework also effects the modulus of elasticity; the extent of the decrease is governed by the level of the admixture dosage.

(d) *Durability:* Very little published information is available on the freeze/thaw resistance of concrete and mortar containing gassing admixtures. Notwithstanding this, grouts, mortar and concrete with gassing admixtures have been used successfully in exterior applications. Microscopic examination of slices obtained from 2" x 2" cubes of a gas generating grout has shown that the bubble spacing and other air void parameters required to ensure freeze/thaw resistance can be obtained in mixes under restrained conditions.[11][12] Cellular concretes (both moist cured and autoclaved) are reported to exhibit greater freeze/thaw resistance than might be predicted by porosity values.[13]

Preparation. Aluminum powder, used in both single and multicomponent admixtures, is produced by stamping or ball milling, sieving and a final polishing process. Stearic acid or other fatty acids are usually added to prevent the pieces from agglomerating. In the unpolished material the last stage of polishing is eliminated. The powder used in multicomponent admixtures is usually precoated and stored in bulk as a premix. Precoating is usually carried out by stirring the Al powder in a solvent or a aqueous solution of water soluble resin (vinsol or carboxyvinyl polymer) until a stiff gel is formed. The mix is then spread out and left to dry in an oven under low heat when chunks of the material are formed. These are then ground using a hammer mill and separated by sieving into the required size (30 mesh).[14]

Fluidized coke obtained from the petroleum refining process is either sieved or separated by the fluidized bed process to the required particle size (30 mesh). The coke is normally dried to remove most of the water contained in the pores and allowed to regain a moisture content up to 3% during exposure to cool air. The nitrogen and oxygen liberating systems are usually industrial grade chemicals which are formulated to obtain the required amount of gas bubbles.

Multicomponent admixtures used with oil well grouting cements and cellular concrete applications are mixed in predetermined proportions with other admixtures or chemicals to give proprietary products that yield desired properties in concrete and mortar.

Dispensing and Addition Procedure. As only a small amount of these fine powdered admixtures is used and because of the tendency of Al powder and coke particles to float in the mixing water, the materials are usually mixed with sand, fly ash or calcium hydroxide, prior to incorporation into the mix.[13] The point of addition is usually at the mixer by manual methods. Most of these admixtures are, however, used in factory blended sand/cement grouts. Except for hydrogen peroxide, all other materials are powders. Due to the small quantities used they are carefully weighed and discharged into the mixer. The materials are usually added to the fine aggregate, mixed for a minute and then mixed for a further period of 3–5 minutes with the other ingredients. Hydrogen peroxide may be metered into the mix with the usual automatic admixture dispensers or by manual methods.

Storage and Shelf Life. Single component admixtures consisting solely of metallic powder should be packaged in durable containers resistant to damage by mechanical handling. Contact of moisture with metallic powders must be avoided. The materials should be stored in areas free from high relative humidity and temperature extremes to avoid condensation. Fluidized coke also requires storage under dry conditions.

The shelf life of all types of admixtures is governed by the type of packaging used and the storage conditions. Adequate storage and packaging of Al powder containing materials, ensures a shelf life of 6–9 months. Precoating of the powder usually extends the shelf life by six months.[1]*

Precautions and Hazards. The duration of gas production determines volume stability. Should the expansion be completed well before the hardening of the concrete or mortar, a gradual settling occurs from the time expansion ceases until the material starts to harden. For concrete, unrestrained expansion must not take place before the concrete gains sufficient strength, otherwise the expanding forces will disrupt the concrete.

In order to limit settling and potential disruption, it is necessary to reduce the intensity of the gas producing reaction and increase the duration of gas generation. Precoating the metallic gassing agent with a water soluble coating usually provides the desired reaction duration and reduced reaction intensity.* The degree of solubility of the coating or its thickness controls the rate and the timing of the gas generation reaction. Extended periods of mixing cause the gas to escape with a consequent loss of expansive potential.

Aluminum powder is highly reactive, often forming explosive mixtures in dust clouds.[14] However, most of the commercially available materials will have been exposed to the atmosphere for some time before use and will not, therefore, ignite without an external source of ignition. Safety precautions are: *(1)* avoid dust clouds, *(2)* prevent potential causes for ignition in the vicinity of the manufacturing and storage areas, *(3)* prevent electrostatic charges by grounding equipment.[14]

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* R&D Report, Sternson Ltd., Brantford, Ontario.

Applications. Gas producing admixtures are used in concrete, mortar and grout for the following purposes:[15]

- Improve the bond of steel to concrete of horizontal reinforcing rebar in deep beams.
- Improve the effectiveness of grouts by offsetting volume changes due to shrinkage and settlement in the bedding of machinery and under pinning applications.
- Filling of watertight joints and grouting of cracks in repair work.
- Void filling applications such as prepacked concrete and prestressed concrete ducts.
- Improving the homogeneity of concrete.
- Production of cellular and self stressed concrete.
- Oil well cementing of porous rock formations.
- In cement-based waterproofing coatings.

Standards and Codes of Practice. Evaluation, selection and quality control of an admixture is done by assessing the performance of the concrete, mortar and grout containing the admixture. The Australian Standards AS 2073-79 (Methods for Testing Expanding Admixtures for Concrete and Mortar) and AS-2072-79 (Methods of Sampling Expanding Admixtures for Concrete and Mortar) are the only current standards which give test methods and the required properties for assessing the performance of these admixtures.[16]

At present, the use of these admixtures is chiefly in grouts and patching compounds. The assessment of performance and control of their quality is covered by the following relevant standards, construction guides, or miscellaneous publications. Standards relating to other chemical admixtures are discussed in other chapters.

American Society for Testing and Materials

ASTM	- 1107-89	- Standard Specification for Packaged Dry, Hydraulic-Cement Grout (Nonshrinkable)
ASTM	- 827	- Early Volume Changes

Corps of Engineers

CRDC - 621-76 - Specification for Nonshrink Grout

- 613 -74 - Method of Test for Expansion of Grout Mixes

- 79 - 58 - Method of Test for Flow of Grout Mixes (flow cone method)

- 81-74 - Method of Test for Expansion of Grout Mixes

CSA Standards

A.23.2 1B - Viscosity, Bleeding Expansion and Compressive Strength of Flowable Grout

Australian Standards

AS-2073-79 - Method of Testing Expansive Admixtures for Concrete, Mortar and Grout

AS-2072-79 - Method for Sampling of Expansive Admixtures for Concrete, Mortar and Grout

SAA-MP-20-3 - Information on Expanding Admixtures for Use in Concrete, Mortar and Grout

British Standards

CP—110 Part 1 1972 - The Structural Use of Concrete, Design, Materials and Workmanship. Grouting of Prestressing Tendons. Clause, 6.12.

BS-5400 Part 7&8 - Grouting of Prestressing Tendons. Clause 3.12 (in both parts) 1978

American Petroleum Institute

API Specification - 10A - Specification for Oil Well Cements and Cement Additives, 19th edition, 1977 Dallas, U.S.A.

API -RP-10B - Recommended Practice for Testing of Oil Well Cement and Cement Additives, 20th edition, April 1977, U.S.A.

Other Tests

(1) Plate Lift-Off Test: A non standard test used to determine bond characteristics of grout to base plate.

(2) *Simulated base plate:* The test is used to assess the performance of the grout under simulated field conditions. Results give approximate values and percent contact area between the grout and base plate. Details of the test methods pertaining to shrinkage compensating grouts are discussed in Reference 15.

Publications: Some important publications on grouting include:

- C. J. Budge, *Construction Guide for Preparing and Grouting Ducts in Prestressed Concrete Members,* Cement and Concrete Association, London, UK (1971).
- *Grouting of Tall Vertically Prestressed Ducts.* Current practice sheet 37, Concrete Society working party on grout, Cement and Concrete Association, London, UK (1968).

There is no consensus on an effective method to measure volume changes. This is mainly due to differing opinions on the desired amount of expansion, chemical mechanism by which volume change should be achieved and the relevancy of the test methods.[17] Therefore, in the interpretation of the results from a given method, the type of admixture and its expansive characteristics must be considered. ASTM 1107-89 covers three grades of grout, classified according to the volume control mechanism exhibited by the grout after being mixed with water. The choice of the test method is, therefore, left to the judgment of the grout user or the admixture manufacturer. The CRDC-621 test method is a relevant quality control test for the uniformity of the admixture or admixture-containing products. The CDRC-613 and ASTM-827 (early volume changes) are useful routine quality control tests after initial correlation tests are carried out according to CRDC-621.10.

2.2 Admixtures Containing Granulated Iron Filings

Background and Definitions. Unlike gas producing admixtures, iron filings-based admixtures cause expansion only after the mortar has hardened. Two basic types, iron particles with rust promoting or rust inhibiting admixtures, are generally used both under restrained and unrestrained conditions in grouting and flooring compositions respectively. They provide other auxiliary functions such as abrasion and impact resistance in the products in which they are used.

Chemical Composition. Single component admixtures contain graded granulated iron filings as the sole active ingredient. Iron filings are generally obtained from metal boring wastes. The metallic raw materials are first processed by firing in a kiln, to rid oily wastes, carbon and other organic material, quenched and magnetically separated. Magnetic separation usually separates the potentially reactive metal particles such as zinc and aluminum from the iron. Depending on the intended application, the metallic particles may either be treated with chemicals to produce a passivated surface layer or directly sieved and graded. Table 3 shows a typical gradation of iron filings used in these admixtures.

Table 3. Typical Range of Gradation Granulated Iron Filings Used in Admixtures Containing Iron Filings*

Sieve Mesh Size	Percent Retained
No. 8	0
No. 16	6-10
No. 30	48-54
No. 50	32-37
No. 100	1.4-3.2
No. 200	0.1-0.4
Fineness Modulus	2.65-2.78

* Courtesy Sternson Ltd.

Both the untreated and treated iron particles may be mixed with rust inhibiting chemicals, water reducers, predetermined proportions of cement and sand, and used in flooring and grouting compositions. Products such as quick setting patching compounds and grouts which expand by the rusting of iron particles contain only the untreated particles. Rusting is usually obtained by oxidation promoting chemicals like calcium chloride, ferric chloride or ammonium chloride. Quick setting patching compounds contain high levels of calcium chloride and type III cement. Grouting and flooring compositions may contain either portland or shrinkage compensating type-K cements. Iron particles used in grouts to provide impact resistance and abrasion resistance in floors are always combined with corrosion inhibiting admixtures (such as sodium nitrite, sodium benzoate, or calcium nitrite) and water reducing agents.

Factory preblended flooring and grouting compositions often consist of mix ratios of cementing material (Type I, Type III, Type K fly ash or slag) to iron particles in the range from 1:2.5–3 respectively. On-site mixing of such grouts, therefore, merely requires the addition of the stipulated water content per bag of grout to produce the desired consistency.

Mode of Action. Oxidation of the iron particles in the presence of rust promoting chemicals occurs in the first few days of hardening, causing sufficient volume increase to offset the settling that occurs before initial set. In compositions containing treated iron particles or those containing corrosion inhibiting admixtures, expansion is produced by the use of expansive cements such as Type K cement or expansive calcium aluminate or lime-based admixtures. Unlike the rust promoting types, these admixtures do not show significant expansion after 48 hours and, therefore, are not susceptible to disruptive expansion when exposed high moisture levels. Flooring compositions are incorporated into the concrete by the *dust on* method. Iron particles containing cement and other admixture components are evenly distributed on a freshly screeded horizontal slab and subsequently trowelled into the surface of the concrete. The closely knit mesh-like structure that results when finishing operations are completed produces a dense energy-absorbing, highly resilient finished floor.

Effects on the Plastic and Hardened Properties of Concrete and Mortar. The mix consistency achieved in a composition containing iron particles is usually a function of water reducing and accelerating admixture present in the product. Grout formulations that contain superplasticizers are generally placed at fluid to flowable consistencies. As in most instances where a superplasticizer is used, slump loss is rapid and the mix may therefore require continuous agitation prior to placing. Fast-setting patching compounds containing high levels of $CaCl_2$ are mixed to a plastic consistency that hardens within five minutes. The water demand of the materials is quite high.

Mortar mixes with poor cohesion caused by high water or low cement contents, exhibit pronounced bleeding and settlement, separating into dense-packed solid layer and supernatant water layer. Compositions containing accelerators produce set acceleration which at the extreme occurs in minutes for quick set compounds. Grouting compositions containing superplasticizers and water retainers often extend the set times by one or two hours in comparison with those containing accelerating admixtures. The setting time is not generally affected by the addition of metallic particles.

Incorporation of iron particles into the mix results in a significant increase in density of concrete and mortar, and the increase is proportional to the amount of iron particles contained in the mix. The degree of vertical confinement provided and the availability of moisture determine the volume stability of the concrete and mortar that contain iron particles and oxidant ($CaCl_2$). In the absence of restraint, concrete and mortar containing high levels of the oxidant, when subjected to wetting and drying cycles, produce self destructive expansion. If expansion continues after the first few days, strength decreases. Strength levels attained by the mixture containing treated iron particles or rust inhibiting agents are usually lower than those produced when rusting occurs. The lower cohesion in high consistency mixes allows the gradual settlement of the denser iron particles causing inhomogeneity in the concrete or mortar, and this results in strength variation.

Materials used in flooring composition have a high loading rate and, therefore, increase significantly the density of the surface layer of a concrete slab and improve the abrasion resistance. The degree of improvement is determined by the amount of admixture incorporated into the concrete. High moisture levels and intermittent exposure to moisture drastically reduce the performance of concretes containing such admixtures.

The ability to accommodate shock impact stresses is considerably improved in mortar and concrete due to the energy absorbing characteristics of the metal particles. This applies to situations where rigid vertical confinement is provided and where no further rusting and expansion occurs. Continued rusting after hardening will dramatically lower the capability of the composite to withstand impact loads due to the cracks that develop within the matrix as a result of the expansive forces generated.

Applications. Granulated iron particle-bearing admixtures, both rust inhibiting and rust promoting (catalyzed) types, are used in the following applications.

- Grouting of machine base plates and column bedding.
- Floors subject to heavy wear such as floors in warehouses, armament and automotive factories and aircraft hangars.

Catalyzed products cannot be used for the applications given below:

- Where there is no rigid confinement as unbolted plates.
- In prestressed concrete.
- In equipment subject to stray electrical currents.

- For anchor cables designed for stresses over 80,000 psi.
- In contact with aluminum concrete embedments.
- Under an equipment which experiences significant thermal movements.

The use of shrinkage-compensating cement, expansive admixtures, and rust-inhibiting admixtures has drastically reduced the demand for grouting compositions based on a rust promoting mechanism, and they are now obsolete. Since shrinkage-compensating cement provides predictable expansions under varied conditions, the application of the newer compositions is less restricted.

Storage and Shelf Life. Processed and graded iron particles are bagged in 25 kg multi-ply plastic lined bags. Cement based products, particularly those containing calcium chloride, should be stored under cool, dry conditions. Shelf life of such materials (i.e., rust promoting) is usually six to nine months. The quality of the materials used after a given storage period should be assessed prior to use. Non-rusting materials may be used up to a period of twelve months, although expansive cements tend to lose expansion properties due to aeration.

Precautions. Some of the problems which arise from the use of grouts and patching compounds which expand by a rusting mechanism include surface staining, disruptive expansion of the matrix and possible corrosion of metallic embedments in concrete. It is, therefore, important to restrict their use strictly to temporary applications such as stopping leaks which have high water flow.

Excessive wetting and drying cycles, particularly in the presence of rust promoting chemicals, produce surface staining and are deleterious at later ages.[15] Salts like calcium chloride and sodium chloride accelerate corrosion. Continued expansion, associated staining, and discoloration are prevented by sealing the exposed surface of the concrete or mortar using a resin-based sealer or, preferably, a sand/cement mortar followed by the sealer. Because of the potential for rusting and continued expansion, the use of such materials should be limited to locations that are relatively dry.

When a decision to use granulated iron admixtures, as grouts or floor hardeners is made, the effect of the placing and in-service conditions should be evaluated carefully. The limitations due to the use of rust promoting materials should be considered. Bleeding, compressive strength and long-term volume stability under job conditions should be determined prior to placement.

Standards and Codes of Practice. With the exception of the methods which measure early volume change (ASTM C-827) and performance under prestressed conditions, all other standards mentioned under *gassing admixture* can be used in the sampling and a testing of both rust forming and rust inhibiting materials.

Quality Control. As in the case of gassing admixtures, there are no recognized performance criteria by which product quality and uniformity can be stipulated. The material that is selected as a grout depends on the users' performance specifications. Routine quality control can be performed for both rusting and rust inhibiting types using the following tests:[18]

Requirement	Test Method	Remarks
Volume change	ASTM 827 CRDC 613-74	To verify whether grout shrinks below placement volume
	ASTM C-157	To ensure that continued expansion does not occur under given set of conditions
Workability Initial set flow	ASTM C-191 CRDC-79	To ascertain placing characteristics
Compressive strength	ASTM C-109	To verify strength developing properties

The plate lift-off test can be done in the field to determine expansion of field mixes.

Materials used in floor hardener compositions suffer similarly from a lack of universally accepted test to determine abrasion resistance. Although ASTM C-131 (Los Angeles abrasion test) and the Taber abrasion test are widely accepted, there is no consensus of opinion as to whether these methods adequately correlate with field conditions of wear.

2.3 Calcium Sulfoaluminate and Lime-Based Expanding Admixtures

Background and Definitions. Two types of admixtures, calcium sulfoaluminate (CSA) and calcium oxide (lime) based admixtures have provided a means of offsetting volume changes due to hardened shrinkage.

Shrinkage compensation is obtained at lower addition rates, while chemical prestressing of the reinforcement is achieved at higher dosages. Other allied admixtures of this type and mixtures of $CaSO_4$ and CaO have also been used. Lime-based admixtures were developed in the early 1970's. A commercially produced product called *Onoda Expan* belongs to this category. Although the types of reactions that generate the expansive force and the magnitude of expansion are different in CSA and lime-based admixtures, the effects produced in concrete and mortar, factors affecting the reaction and application, are not different.

Chemical Compositions. The most widely used single component, calcium sulfoaluminate admixture is composed of 30% (C_4A_3S), 50% $CaSO_4$ and 20% CaO with small amounts of a glassy phase. Particles size is coarser than that of portland Cement. Larger particle size ensures that the potential expansion due to hydration is extended over a period of time. Chemical and physical properties of the most widely used proprietary Denka CSA, are product are given in Table 4.[19]

Other CSA type materials include mixtures of C_4ASH_{12} and 2CS (monosulfate and gypsum) and mixtures of Type I cement, high alumina cement, $CaSO_4•2H_2O$, $Ca(OH)_2$ and CaO.

Table 4. Chemical and Physical Properties of Calcium Sulfoaluminate Expanding Admixture (Calcined Denka CSA)*

Chemical Composition	
Oxides	
SiO_2	1.4%
Al_2O_3	13.1%
Fe_2O_3	0.6%
CaO	47.8%
MgO	0.5%
SO_3	32.2%
Free CaO	19.4%
Ignition loss	0.9%
Insoluble component	1.4%
Physical Properties	
Specific gravity	2.93
Specific surface area	2, 280 cm^2/g

*Courtesy S.Matsumoto.

For use in special fields of construction such as structural grouting and oil well cements, the anhydrous calcium sulfoaluminate is combined with two or more of the admixtures listed below.[20][21]

- A dispersing admixture.
- A gas liberating agent, e.g., Al powder or fluidized coke particles.
- A powdered acrylic latex to increase bond strengths.
- Mortar density-increasing or decreasing-ingredients such as barytes or bentonite.

Products with a range of CaO contents (80–96%), particle size and particle size distribution are used as single component lime-based admixtures. Typical physical and chemical properties of a commercially available material is given in Table 5.[22]

Table 5. Chemical and Physical Properties of a Lime-Based Expanding Admixture *(Courtesy S. Matsumoto)*

Oxides	%
SiO_2	13.1
Al_2O_3	2.9
Fe_2O_3	2.0
CaO	76.9
MgO	1.1
SO_3	3.0
Total	99.0
Specific Gravity	3.21

* Courtesy Onada Expan. The Onoda Cement Co.

A material made by encapsulation of the lime particle with a protective film of calcium carbonate or calcium hydroxide has been patented.[23]

Mode of Action. The expansion mechanism associated with the formation of ettringite in cement is not clear and several hypotheses have been advanced.[25] A mechanism advanced by the manufacturers of a CSA type admixture and supported by the work of other investigators[24]-[26] is as follows. On reacting with water, CSA type admixtures form ettringite and expand. Formation of ettringite is thought not to occur in the liquid phase of the cement. The $C_4A_3S^{-}$ compound and lime react to form a solid solution consisting of hexagonal platelike crystals of monosulfate and calcium aluminate hydrate of type C_4AH_{13}. Subsequent reaction of the monosulfate with gypsum produces acicular crystals of ettringite. Monosulfate apparently does not contribute to expansion whereas the formation of ettringite involves expansion. The reaction is schematically represented in Fig. 3.

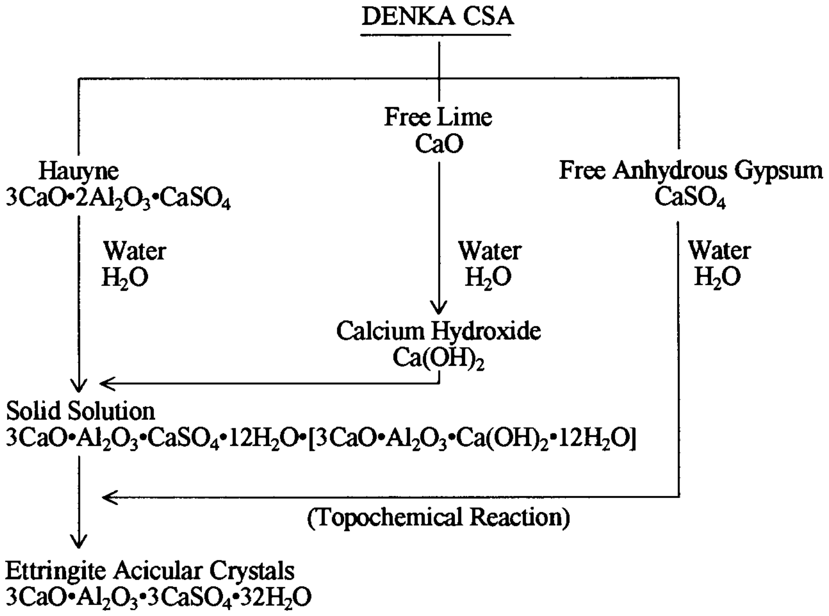

Figure 3. Schematic representation of the reaction which occurs when calcium sulfoaluminate type admixture hydrates to form ettringite. *(Courtesy Denki Kayaku Kabushiki Kaisha Co., Tokyo, Japan)*[19]

Expansion in the lime-based system is due to crystal growth and the pressure that results when CaO particles hydrate to form $Ca(OH)_2$. Particle type, size, thickness of protective coating, and presence of moisture determine the rate and extent of expansion. Although the mechanism of expansion is the same as above for multicomponent admixtures, the rate and extent of expansion is also determined by the resulting modification produced by other components in the admixture. A comparison of the 24-hour early volume change and 28-day hardened volume change values obtained for grout compositions containing two sulfoaluminate-based (CSA) and two lime-based with that obtained for Type K cement is shown in Figs 4 and 5.[27]

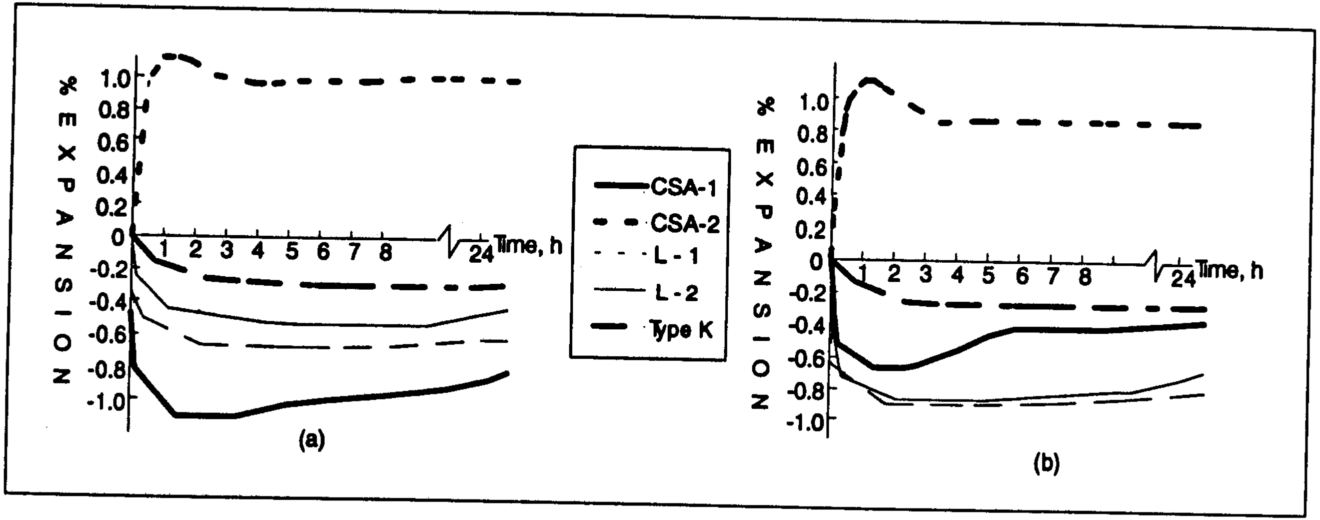

Figure 4. Early volume change vs time for *(a)* low dosage and *(b)* high dosage of expansive admixtures vs Type K cement. *(Courtesy Mailvaganam, N., Nunes, S., Bhagrath R., Effectiveness of Expansive Admixtures in Structural Grout Compositions,* Concrete International, *15[10]:38-43, 1993)*

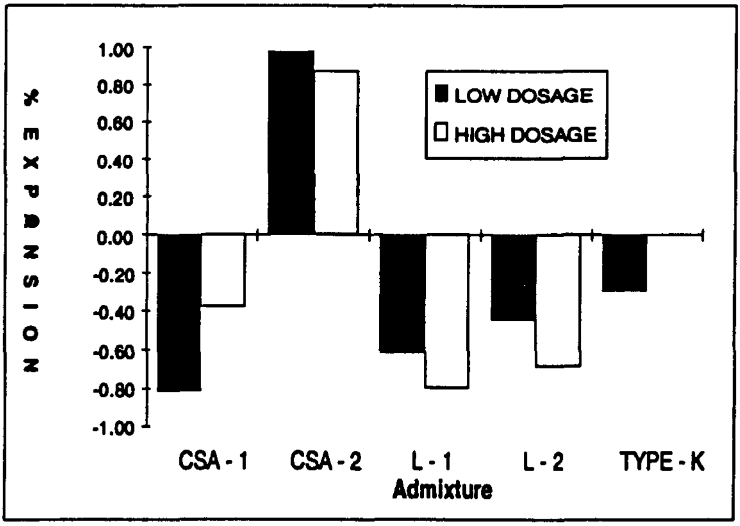

Figure 5. Comparison of 24 hr early volume change using low and high dosages of expansive admixtures vs Type K cement. *(Courtesy Mailvaganam, N., Nunes, S., Bhagrath R., Effectiveness of Expansive Admixtures in Structural Grout Compositions,* Concrete International, *15(10):38-43, 1993.)*

The deformation that accompanies expansion as strength increases, induces compressive stresses in the concrete, reducing the tensile stresses due to drying shrinkage. Consequently, both cracking and contraction that occur on drying are decreased. In chemical prestressing, the expansive force generated produces tension in steel to a degree corresponding to the expansion produced. Concrete is simultaneously subjected to an equivalent compressive stress because of the restriction imposed by the reinforcement.

Factors Influencing the Reaction. The following factors affect the reaction :

(a) *Composition and fineness:* Type and amount of aluminates, calcium sulfate, and free lime present in the mixture govern the rate at which ettringite forms. The presence of lime is reported to be essential for both the initial and subsequent stages of ettringite formation because it maintains a solution phase saturated with calcium ions.[28][29] Crystal habit, particle size and range of particle size in CSA admixtures determine its rate of hydration and duration of expansion. Protective coating [$Ca(OH)_2$ or calcium silicate] and its thickness influence the rate of the reaction in lime admixtures.

(b) *Cement content:* Higher expansion is attained in rich mixes and this decreases as the cement content is lowered. In general, a minimum cement content (280 kg/m^3) is required to obtain desired expansion values.

(c) *Ratio of water to cementing materials:* At admixture dosage levels ranging from 9–13%, concretes with CSA admixtures show significant increases in both total expansion and compressive strength at W/C ratios less than 0.50.[29] At high consistencies and W/C ratios lime produces higher expansion than CSA . Increased expansion due to W/C reduction is not exhibited by lime admixtures. At higher W/C ratios, or prolonged exposure to wet conditions, the increased expansion produced in lime admixtures acts detrimentally on all properties of the hardened concrete if adequate restraint is not provided.

(d) *Ratio of admixture to cements:* The commonly used ratios of admixture:cement for the purpose of shrinkage compensation are 9–11:91–89 (admixture:cement). At these ratios, the properties of CSA concrete are similar to portland cement concretes of similar mix proportions. At admixture dosages exceeding 11% however, concrete workability and strength decrease while expansion and air entrainment increase. When expansion is unrestrained and exceeds 0.3%, strength is reduced.[19]

The 6–7% dosage of lime admixture produces concrete with properties similar to those of portland cement concrete. The strength reduction caused by higher dosages (in the absence of restraint) is more drastic because of greater expansion and moisture sensitivity of the admixture. At increased dosages (~ 9%), foaming and increased air entrainment occurs.

(e) *Curing conditions:* At 8–11% dosage for CSA and 6–7% for lime-containing concretes, larger expansions are produced when the concrete is water cured or cured at 100% RH than when sealed with curing compounds. When cured at 50% RH (air cured), little expansion (~ 0.05%) occurs and shrinkage occurs after seven days. Compressive strength for water cured material is slightly lower than that of the air cured material. The effects produced above are more drastic in prestressed applications since higher dosages are used. If no restraint is provided during moisture cure, disruptive expansion can occur.[27]

(*f*) *Temperature:* Higher mix and ambient temperatures result in increased slump losses and reduced ultimate expansion. Reduced expansion also occurs at lower temperatures. In general, greater expansions are obtained at moderate (18–25°C) temperatures.[29]-[31] At higher temperatures (>35°C), the rate of ettringite formation is accelerated and, although a high rate of expansion occurs at early ages, the resistance offered by the concurrent acceleration of strength development results in a lower ultimate expansion value. At lower temperatures and early ages, the rate of ettringite formation is slower and the expansion produced is dissipated by higher creep. The reaction of lime-based admixtures is not markedly affected by temperature.[28][29][32]

(*g*) *Degree of restraint:* Adequate restraint during expansion must be provided to induce compressive stresses required for shrinkage compensation or prestressing of steel. This is usually provided by the reinforcement, subgrade friction and forms. For a given admixture dosage, cement content and mix proportions, expansion decreases with increase in steel reinforcement. In the absence of restraint, the level of compressive stresses necessary to offset shrinkage stresses is not achieved at lower dosages, while disruptive expansion results in self stressing applications.

(*h*) *Mixing time:* Since the expansion produced is dependent on the uniformity of particle distribution, longer than normal mixing times are required. However, prolonged mixing will result in a significant reduction of the expansive potential, especially at higher temperatures.

(*i*) *Compatibility with other admixtures:* Some water reducing admixtures have been found to reduce the expansive potential of CSA type admixtures, due to their effect on ettringite formation. For example, superplasticizers used to provide flowable consistencies and accelerators employed for rapid strength development have been shown to reduce expansion significantly.[33][34] The magnitude of the effect is dependent on whether the admixture retards or accelerates set. Retarders tend to increase ultimate expansion at normal temperatures.[29] Under hot weather conditions, however, retarders offset the accelerating effects of high temperatures and allow the normal level of expansion to occur. Air-entraining agents do not influence the expansive reaction; higher air contents may result when CSA and lime admixtures are used in air entrained concrete. The use of $CaCl_2$ with expansive admixtures is not recommended generally, due to its adverse effect on shrinkage. The inclusion of silica fume in grout compositions made with Type K cement or CSA type expansive agents may reduce expansion.[35] The silica fume is said to decrease the formation of ettringite by reducing the concentration of cations and anions like Ca^{2+} and OH^- involved in the formation of ettringite.[35][36]

The expansion reaction of lime admixtures is not affected by water reducing admixtures to the same extent as observed for CSA admixtures. Set retardation may result due to the presence of increased amounts of $Ca(OH)_2$.

(j) *Aggregate type:* Aggregates influence expansion and shrinkage characteristics of concrete. In concretes (containing CSA or lime) use of aggregates of high elastic modulus results in larger expansion.[29]

(k) *Age of admixture:* CSA and lime admixtures are more prone to loss of activity due to CO_2 and moisture pickup than are shrinkage-compensating or portland cements.[24][30][31] Consequently, the use of materials with ages exceeding the shelf life may seriously reduce the expansive potential.

Effects on the Plastic Properties of Mortar and Concrete. The water requirement for equal slumps is generally higher for concretes containing these admixtures and they show significant reduction in bleeding. Both the high water demand and reduced bleeding are related to the high water demand for the ettringite formation.[27][28] When used at lower dosages (6–8%), they do no entrain any significant amount of air. However, at increased dosage levels, they have a tendency to foam. Since concrete mixes containing CSA and lime admixtures show increased cohesion and reduced bleeding, finishing operations should occur sooner than for portland cement concretes. Due to the lack of bleed water, conditions that promote rapid moisture loss may cause plastic shrinkage. Precautionary procedures detailed in ACI 614-59 practice should be followed for satisfactory results.

Effects on the Hardened Properties of Mortar and Concrete. Physical properties such as compressive strength, creep, modulus of elasticity and durability of CSA and lime admixture-containing concretes are comparable to those of corresponding portland cement concretes, especially when dosages are within a range (8–11% CSA and 6–7% lime).[19][22] When the dosage exceeds the ranges mentioned above and no restraint is provided either internally (by reinforcement) or externally, a point is reached when the expansion will have a disruptive effect on mechanical properties. Although higher levels of expansion are produced for a given dosage in concretes with the lime admixture, the expansion and shrinkage characteristics produced by both the lime and CSA types are not very different. Both admixtures produce most of the expansion at early ages of wet curing. Subsequently, on exposure to lower relative humidity levels as in air curing, a gradual decrease in the amount of expansion occurs with age. Depending on the extent of expansion achieved in the curing period and the rate of shrinkage soon after water curing ceases, significant contraction can occur (Fig. 6).[10]

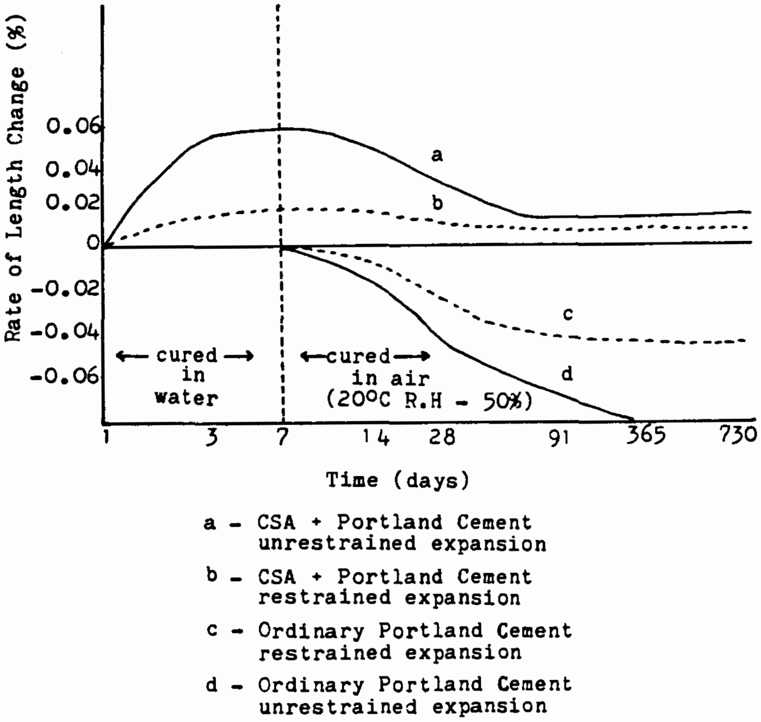

Figure 6. Volume change at various ages for portland cement concrete with and without CSA admixture and with and without restraint. *(Courtesy S. Matusumoto)*[19]

Expansion increases with dosage and the effectiveness in controlling shrinkage will be influenced by the degree of restraint present during expansion. Under conditions of internal restraint, the expansion produced is proportional to the ratio of steel to concrete and the dosage of the admixture. At a given dosage, expansion decreases as this ratio exceeds the optimum value for that dosage. Restrained expansion increases the density of the matrix and produces concrete or mortar with a lower coefficient of permeability than that of corresponding portland cement concretes and mortar.

Applications. Shrinkage compensation is highly advantageous in many applications such as architectural precast and pneumatically applied concrete, water retaining structures, and for most horizontal slab applications such as floors, roofs, and parking decks. The capacity for minimizing cracking, thereby allowing a reduction in construction joints makes the admixture ideally suited for these applications. In structures where water leakage is a problem, use of these admixtures can result in the reduction of the number of cracks. Chemical prestressing is used in the production of pressure pipe, water tanks and tunnel linings.

Multicomponent admixtures are widely used in structural grouting of machine bases, column bases, repair of cracks and oil well cementing operations.

Preparation and Addition Procedure. Anhydrous calcium sulfoaluminate is formed by calcination of lime, gypsum and bauxite. The active expansive ingredient $C_4A_3S^-$ is formed by solid state reaction from mixtures of compounds composed of calcium oxide, aluminum oxide, and sulfur trioxide gas formed during the calcination of gypsum and bauxite. Crystal growth of CSA is encouraged to proceed at a slow rate to preserve the potential force of expansion for extended periods.[24]

A commercially available material (Onoda Expan) is manufactured from the same raw materials as used in the manufacture of portland cement. It is calcined in a rotary kiln and ground to the required size in a ball mill. The finished product (a whitish grey powder) includes 35% of the specially treated calcium oxide.[22] Encapsulated lime products are also produced by calcination. The product cited in this discussion contains 90–96% CaO and after grinding is exposed to CO_2, H_2O or $Ca(OH)_2$. Particle size of the product is usually < 250 m.[23]

Admixture dosages for the calcium sulfoaluminate material vary from 8 to 11% by cement weight for shrinkage compensation and 12–17% for prestressing applications. Recommended dosage levels for the lime-based admixtures vary from 6 to 10%, depending on the desired level of expansion . For shrinkage compensation and crack prevention, a dosage of 6–7% suffices, while for prestressing applications, the requirement is in excess of 8%.

When CSA or lime-based admixture are used, cement is replaced in the mix and the proportions adjusted by reducing the sand by an amount corresponding to that of the admixture. Measurement of the powdered admixture quantities into the mix may be based on a given number of bags or a weighed amount of the material per weight of cement in the mix. In both cases the admixture is batched by weight and not by volume. The point of addition in both precast and ready mix applications is with the fine aggregate prior to the addition of the mix water.

Satisfactory performance of the admixtures will depend to some extent on the degree of mixing. Slightly longer mixing times than those used for portland cement mixes may be required, especially when small amounts of admixture are used. In hot weather, the sequence of charging the concrete ingredients into the ready mix truck can be changed. The truck drum is kept stationary until it reaches the destination when a 3–5 minutes of mixing is carried out prior to discharge. This method minimizes slump loss and ensures that the expansive potential is not seriously affected. When mixing in cold weather using hot water, water should be added to the aggregate, followed by the cement and admixture; otherwise fast setting may occur.[27][31]

Storage and Shelf Life. Lime and CSA admixtures are more sensitive to moisture and atmospheric CO_2 than are portland cements. The materials are, therefore, packed in waterproof bags and should always be stored in a dry place. Once a bag is opened it should preferably be used the same day to maintain the activity. Shelf life is usually 9–12 months.[19][22]

Standards and Codes of Practice. Standards mentioned under *gassing admixtures* can be used in the sampling and testing of these materials.

Precautions. The expansion achieved in concrete containing these admixtures is dependent on the type of aggregates used in the mixture.[29] Thus, the desired level of shrinkage compensation should take into account the modulus of the aggregate to be used on the job. The effect of cement and water contents on the extent of expansion should also be considered. Minimum cement content required to achieve desired expansion should be determined through mix trials. Compatibility with other admixtures may also need trials and the manufacturer's recommendation should be followed.

Admixture dosage and post placing curing conditions affect the properties of concrete, hence, selection of an appropriate dosage would depend on *(1)* desired level of expansion, *(2)* degree of restraint of the structure, and *(3)* curing conditions. In situations where adequate curing cannot be provided, a slightly higher than normal dosage should be used to ensure effective shrinkage compensation.

Since more than normal amount of water is required at the initial stages to produce effective expansion, water suction into the dry substrate should be minimized by thoroughly wetting the base or subgrade. Special care should be taken to ensure that reinforcement is located in its proper position during placement and consolidation so that adequate restraint and good bond to steel is obtained.

3.0 PIGMENTS

3.1 Background and Definition

Concrete is colored either by an integral method or by the application of color after the concrete has set and hardened. The latter method is excluded from this discussion. Integral coloring consists of introducing the coloring agent during the mixing cycle. Integrally colored concrete utilizes three types of products: *(a)* natural and synthetic products, *(b)* multicomponent coloring admixtures, and *(c)* mortar coloring aids.

A pigment, as related to its use in concrete, mortar and cement paste is defined as a fine dry powder, aqueous suspension, or slurry, of that powder, insoluble and inert to the concrete ingredients and which imparts a specific color to the product.[37] Pigments used in colored concrete are either natural or synthetic. Synthetic pigments produce stronger tints and have also the advantage of high brilliance and greater uniformity in color shade because of the uniformity in particle size.[38] Despite the low cost of natural pigments, their use in concrete is gradually diminishing due to the lack of purity and the adverse effect that high pH has on their color permanence.

Multicomponent admixtures contain components which not only impart color but also react chemically with the cement influencing the hydration reaction and morphology of the hydrated phase. Mortar coloring aids also contain ingredients other than pigments such as wetting agents and in inert fillers. They are distinguished from pigments because they influence some plastic properties of the cement phase, and from normal admixtures because they do not induce effects characteristic of typical chemical admixtures such as water reduction and strength increase. These materials are not satisfactory for use in integrally colored concrete because of their lower coloring strength per cement weight, which largely limits their use to masonry work. Pigments or coloring admixtures find wider acceptance than mortar coloring aids both for reasons of economy and quality. Multi-component coloring admixtures are sold both in liquid and powder forms and a variety of colors is produced by blending two or more pigments.

Pigments in the form of slurries or dispersions are used for three main reasons: *(a)* to enhance the wetting and dispersion characteristics of materials containing very fine particles with inherently poor wettability; *(b)* enable dispersion through commonly used equipment; and *(c)* reduce health hazards that may result by handling fine powders.

3.2 Chemical Composition

Pigments used in concrete include metal oxides, organometallic complexes and finely divided carbon. Typical pigment types are listed below.

- Natural or synthetic iron oxides for brown colors.
- Synthetic yellow iron oxide for buffs and yellow.
- Synthetic chromium oxides for greens.
- Natural and synthetic iron oxides for reds.
- Synthetic cobalt oxide and organic pigments based of Cu-complexes of phthalocyanine for blues.[39]

Detailed chemical and physical characteristics of pigments required for use in concrete and mortar have been discussed in specifications listed in some references.[39][40]

3.3 Chemical and Physical Properties

The color of a pigment can be described in terms of three properties: hue, value, and chroma,[41][42] which are indicative of the purity (oxide content) and the brightness of the pigment. Hue is the property of a color which distinguishes red from yellow, blue, etc. It is a measure of the relative intensity of light reflected from the surface of a colored body at different wave lengths of the visible spectrum. Value or lightness denotes the light reflecting quality or lightness of a color. Chroma or saturation is the richness or depth of hue or a color and is a measure of its departure from a grey or neutral (black and white or grays) of equal value. It is, therefore, an indication of the purity of the pigment.

Pigments intended for use in concrete or mortar should not react with any of the concrete ingredients. The pigment should have the ability to resist the action of lime.

Hiding power of a pigment is particularly important in applications where maximum light reflection is required. It depends not only on the specific characteristics of the pigment such as refractive index, particle size, and selective absorption of light, but also on factors such as pigment concentration and degree of dispersion in the material. In general, hiding power increases when:

- Difference in refractive indices of the pigment and cementitious binder is large.
- Distance between pigment particles decreases (i.e., increased pigment concentration).
- Particle size decreases.
- Light absorption decreases in white pigments.
- Light absorption is selective as in the case of colored pigments.

Ease of Wetting Dispersion. Pigments in the dry form exist as aggregates of particles. The ease with which the aggregates are broken down and dispersed in concrete, mortar and cement paste depends on the extent to which the forces of attraction between the particles is reduced. Since manufacturers treat the pigment surfaces, easy wetting is obtained. The addition of selected wetting or dispersing agents also accomplish similar easy wetting characteristics. However, some investigators,[37] discourage the use of such wetting agents because the *wetting action* also results in the increased masking effects produced by lime.

Water Absorption. In general, oil absorption values correspond to water absorption values. The water absorption value indicates the amount of water necessary to produce a paste with a specific amount of pigment. High values tend to impair the rheology of the paste.

Resistance to Light and Heat and Weathering. Certain pigments when exposed to high intensity of sunshine undergo degradation by UV radiation, possibly due to physical or chemical changes. All colored products tend to "bleach" in the autoclave, primarily due to the lightening effect on the cement. Some colors are not suitable for use under autoclaving temperatures; for example, black iron oxide will begin to redden at approximately 300°F, the degree of change being proportional to the temperature. Also, since black is used in combination with red and yellow to make brown, a "pinking off" will occur in most blends. Yellow oxides of iron ($Fe_2O_3 \cdot H_2O$) lose water of hydration at temperatures of 350°F and change to Fe_2O_3. Other pigments change their crystal form and produce changes ranging from slight darkening to drastic loss of hue when curing temperatures higher than 300°F are to be used. Certain manufacturers offer special colors or suggest procedures to be adopted.[43]-[46]

Resistance to Aggressive Chemicals. In general, the chemical resistance is offered by the cementitious binder, but the pigment type and concentration should be chosen depending on the required chemical resistance. For example, basic pigments shouldn't be used where acid resistance is required and organic pigments which bleed in oils should be avoided for grease and oil resistant floors.

Particle Size. The effect a pigment produces is governed to a large extent by the size of the particles and is characterized by the particle diameter and specific surface area. Properties such as color and mix consistency depend on particle size. Particle diameter governs color shade since it determines the light scattering and absorption characteristics of the pigment.[44] Particle size and shape of both natural and synthetic pigments are determined by their chemical composition, crystal form and methods of preparation.

3.4 Mode of Action

Color in concrete surfaces is due to the selective absorption and reflection of certain components of white light which falls on them. When certain wavelengths are absorbed and others reflected, the surface appears to have the color of the reflected wavelength. The basic factor responsible for the production of color in concrete is the arrangement and characteristic vibrations of the electrons in the atomic and molecular structures of pigments.[45] When the frequencies of vibration of the electrons correspond to some of those in the visible spectrum, the pigments absorb the light having these frequencies and reflect the remainder. Differences in color are produced by differences in frequency of vibration of electrons in their structures. The coloring of concrete is therefore characterized by the specific size and shape of the pigment particle, the degree of dispersion (the ability to smear the mix ingredients), and the nature of the material (shade of the cement & color of aggregate) being colored.

3.5 Factors Affecting the Coloration of Concrete

(a) Exposure Conditions: The most noticeable effect due to weathering of colored concrete is a progressive weakening of the color intensity (chroma) and a lowering of the brightness (value). The effect increases with age and comparatively large changes in chroma and hue are observed due to the erosion of the surface cement layer and exposure of the underlying aggregate. The mortar then assumes a mass color which is a composite of the colors of the aggregate, cement paste and pigment. The direction of the change of color is usually towards that of the aggregate. The extent of change, however, is dependent on the color of the pigment. The color intensity is also affected by the formation of a whitish deposit of $CaCO_3$ due to efflorescence. When the process of efflorescence occurs on colored concrete products, the contrast is more noticeable. The migration of $Ca(OH)_2$ to the surface and the subsequent formation of the whitish deposit occurs when high water contents are used or due to the ingress of water from external sources.[47]

Methods and measures used to reduce efflorescence are:

- Use of concrete ingredients (cement, sand, water and pigment) with a minimum soluble salt level, e.g., low alkali and SO_2 content-cements and washed aggregate.
- Use of integral waterproofing admixtures.
- Increased rate of strength development by the use of finely ground cement.
- Keeping surface trowelling to a minimum.
- Use of a chemical such as $BaCO_3$ to convert soluble alkali salts to an insoluble form, e.g., $BaSO_4$.

(b) Mix proportions: The coloring action of pigments is dependent on the extent of smearing over the cement and fine aggregate in the mix. Therefore, cement and fine aggregate contents will significantly influence the degree of coloration achieved. In general, the higher the water content of the mix, the lighter will be the final color.

(c) *Cement type:* Different cement types and even those within a group with different fineness produce varying color intensities.[44][48] The variation is attributed to differences in the brightening power.[44]

(d) *Aggregate color:* Aggregate color affects not only the shade of new concrete but also determines the extent to which a color detracts from the original shade due to weathering. For example, green and red mortars undergo changes in hue and chroma close to those of the aggregate, while yellow mortars are not greatly affected.[42] In colored concrete, it is important to select an aggregate the color which harmonizes with that in the cement paste.

(e) *Construction methods:*

- *Formwork and finishing:* The degree of absorption and rigidity of the mold lining materials affects the textures and, thereby, the apparent color shade of colored precast concrete. High gloss mold materials should be avoided as they give mirrorlike finishes which are readily prone to surface crazing. Hence, all finishes should be matte-like.
- *Releasing agents:* Mold release agents based on mixtures of furnace oil and oil in water type emulsions cause surface blemishes due to staining and streaking. Preferred types include water in oil emulsion and surfactant type release agents.
- *Curing conditions:* Consistent curing conditions during the initial period are important for color uniformity. Polyethylene and similar types of covers are not recommended as they cause condensation and staining. Curing should begin immediately by applying a suitable curing membrane for vertical surfaces or a wax based formulation made specially for colored floors.
- *Finishing procedures:* Faulty finishing such as excessive trowelling by steel tools or conducting finishing operations at the wrong time will result in staining or mottling. The appearance of integrally colored concrete is generally enhanced by a textured finish due to improved color refraction.

3.6 Effects on the Properties of Plastic and Hardened Concrete and Mortar

(1) Workability: Addition rates under 6% generally do not affect the consistency of mortar nor the workability of concrete significantly. Higher dosages increase the water demand and premature stiffening of the mix, particularly when synthetic pigments containing very fine particles are used. Large specific surface area of carbon black has a marked influence on the consistency—a physical or colloidal reaction may occur that increases the rate of stiffening of the mix.

(2) Setting characteristics: Most pigments and coloring multicomponent admixtures, when used at the recommended addition levels, do not alter the setting times. Carbon black and certain iron oxides, however, may produce *flash setting.*[46]

(3) Air content: The use of carbon black or other pigments of very high surface area in air-entrained concrete results in a reduction of the quantity of air entrained.[46] Consequently, increased dosages are required to provide sufficient air contents for adequate freeze/thaw resistance. Most of the carbon black pigments currently marketed contain air entraining agents.

(4) Bleeding and settlement: Pigments and mortar coloring aids used at permissible dosages do not alter the bleeding characteristics of a mix. Multicomponent coloring admixtures and pigment dispersions, when used at higher than recommended dosages or with cements of low C_3A content, can reduce the cohesiveness of the mix and promote bleeding.

(5) Compressive and tensile strength: Strength values are not adversely affected at addition rates under 6% for most inorganic synthetic and natural pigments. Organic pigments, such as phthalocyanine and carbon black which contain very fine particles, are limited to dosage levels under 3% due to the drastic effects they have on water requirement and, consequently, on compressive and tensile strengths. The British Standard[39] and American Draft Standard[35] require that the mean compressive strengths of concrete containing the pigment not differ by more than 10% and 20%, respectively, from the mean compressive strengths of the mix without pigment.

Iron oxide pigments (when added in excess of 10%) and ultramarine blue may produce concrete of high compressive strength. The effect has been attributed to a lowering of the effective W/C ratio with the former and a pozzolanic activity due to the latter admixture.[42] Abrasion resistance values are affected similarly.

(6) Permeability: The use of high dosages of materials with high surface area or the addition of large amounts of pigment dispersions produce concrete with a high W/C ratio. The permeability of such concrete will accordingly be lowered.

3.7 Preparation

Natural pigments are obtained from soft rocks or deposits such as clay by crushing, grinding and size separation. Synthetic pigments are produced by four general methods: *(i)* chemical precipitation, *(ii)* heat fusion, *(iii)* fume process, and *(iv)* partial combustion.

Pigment dispersion consist of pigment-water mixes which may contain a surface active wetting agent. Common pigment-water ratios range from 1:1 to 1:10 by weight depending on the pigment used. The aqueous mixes usually contain suspending agents (thickeners) to prevent the rapid settling of the particles. Multicomponent admixtures are usually prepared by blending compatible ingredients, consisting chiefly of synthetic pigments, water reducing admixtures, thickeners and fine fillers like sand. Mortar colors are products made from naturally occurring ores of low coloring power, or from synthetic pigments which have been diluted with inert fillers like fine sand or calcium carbonate.

3.8 Dosage and Dispensing and Addition Procedure

In general, most standards and specifications restrict the proportion of pigment allowed to a maximum of 10% by weight of cement. The dosage is generally 3–6%. However, the exact concentration will depend on the desired architectural effect, 1% level being used for tinting, 5% for definite color and 10% for a deeper shade.[37] Most iron oxides impart total color value at approximately 7%.[45] Materials, such as carbon black and phthalocyanine pigments, which have high specific surface areas use lower pigment loadings of 0.1 to 1.0%. Steam cured products require the choice of an appropriate heat stable pigment and a 3–4 fold increase in concentration to offset the lightening effect.

In considering the use of multicomponent admixtures and mortar colors, the secondary effects produced in the concrete due to other components should be taken into account before a decision on the dosage can be made. Both admixtures are used at addition levels ranging from 3–6% depending on the application.

Three methods are normally used to dispense coloring admixtures.

(a) Dispensing of powder by a volumetric method.

(b) Dispensing of powders by weight.

(c) Metering of pigment slurries or suspensions by volume.

Although the dispensing method is largely automated in the industry, it is still a common practice to add the powders manually. The pre-weighed amount or certain volume of the powder admixture required for the batch is added by the mix operator during the mixing cycle. Manual volumetric dispersion of powdered admixtures produce color variation in the concrete products because of the varying amounts added in consecutive batches due to the bulking of pigments. The method is limited to small operations. Higher metering accuracy is obtained by the use of automatic dry volume metering devices. Although uniform volumes can be dispersed with the aid of this type of equipment, caking of the powders in the supply lines may significantly reduce accuracy in batching. Due to the problems associated with powders, the use of pigment slurries and dispersions is gaining wider acceptance.[49]

The order of introduction of concrete ingredients is important in colored concrete work. For most precast and small on-site batching operation using powdered admixtures, the most suitable method of batching materials for colored concrete is as follows.

Preblend the cement and pigment admixture prior to batching. Combine the dry aggregate and cement/pigment mixture and mix for four minutes. Following this, add the required amount of water and resume mixing for an additional three to five minutes. In ready mix operations the pigment of powdered admixture is added with the cement and the truck drum is rotated at charging or mixing speeds prior to the addition of water. Another method more suited for ready mix plants is to add the powder admixture or pigment to the dry aggregate and mix for four to five minutes before water is added to the mix.

Pigment slurries and suspensions are added to the concrete mix like normal liquid chemical admixtures by automatic dispensers with the gauging water. For suspensions or slurries stored in the tank, a means for continuous agitation should be provided to prevent settlement of the pigment. The dilution of the slurry or dispersion needs to be known accurately so that the automatic dispenser can be set to dispense the requisite amount of active pigment material to the mix. In addition, the automatic metering of water needs to be adjusted to a lower level to make allowance for the additional water that is incorporated within the pigment. Proper mixer clean up procedures are required to minimize batch color variation.

3.9 Applications

Colored concrete slab work is used in side walks, driveways, patios and swimming pools. Decorative precast concrete panels and tilt-up panels are used in public buildings and residences.[44] Colored concrete is also used to create permanent caution signs in factories, highways and airport runways. Table 6 summarizes the methods available for coloring concrete and also the possible effects they produce.

3.10 Storage and Shelf Life

Dry pigments and mortar colors are packaged in multiwall bags usually filled to a predetermined weight. Some multicomponent coloring admixtures are sold by the units and not by the pound or kilogram weight since units of different colors have different weights. The materials should be stored in areas that are adequately heated to maintain dry conditions. Liquid products stored in tanks should always be equipped with circulating or agitating devices to prevent settling of the solid particles. The shelf life of most pigments and powdered admixtures is stipulated by manufacturers as two years providing proper storage is provided. The shelf life of aqueous slurries or pigment dispersions is limited to 9–12 months.

3.11 Standards and Codes of Practice

BS-1014 1975. This standard specifies requirements of a range of pigments suitable for coloring portland cement mixes. Although a note states that pigments applicable for portland cements may be suitable for high alumina cement and supersulfated cement, the use of pigments in these cements is not covered in this standard. Required pigment characteristics and the methods of determining these are presented in a tabulated form. Appendices A–F give test methods for determining oxide content of pigments, comparison of coloring power, and effects on the properties of concrete. Appendices G and H contain comments on pigment dispersions and method of incorporation of the pigments.

Table 6. A Comparison of Alternate Methods Available for Coloring Concrete in New Construction

Property	Colored Cement	Pigments	Multi-component Coloring Admixtures	Colored ("Dry Shake") Hardeners
1. Color Intensity and Uniformity	Moderate color intensity. Higher values may require addition to pigments. Uniformity better than other methods.	Pigment loading determines intensity. Uniformity dependent on mix proportions and construction techniques. Batch to batch variation in pigment supply may hinder color match in later jobs.	Admixture type and loading determines intensity. Uniformity better than pigments due to better dispersion. Color variation more than dry shake due to cement and slump variation of fresh concrete.	Highest intensity of all methods, due to manner of incorporation onto mix. Uniformity quite dependent on skills of finishing operator and curing methods. Differences in color of local cement affects desired color.
2. Color Range - Special Shades	Range limited. Specials difficult to obtain.	Wide range of specials more readily obtained.	Limited range if white cement is not used. Specials less readily obtained.	Range of available colors better than cements. Often custom made. Number of color shades less than for pigments, or multicomponent admixtures.
3. Areas of Application	Can be used for both vertical and horizontal applications.	Both horizontal and vertical applications possible.	Both types possible.	Limited to horizontal applications only.
4. Batching and Handling Characteristics	Readily stored and handled when delivered in bulk.	Powders require special methods for accurate dispersions in ready-mix operations. Liquid dispersions or suspensions can be handled by automatic dispensers. Not easily stored in bulk.	Handling characteristics similar to that of pigments. Packaging and storage limited to bags.	Handled mainly in bags. Incorporation determined by skill of operator.

Table 6. (Cont'd)

Property	Colored Cement	Pigments	Multi-component Coloring Admixtures	Colored ("Dry Shake") Hardeners
5. Placing and Finishing Techniques	Skill required similar to uncolored concrete. Faulty finishing techniques do not affect finish as much as dry shake method.	Techniques and skills same as for uncolored concrete. Surface less prone to trowel burn than the dry shake method.	Essentially same as for pigments, but formulations containing retarders or accelerators require knowledge of their effects and the required timing of finishing operations.	Requires special skills of operation. Quite prone to severe discoloration if timing and extent of trowelling is incorrect.
6. Incorporation of Surface Texture	Color puts no limit to depth to which texture can be incorporated.	Same as for colored cements.	Same as for pigments and colored cements.	Depth of texture limited to thickness of colored surface, usually 1/8" thick.
7. Compatibility with Other Admixtures	Usually established by cement producer. May require test with actual job materials.	Must be established by user with actual job materials.	Does not require the use of other admixtures.	Compatibility must be established. Chloride admixtures may produce mottling.
8. Effects on Properties Other than Color of Concrete	Normal properties unaffected. Same as for unpigmented concrete.	Dosage of pigments may effect the water requirement and strength values. Efflorescence and laitance effects highlighted due to background color.	Strength increased by water reducing action of wetting agent ingredient. Bleeding, efflorescence and laitance reduced.	Incorporation of the material greatly improves density and wear resistance of surface. Permeability also improved. Faulty finishing techniques could nullify above improvements and reduce properties to less than that in normal concrete.

Table 6. (Cont'd)

Property	Colored Cement	Pigments	Multi-component Coloring Admixtures	Colored ("Dry Shake") Hardeners
9. Correction of Color Variation	Variations that occur over a period of time may be difficult to correct.	Batch to batch variation in color is more readily corrected, by adjusting loading level of pigment so that standard color of product is matched.	Less readily corrected than situations where pigments are used, due to concurrent effects produced by the admixture on other properties of concrete such as bleeding, set retardation and strength.	Since color uniformity is dependent on consistency, distribution of the material on the surface, variation due to operator's skill quite likely. Correction difficult after material incorporated, because of problems arising from over trowelling. Color variations usually overcome by applying companion sealer matched with concrete color.
10. Costs	Depending on the availability, costs may be less than multi-component admixtures but higher than colored hardener, since entire concrete is colored.	Varies according to pigment type, desired color, shade and depth. Usually higher than dry shake method because whole concrete is colored.	Great variation in cost, depending on color, shade and intensity. Probably, highest cost of all methods. Some cost increase may be offset by greater efficiency of color dispersion.	Material cost relatively constant for all colors, except blue. Less costly than other methods since color limited only to surface layers of concrete.

ASTM D 1208/ASTM C 979. These standards define the basic requirements for pigment types to be used for the integral coloration of concrete.

Methods of preparing mortar test specimens and typical pigment types used in concrete are listed in Annex I and Appendix I, respectively. The specification does not cover the use of pigments under low and high pressure steam curing conditions.

The specification in both standards apply only to the pigment constituent of a multicomponent admixture. Components such as water reducing agents are required to meet BS 4555 and ASTM C 494.

ACI Manual of Practice. Coloring admixtures are also discussed in the ACI Manual of Practice, Part I 1992, *Materials and General Properties of Concrete.* The information presented is part of ACI Committee 212 Report, 212 IR on admixtures. Requirements for commonly used coloring admixtures and the corresponding oxides are described. Dosages generally used, mixing procedures for incorporation of the admixtures and the limitations of some pigments under certain curing conditions are also discussed.

3.12 Product Uniformity

Two distinct criteria apply in assessing coloring materials, *(a)* quality and *(b)* consistency of the manufactured product.

BS 1014 and the German Standard 5593 employ pigment/cement or barytes mixtures in smear test for the control of quality and consistency of the product. The tests involve the visual comparison of two mixtures, the control and test mix with the pigment. In order to serve as a valid control during the course of a job, the product should be sealed in an air tight container, dated and coded. The test method monitors both batch to batch variation and differences in particle size due to grinding.

The ASTM Draft Standard provides for quality control through color matching of concrete specimens made from mixes containing the standard pigment sample in one and a sample obtained from the shipment in the other. Pigment loading levels used are either the prescribed ½ and 6% levels or a dosage agreed upon by the buyer and seller. This standard discourages the comparison of the colors of pigment powders as a test for quality control.

In manufacture of colored precast concrete panels, control of the consistency of color is very important. Tests are carried out under field conditions representative of the actual job conditions. At least two large-scale test samples incorporating all the variable factors in design, material, fixtures and atmospheric conditions that will be encountered in the manufacture of the product are made. Once the desired color and effect have been established, the sample should be kept as a control on site or in the precast factory so that the manufactured product can be compared with it.

3.13 Precautions

In the use of pigment mixtures to obtain desired color shades, two or more pigments are blended. However, care should be exercised to ensure compatibility of the particle sizes of the individual components in the mixture. Wide differences in the particle size often result in a color change of the pigment due to preferential weather erosion of the finer particles.[38] Longer mixing times are also required to obtain proper dispersion and color shade. When pigment dispersions are used, the increased water contents used should be taken into account in mix designs; accurate dispersion of the correct pigment concentration should be affected and possible adverse effects that wetting agents may have on finished products should be considered. Settling should not take place during storage. In order to minimize batch to batch color variation in ready mix operations, it is necessary that a permanent record of the mix data be kept. The use of newer with older batches of pigments and powdered admixtures could result in color variations. Therefore, proper care should be exercised in manufacture to exclude such mixtures of materials.

3.14 Hazards

Pigment particles are easily air borne and although none of them are toxic, they are ocular and respiratory tract irritants. Air extractors should, therefore, be provided over mixers to ensure that the dust is kept to an acceptable level.

4.0 DAMPPROOFING AND WATERPROOFING ADMIXTURES

4.1 Background and Definitions

Admixtures grouped in this category have been used for roofs, slabs on ground, basements, water retaining structures, concrete blocks, in the manufacture of architectural precast concrete and clay bricks. Waterproofing admixtures that reduce the permeability of concrete are effective in reducing the transport of moisture under pressure; whereas materials that impart water repellency (dampproofing) may reduce moisture migration by capillary action. Most dampproofing admixtures are ineffective in reducing water passage under a positive hydrostatic head.

Dampproofing and waterproofing admixtures may be grouped in accordance with their physical and chemical characteristics as follows:[50][51]

(a) Water repelling materials including soaps and fatty acids, which react with cement hydrates, and substances like wax emulsions.

(b) Finely divided solids which are inert pore filling materials.

(c) Chemically reactive finely divided solids.

(d) Conventional water reducing, air entraining, and accelerator admixtures (discussed in Chs. 5, 6, and 8).

(e) Miscellaneous, e.g., methyl siliconates.

Materials in group *(a)* are dampproofing admixtures, while materials in groups *(b)*, *(c)*, and *(d)* are more effective in reducing the permeability of concrete and are, therefore, designated waterproofing admixtures.

4.2 Chemical Composition

The most widely used water repelling materials in group *(a)* are the Ca or NH_4 salts of fatty acids such as stearates. Liquid materials include fatty acids such as oleic, caprylic, capric and ammonium stearate dispersions in water and butyl stearate. Certain vegetable and animal fats and emulsions based on white grease, tallow or soya bean oil and paste have also been used. Other products in this category derived from petroleum residues include heavy mineral oil, paraffin waxes, and bitumen emulsions. Very finely divided wax emulsions, produced from waxes with melting points 57–60°C, and an emulsifying agent are also used. Heavy mineral oils have proven effective against absorption and, to a degree, against water under pressure. Finely divided solids may either be inert or reactive with the cement hydrates. Reactive materials include some silicates, finely ground blast furnace slag, and pozzolans such as fly ash and diatomaceous earth. Inert materials used are fullers earth, talc, bentonite, and other siliceous powders. Sodium methyl siliconate solutions have been used in limited quantities in the U.S.A for bridge deck resurfacing, but more widely in Russia. Although absorption of water is significantly reduced, this admixture extends its effect through a reduction in permeability and impartation of dampproofness without strength loss. A waterproofing admixture called *Hydrophobic Blocking Ingredient (HPI),* based on two principal components: reactive aliphatic fatty acids, and an aqueous emulsion of polymers and aromatic globules, has been introduced to North America.

4.3 Mode of Action

Both types of admixtures increase resistance to water penetration, either by acting as pore fillers or by creating a hydrophobic coating within the pores, or by combining both effects. Materials which produce hydrophobic coating (fatty acids, wax, and bituminous emulsions) function as follows. Normally, concrete *wets* because the pressure needed for wetting is low due to the surface tension forces which pull the water into the pores. When waterproofing admixtures such as stearates are used, insoluble calcium stearate produced by the reaction of the soap with $Ca(OH)_2$, coats the surfaces of the pore. Similarly, wax or bituminous emulsions, on contact with cement hydrates, deposit minute droplets of wax or bitumen on the wall of the fine pores and capillaries forming a hydrophobic coating. The result is that the hydrophobic coating causes a reversed angle of contact that the surface tension forces now push the water out of the pore. (Fig. 7)

$$\underset{\substack{\text{Calcium}\\ \text{Hydroxide}}}{Ca(OH)_2} + \underset{\substack{\text{Stearate}\\ \text{admixture}}}{RCOOH} \rightarrow \underset{\substack{\text{Insoluble calcium}\\ \text{stearate}}}{Ca^+ COOR^-} + H_2O$$

Theoretically, the effect of high contact angle produced by the use of the admixture means that 1–4 m head of water would be required to penetrate the surface through the largest capillaries. In practice, however, nonuniform and incomplete coating and the presence of voids in concrete usually reduce the resistance to a few centimeters head of water. Consequently, dampproofing or admixtures that merely increase water repellency are only effective in keeping out rain and preventing rising damp but are of little help in water retaining structures.

The HPI admixture system claims to have been designed to deal with the problem of water penetration, not on permeability, but sorptivity, or capillary suction which the manufacturers contend is the primary mechanism of water and salt penetration, under conditions of wetting and drying, or partial immersion.[52] Both components in the admixture system increase resistance to water penetration, either by acting as pore fillers or by creating a hydrophobic coating within the pores, or by combining both effects. The principle of the HPI system is to exclude water and moisture along with any dissolved salts, or other aggressive solutes. Each component of the admixtures has distinct action (Fig. 8). During mixing, reaction of the fatty acids with the initial hydration products creates a water and moisture repelling lining on the capillaries and concrete surfaces. This component increases the contact angle to well above 90°, and the resulting force at the entrance of the capillary pores and microcracks act to keep water out. When hydrostatic pressure is applied, the globules are pushed in front of the water until they jam together forming a physical plug in the capillary, preventing further penetration.[52]

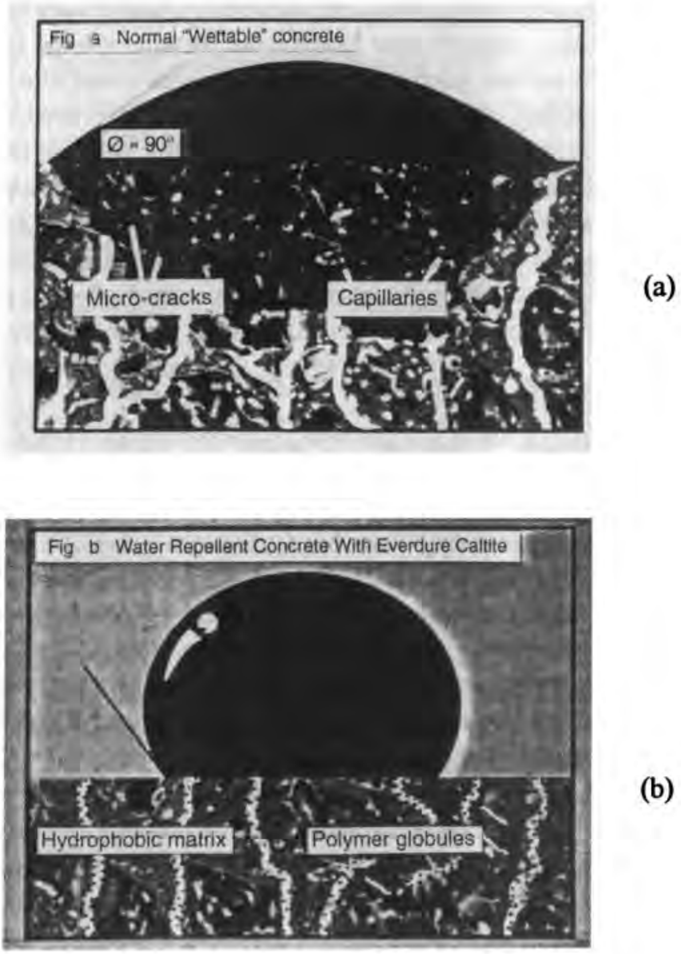

Figure 7. Mechanism by which water penetration into concrete is reduced: *(a)* concrete with no admixture, and *(b)* concrete containing an integral dampproofing admixture.

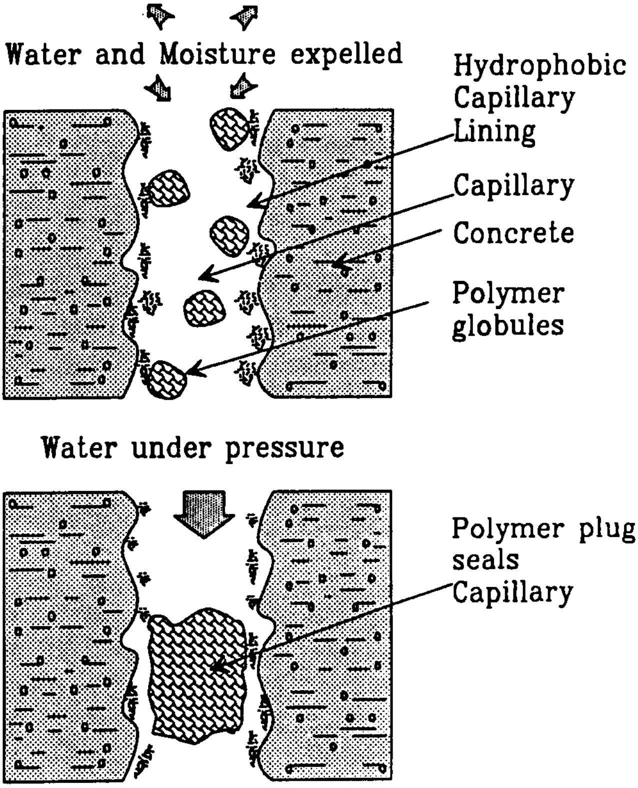

Figure 8. Capillary blocking actions of hydrophobic pore blocking ingredient.

4.4 Effects on the Plastic and Hardened Properties of Concrete and Mortar

These admixtures modify workability, bleeding and settlement, set-time, air content, finishing characteristics, compressive strength, durability, and permeability as follows.

Most of the materials in group *(a)* (enumerated on p. 986) entrain air and will therefore show improvement in workability when compared to concretes with no admixture. Other lubricating actions may also result from the small particles of waxes and bituminous emulsions.

In medium cement content mixes of low slump and at normal temperatures, they increase the cohesiveness of the mix. Finely divided admixtures impair the workability of cement rich mixes due to the increased water demand. Workability of mixes with low cement and fine contents benefit by the incorporation of these materials.

At the recommended dosages they do not alter setting times significantly. However, when high air entrainment results due to use of large dosages and high mix consistencies, pronounced set retardation can occur specially at lower curing temperatures (< 15°C). The effect is significantly increased if a water reducing admixture is also present.

When high dosages of soap-based admixtures are used at high workabilities, frothing of the mix results due to very high air contents. This is more prone to occur in concrete where a combination of admixtures (waterproofing/water reducing) is used.

Depending on the dosage of the admixture used and the consistency of the mix, increased cohesiveness may result producing "sticky" mixes. This occurs mainly in mixes with high cement and fines contents, at low W/C ratios. A change in mix proportions and the use of coarse sand may be needed.

Some strength reduction results from the use of soaps and wax emulsions, particularly in high strength mixes due to the air entrainment induced by the admixtures. Lower cement content and dry harsh consistency mixes containing the admixture often show increased strength values in comparison with corresponding plain mixes due to improved consolidation and bleeding characteristics. Similarly, fine particulate materials adversely affect the strength of rich mixes due to their increased water demand, resulting in high water contents in the mix. In cement-poor mixes an admixture acts as a pore filling and workability aid.

Although dampproofing and waterproofing admixtures show marginally improved resistance to water penetration, the presence of even small amounts of these admixtures is said to improve freeze/thaw durability.[53] Wax emulsions have been shown to significantly improve freeze/thaw characteristics.[54] However, the results cannot be directly attributed to waterproofing effect, since the admixtures reduce W/C ratio and entrain up to 4% air.

Materials, such as soaps and finely divided inert fillers, which decrease the density by increasing the voids content of concrete, decrease the water tightness. Also, materials which reduce the strength of concrete increase the permeability of concrete. The effects are pronounced at earlier ages. However, some finely divided inert pore filling materials such as bentonite and chemically reactive finely divided solids, when used at dosages which do not significantly increase the water demand of the mix, can result in improved water tightness of the concrete.

4.5 Factors Influencing the Effects of the Admixtures

Mix proportions, mix consistency, admixture dosage, poor mixing and curing conditions markedly influence the effects produced by the admixture. In cement-rich mixes void content is often increased, resulting in increased permeability, although absorption rates may decrease. Since the admixtures produce air, mixes with high fines content may promote air entrainment. Higher workabilities produce a frothing action with soaps, waxes and bituminous emulsions, particularly if large admixture dosages are used. The use of higher than recommended addition rates results in reduced density, strength and watertightness.

When fatty acid or wax emulsion type waterproofers are used in conjunction with other lignosulfonate or hydroxycarboxylic water reducers, heavy air entrainment results with attendant strength reduction. Both these effects decrease waterproofing characteristics. At high workabilities, lignosulfonates counteract the reduced bleeding effect obtained with waxes and increase bleeding rates.[55]

Poor mixing may result in discontinuities in the water repelling character. Consequently, adverse effects may be produced in the structure due to differential moisture movement. The effectiveness of these admixtures is closely related to the prevailing curing conditions at early ages. Watertightness of the concrete increases with curing. The first seven days are crucial because major improvements occur during this period.[56] Concrete with these admixtures should not be left to dry out before the seventh day. Intermittent curing cannot be readily wetted again.

4.6 Preparation, Storage, and Addition Procedures

Water repellent materials such as soaps and fatty acids are available as dry powders. Usually a stearate soap is blended with talc or fine silica sand and used at the prescribed dosage per weight or bag of cement. In commercial liquid preparations, the fatty acid salt (soap) content is usually 20% or less, the balance of the solid material is made up of lime or $CaCl_2$. $CaCl_2$ is used to offset the strength reduction that occurs at early ages when soap-based materials are used. Butyl stearate, which has an action in concrete similar to that of the soaps, is usually added as an emulsion. Unlike the soaps it does not have a frothing action and can therefore be used at a higher dosage without adverse effects on strength and permeability. The emulsion is said to provide better dispersion throughout the mix and, when used at the recommended dosage of 1% by weight of cement, gives water repellent effects superior to that of soaps without affecting the strength.

Heavy mineral oil (a fluid petroleum product) should be free of fat or oils that saponify. Petroleum residues which emulsify with water, have been found satisfactory. Dosage rates up to 5% by weight of cement show desired results with only slight strength reduction. Finely divided inert pore filling and reactive materials are generally used in mixes that have low cement and fines contents. Improvements in strength and permeability are attained. The materials are used at addition levels ranging from 0.5% to 10% by weight of cement for the production of watertight concrete. Dosage used is dependent on the cement content, percentage fines in the mix and the type of admixture. Liquid sodium methyl siliconates dosage is limited to 2–3% because of its severe set retarding action. Significant advantages could be achieved by the use of increased dosages but the potential waterproofing character of the admixture cannot be realized due to this limitation.

Admixtures based on soaps and finely divided inert solids are relatively stable and not sensitive to moisture or temperature variation. Shelf life of the material would, therefore, exceed the customary twelve month period stipulated for most proprietary products. Wax and bituminous emulsions, however, are susceptible to freezing and can be precipitated out of the emulsions and appropriate storage conditions should be provided.

Addition of powdered materials is mainly done by a manual operation where the mix operator adds a measured weight of the material at the mixer. The dispersion of liquid materials can be done by the use of automatic dispensing equipment used for conventional admixtures. Admixtures that are fine powders are usually blended with silica sand to enable better dispersion. Aqueous bentonite dispersions and wax emulsions are dispensed at the mixer in a manner similar to that used for other liquid admixtures. The materials are added just after the batching of aggregate mixed for a brief period and followed by the addition of cement. Because they are solid powders they need vigorous mixing with other solids.

4.7 Precautions

In the selection of a dampproofing or waterproofing admixture for use in concrete, the following criteria should receive consideration: *(a)* type of waterproofing admixture, *(b)* dosage, *(c)* compatibility with other admixtures, *(d)* placing and curing temperatures, *(e)* limitation of the admixture.

Certain vegetable and animal fats and emulsions based on white grease or soya oil may produce significant strength variation. The quantity of soap-based materials used in the mix should be limited to a maximum of 0.2% by weight of cement, since higher dosages result in larger air contents and strength reduction. This effect is particularly evident with concrete of slump exceeding 3" (75 mm). The use of an integral waterproofing admixture in conjunction with a water reducer may show side effects. At normal dosages for both admixtures at slumps greater than 3", setting time, bleeding characteristics and air content are increased. If a water repellent material is to be used in mixes containing a conventional water reducer, the following control measures should be taken.

- Use mixes with low W/C ratio (slump <3").
- Use reduced dosages for both water reducer and waterproofing admixture.
- Use a set accelerating water reducer

Placing and curing temperatures play an important role in the effects produced by waterproofing admixtures. Temperatures below 15°C may promote set retardation. Some waterproofing admixtures may affect the hydration of the cement because they impede the entry of water into the cement particle. When these admixtures are considered for use in floors and walls it is important to determine whether the admixture will interfere with the adhesion of subsequently applied coatings, adhesives, or plaster.[51]

4.8 Standards and Codes of Practice

There are no nationally recognized standards covering the performance and use of these admixtures. Establishing the effectiveness of the admixtures has always been a problem due to the difficulty of obtaining consistent results in the permeability tests.[57][58] Consequently, available test methods and often those quoted by manufacturers relate to simple absorption or permeability tests which are related to a highly permeable control specimen. Some of the test methods available for determining waterproofing properties are as follows:

(a) Test methods for dampproofers. Determination of percentage absorption: The method is detailed in BS.556, Part 2, 1972. Water absorption is measured as the weight change at fixed immersion times. Although no absolute values can be obtained, the method finds use in screening test, where comparative evaluation is required. In the initial surface absorption test, BS.1881, Part 5, 1970, rate of flow of water into concrete per unit area, after a given interval from the commencement of the test, is determined.

Another more refined test described in Ref. 51 provides a method of determining liquid/vapor transport through concrete, or establishing the effects of material properties upon moisture flow. The methods facilitate the comparison of the effectiveness of various integral dampproofing admixtures.

(b) Test methods for permeability reducing admixtures: The tests measure the effect of the admixture on modifying the hydraulic permeability. A common qualitative method utilizes porous concrete tablets which are subjected to steadily increasing pressures and maintained for short periods. The pressure at which moisture beads appear is noted and compared against a control sample from the same batch of concrete containing no admixture. Another method, less frequently used, measures the flow coefficient of the concrete under saturated conditions.[57] Measurements for a seven day period allows useful comparison.

(c) Admixture uniformity tests: The parameters used are active solid content, specific gravity (for liquids) and ash content.

5.0 PUMPING AIDS

5.1 Background

Although a number of chemical admixtures (air entraining agents, water reducers and superplasticizers) are used to enhance pumpability in concrete, they are considered normal constituents of concrete because of their wide use. They therefore, are excluded from the category of pumping aids. Pumping aids are admixtures that are generally used to pump marginally pumpable concrete rather than those that are readily pumped; their use is mainly for the purpose of improving the plastic properties of mortar or concrete in situations where strength requirement is not of primary concern.

5.2 Chemical Composition and Categories

Materials that have been used for pumping may be classified according to their physical action in concrete as follows:[59][60]

Class A. Water soluble synthetic and natural organic polymers, which increase the viscosity of the mixing water. They include cellulose ethers, pregelatinized starches, polyethylene oxides, alginates, carrageenans, polyacrylamide, carboxy vinyl polymers, and polyviny alcohol.

Class B. Organic water soluble flocculants which are adsorbed on the cement particles and increase viscosity by promoting interparticle attraction. These materials are styrene copolymers with carboxyl groups, synthetic polyelectrolytes, and natural gums.

Class C. Emulsions of various organic materials which increase interparticle attraction and also supply additional superfine particles in the cement paste. Materials consists of paraffin wax emulsions which are unstable in the aqueous cement phase, as well as acrylic emulsions and aqueous clay dispersions.

Class D. Inorganic materials of high surface area or unusual surface properties which increase the water retaining capacity of the mix. These include very fine clays (bentonites), pyrogenic silicas, condensed silica fume, milled asbestos, and other fibrous materials

Class E. Inorganic materials which supply additional fine particles to the mortar pastes and, thereby, increase the thixotropy, consist of fly ash, hydrated lime, kaolin, diatomaceous earth and other raw or calcined pozzolanic materials and various rock dusts. Other fine filler materials may also be used.[61][62]

5.3 Mode of Action

Successful pumping of concrete necessitates two requirements in the mix: *(a)* sufficient paste content to form an annular grout film against the pipe wall to act as a slip surface, and *(b)* suitable grout consistency and interstitial void structure to offer good resistance to the forced bleeding of water from the cement paste so that de-watering of the paste under pressure of pumping can be prevented. Admixtures in classes A, B, and C act by increasing the viscosity of the cement paste. Materials in classes D and E influence the void structure by acting as pore fillers, although the increased fines content often also increases lubrication of the mix.

5.4 Factors Influencing the Effect of the Admixture

The following factors adversely influence the effect of pumping admixtures in concrete and mortar mixes. Since pumping delays can be time consuming and costly, it is important that the pump operator pay due regard to these items and the engineer designs the concrete mix taking into account these effects.

Cement content. Medium to high range cement contents respond poorly to the use of pumping aids. Often highly thixotropic mixes are produced even at minimum recommended dosages. It is, therefore, important that the suitable dosages be evaluated for the specific mix prior to field use, if their use is contemplated.

Temperature. High temperatures may cause rapid slump loss and it may be necessary to use a retarder in conjunction with the thickener.

Fine Aggregate Characteristics. Mixes containing a high percentage of fine sand (FM < 2.6) give heavy bodied mixes which impair pumpability due to the high cohesion and friction produced in the pipeline.

Compatibility with Other Admixtures. Due to the inherent surfactant properties exhibited by most of the materials in classes A, B, and C, their use with other admixtures such as water reducers should be evaluated in terms of the side effects on the plastic and hardened concrete, such as severe set retardation and excessive air entrainment.

5.5 Effects on the Plastic and Hardened Properties of Concrete and Mortar

Workability. Since the admixture is mainly used in lean (low cement) and harsh mixes, the admixture usually enhances workability. The effect, however, is governed to a large extent by the mix proportions of the concrete. High dosages of admixtures in classes A, B, and C, may result in substantial thickening and high water demand in medium cement content mixes, thereby impairing workability. The effects produced on workability due to the addition of fine inorganic powders (class D) will depend on the dosage used and the mix proportions. High dosages in low cement content mixes improves workability significantly, while similar levels of addition will adversely affect the workability of medium and high cement content mixes.

Setting Characteristics. Cellulose ethers, starches and polyethylene oxide are potent retarders. Even at recommended dosages prolonged set times are likely to occur at the high W/C ratios used for pumping.

Bleeding and Settlement. Most of these admixtures decrease both bleeding rate and bleeding capacity, the effect, in general, increasing with the amount of admixture used. The use of polyelectrolytes and wax emulsions at higher than prescribed levels may produce significantly higher bleeding rates which, in effect, would be counterproductive to the purpose of their use. Also, certain polyelectrolytes and wax emulsions, while reducing bleeding capacities, tend to increase the initial rate of bleeding.[55][63] Materials with high surface area such as fly ash and silica fume increase the water retaining capability of the mix.

Air Content. Class A, B and C admixtures have inherent surfactant properties that lower the surface tension of the aqueous phase of the mix. Consequently, dosages above optimum levels will entrain unwarranted air.

Compressive Strength. Slight strength reduction, particularly at early ages, results in medium cement content range mixes; the extent of reduction depends on admixture dosage, percentage of entrained air, slump or consistency, and degree of set retardation. High levels of inert, finely divided admixtures from classes D and E increase the water demand and, consequently, produce a weaker matrix. Mixes with low cement content usually benefit from their use due to improved workability that enables lower W/C ratios to be used with attendant increased strength values.

Shrinkage. Admixture types and addition levels which necessitate the use of increased water contents in the mix will increase drying shrinkage.

5.6 Storage and Addition Procedure

Some powder forms readily imbibe moisture, while emulsions are susceptible to coagulation or precipitation of the solid phase when subjected to freezing temperatures. These materials should, therefore, be stored under dry and normal temperature (20–22°C).

The range of admixture dosages used for the five classes is as follows:

Class A: 0.2–0.5% solid by weight of cement.

Class B: 0.01–0 0.10% solid by weight of cement.

Class C: 0.10–1.50% solid by weight of cement.

Class D & E: 1–2.5% solid by weight of cement.

Dosages exceeding 2% (Classes D & E) are only used with materials which have an inherent pozzolanic or hydraulic activity. The addition is usually made as a cement replacement where the cement content is usually decreased by the amount of the admixture added. In some instances, where design strength is important, no reduction in cement content is made; instead, the admixture is added usually at lower dosages.

Due to the small amounts of admixtures used, the addition of the proper quantity should be ensured. Suitable automatic dispensing equipment should be used for liquid materials. For the powders, a general volume dispenser such as a volume cup of the correct size or a measured weight of the material by weight of the cement may be used. Some manufacturers market the material packaged in water soluble packages which contain the prescribed addition rate (in weight) of the admixtures. The packages are added directly at the mixer.

Liquid materials (such as bentonite slurries, wax dispersions) are generally dispensed through suitable automatic dispensing equipment, with the gauge water. Fine powders are mixed with fine sand because of the small quantities involved and because of their tendency to float on the mixing water. The material is added just after the aggregates are discharged and a brief mixing period follows prior to the addition of cement. Due to their solid form, longer, more vigorous mixing may be required to ensure thorough distribution. Materials such as polyethylene oxides, cellulose ethers, and some synthetic polyelectrolytes are hygroscopic and tend to produce slow dissolving "clumps" when they come in contact with moisture. Therefore, to ensure uniform distribution in the concrete, they should preferably be dissolved in water prior to addition into the mix. With polyethylene oxides gradual dispersion of the powder in a large volume of water containing a little isopropanol and vigorous stirring, prevents the formation of clumps.

5.7 Applications

These types of admixtures are widely used for pumping of low strength concrete mixes (cement content < 150 kg/m^3) such as fill concrete. Such mixes will, in general, be short of fine material and a failure to pump will normally be due to segregation that occurs when the flow of grout through the void channels is extremely rapid. The admixtures increase viscosity of the water enabling formation of a cohesive paste with reduced bleeding. Pressure generated at the pump is then transmitted to all the constituents. They are also used in conjunction with water reducing admixtures in oil well cementing grouts to reduce pipeline friction and rapid water loss. Other uses include the grouting of pre- and post-tensioned concrete ducts. The following general rule can be used as a first approximation in the proportioning of mixes. Mixes with low cement contents (< 200 kg/m^3) and cement aggregate ratios of 1:7 to 1:10 normally used for non-structural applications would benefit by the use of the admixtures under classes A, B and C. For mixes with cement-aggregate ratios higher than 1:10 admixtures in classes D and E would be most suitable.[55]

Many of the flocculating admixtures discussed in the next section can be successfully used to aid the pumping of low cement content concrete. Table 7 may be referred to for details on the materials used.

5.8 Standards

There are no North American or European standards or specification which regulate the use of these admixtures. The Australian Standards Association has published a document[60] which gives information relating to the properties, effects, and methods of use of these admixtures. No recognized test method or equipment is available for laboratory determination of pumpability. Pumpability is, therefore, deduced indirectly by determining other properties of concrete which correlate to some degree with this property. Indirect indications of the effectiveness of the admixture can, therefore, be obtained from the values of these properties. Test methods used to determine such properties include the following.

- *Bleed test:* ASTM-C-243 test method for bleeding of cement paste and mortars, and the modification of this method to test concrete mixtures,[64] have been used to provide data on bleeding capacity and bleeding rates of concrete. Such data give information relating to potential for segregation of the mix.
- *Test methods for determining water loss under pressure:* Methods used to determine water retentivity of concrete and mortar placed with the help of pumping aids are as follows:
  - *(a)* American Petroleum Institute Test for fluid loss in oil well cements.[65]
  - *(b)* Pressure Tests on strand tendon mode.[66]

Both methods use pressure filter which measures the volume of water that separates from a grout subjected to pressure.

- *Pumpability test, Pressure Bleeding Tests:* In this method, concrete is subjected to a pressure of 3.5 MPa. The difference in the volume of bleed water that exudes at two time intervals is said to correlate directly with pumpability of a concrete of a given slump. The plot of the values obtained for the difference in the volume of bleed water at the two time intervals at various slumps gives a demarcation line which delineates mixes which can and cannot be pumped.
- *Concrete pumping circuit model.*[68] This test method ascertains the effects of aggregate void size, void volume and the effectiveness of admixtures for marginally pumpable concrete. ASTM-C-494 is used to determine the secondary effects of the admixture on properties such as strength, setting time and percent air entrained. The conclusion drawn from the results of such tests will provide information suitable for mix proportioning purposes. However, further confirmatory, full scale tests should be done under a variety of field, and actual job conditions anticipated for batching, truck mixing, pump type and operator, hose layouts of height and distance contemplated. Such trials will furnish information required for establishing the correct admixture dosage for the job, and alert the user to potential problem areas.

5.9 Precautions

When powders are used, initial mixing produces a stiff consistency; however, further mixing results in the production of a wetter consistency as the polymers gradually dissolve. It is, therefore, advisable to restrict additions of extra water at the initial mixing stages.

6.0 FLOCCULATING ADMIXTURES

6.1 Background and Definition

Physical characteristics of a concrete mix, both in the plastic and hardened state, are determined by the manner and extent of interparticle attraction.[58][69] The phenomenon of bleeding is one of the properties where such interparticle attraction plays an important role. Although several factors affect the bleeding characteristics of concrete,[69] this section deals only with the influence of the chemical environment of the cement particles on such properties of the mix. The chief function of flocculating admixtures is to reduce the type of bleeding from a destructive form (channel) to a more gradual seepage (normal) in mixes, where for reasons of raw material deficiency, high bleeding rates and capacities are anticipated.

A flocculating admixture is a chemical compound which influences the colloidal state of the aqueous cement phase by alteration of the interparticle forces that exist in the system. Four types of materials have been used; these include polyelectrolytes, wax emulsions, aqueous suspensions of clay materials, and natural water soluble gums.[60][63][69]-[72]

6.2 Chemical Composition

The following polyelectrolytes have been used successfully in both laboratory investigations and field applications: Sodium polyacrylate, isobutylene maleic anhydride copolymer, sodium salt of styrene maleic anhydride copolymer, sodium salt of styrene maleic anhydride copolymer, polymethacrylic acid, polyacrylamides, polyacrylonitrile, and the calcium salt of vinyl acetate maleic anhydride copolymer.

Two types of paraffin wax emulsions containing 20–30% solids by weight, with particle sizes ranging from 0.5–1.0 mm, which may or may not be stable in the aqueous cement phase, are used. Suitable emulsifiers include mixtures of sorbitan monostearate and polyethylene stearate, and stearyl oleyl alcohols condensed with ethylene oxide. Aqueous suspension of clay materials such as kaolin and bentonite contain 2 - 6% solids by weight. The particle size of the kaolin suspension is usually much finer than that of the bentonite suspensions.

In the natural water soluble gums category, gum arabic, gum ghatti, and alginates are used as viscosity increasing and anti-fluid loss agents in normal weight pumped concrete and oil well cementing applications. Gum arabic produces a low viscosity system in cement paste while gum ghatti imparts high thixotropy to mortar. All three materials are susceptible to viscosity decrease at high pH and high concentration of electrolytes.

Other miscellaneous materials used for similar purposes include condensed silica fume and ammonium stearate. Table 7 gives a list of materials which have been used as flocculating admixtures and their manufacturers.

Table 7. Materials Commonly Used as Flocculating Agents.

Product Name	Manufacturer	Chemical Identity	Physical Characteristics	Effects in Cement/Water System	Product Application
			.... Class A		
Natrosol	Hercules Inc. U.S.	hydroxy ethylcellulose	fine white powder soluble in hot and cold water	increases viscosity of water phase	thickener suspending agent, water retainer
Carbopol 801	B.F. Goodrich Canadian	polyacrylic acid polymer	powder soluble in water and polar solvents	increases viscosity of water phase	thickener increases cohesion
Methocel F	Dow Chemical U.S.	bydroxy propylmethylcellulose	powder treated form dispersible in in water, solubility pH controlled	increases viscosity of water, mix thixotropy	thickener, suspending agent
Methocel A	Dow Chemical U.S.	methylcellulose	water-dispersible powder	increases viscosity	thickener, water retainer
Modocol E	Modo-Chemie Sweden	hydroethylmethyl	fine powder, soluble in water	increases viscosity and thixotropy of mix	thickener, bonding agent
Polyox WSR 301	Union Carbide U.S.	polyethylene oxide polymer	slowly dissolving in water, solubility increased by addition of isopropanol	increases both viscosity and thixotropy; stringy mix at higher dosages	thixotropic agent, flow agent
Alginates	Alginates Ind. U.K.	natural water-soluble gum from brown seaweed (alginic acid)	powder, water-soluble dependent on divalent ion (Ca^{2+}) concentration and rate of shear	increases viscosity and mix lubricity	thickener, workability aid

Table 7. (Cont'd)

Product Name	Manufacturer	Chemical Identity	Physical Characteristics	Effects in Cement/Water System	Product Application
Calgon	Calgon Corp. U.S.	polyacrylamide	water-soluble	flocculation; increases viscosity by bridging cement particles	thickener for reducing bleeding
Separan	Dow Chemical U.S.	sulfated polysaccharide	slowly dissolving in water	increase viscosity of water phase	water retainer
Class B & C					
Acrysol ASE 75	Rohm & Haas Co. U.S.	natural salt of acrylic acid polymer	water-dispersible solid	increases viscosity of water	thickener, workability aid
Krilium	Monsanto Chem. Aust.	Ca^{2+} salt of vinyl acetate maleic anhydride copolymer	powder, soluble in water	increases thixotropy effect, increasing alkali content of cement	increase cohesion of mix, reduces bleeding capacity
Stymer S	Monsanto Chem. U.S.	Na^+ salt of styrene-maleic anhydride copolymer	soluble in cold water	increases viscosity of water phase	thickener suspending aid
Class D & E					
Silica fume	Elborg Technology Co., U.S.	fumed silica	insoluble in water	shear thinning thixotropic agent	increase cohesion of mix, improve pumpability
Aerosil	Degusa U.S.	finely divided silica	insoluble in water	viscosity increased	improve bleeding characteristics
Volclay		bentonite	insoluble in water	viscosity increased	improved bleeding characteristics

6.3 Mode of Action

Flocculation is thought to occur by the interaction of the highly charged groups in the chain-like molecule of the flocculating agent with the cement particle. The chains are adsorbed on to the cement grains, linking them together. The net result is the increase in interparticle attraction which greatly increases the tendency to behave as a large floc. Unstable wax emulsion, in addition to the above behavior, exerts its effect by also filling the voids between the cement and aggregate particles passing the 25-mesh sieve. Silica fume has a very high specific surface and ability to imbibe large quantities of water in a loose arrangement through hydrogen bonding. These characteristics enable concretes containing silica fume to be more structured yet quite responsive to vibration and pressures used in pumping.

6.4 Factors Influencing the Performance of the Admixture

Three principal factors affect the performance of the admixture: admixture dosage, cement composition, and compatibility with other admixtures present in the mix synergy or antithetical effects.

(a) *Admixture dosage:* Dosages beyond the optimum addition rates impair workability due to high thixotropy, and result in the extension of set time and strength reduction.

(b) *Cement composition:* The effectiveness of polyelectrolytes is influenced by the alkali content of the cement.[55][69] Low alkali cements produce a lower degree of flocculation than high alkali cements; a certain alkali content (up to 1%) is required to increase the stiffness of the paste.

(c) *Presence of other admixtures:* Concrete or mortar mixes containing lignosulfonate or hydroxycarboxylic type water reducing admixtures generally require higher admixture dosages. Accelerating admixtures like $CaCl_2$ require lower dosages of the flocculating admixture.

6.5 Effects on the Plastic and hardened Properties of Concrete and Mortar

Workability. When used at the recommended dosages in cement-rich concrete and mortar, these admixtures produce low slump and flow table values. Increased cohesion of the mix impairs significantly the workability in such mixes. In low cement content mixes, although increased cohesion results, the slump values are not affected markedly.[55]

Bleeding. All admixture types generally reduce the bleeding capacity, sometimes up to 50%. The effect on bleeding rates, however, can vary depending on the type of admixture. Some of the polyelectrolytes and stable wax emulsions may increase bleeding rates while decreasing bleeding capacity. Bentonite suspensions and unstable waxes are more effective than kaolin or stable wax emulsions in reducing both bleeding rates and capacities in cement pastes. In mixes where reduced bleeding capacity is observed when the admixtures are used, a concurrent reduction in the compactness of the sedimented cement and subsieve aggregate particle also occurs.

Compressive Strength. Materials that produce strong interparticle attraction such as polyelectrolytes, gums, and unstable waxes produce beneficial effects when used at dosages up to 0.025%. Beyond the 0.025% level, strength reduction occurs in low cement content mixes, while richer mixes are able to tolerate addition levels up to 0.1% before strength begins to decrease. Materials which supply supplementary fines to the mix (stable waxes, kaolin suspensions) give improved strength up to 10% for inert materials and up to 25% with the pozzolanic materials.

6.6 Preparation, Dosages, and Addition Procedures

Polyelectrolytes are added in small amounts, generally not exceeding 0.15% by weight of cement. Since all these admixtures dissolve slowly, the preparation of these solutions should be done in advance. In order to ensure full hydration and dispersion of the bentonite particles, it is preferable to prepare these suspensions at least 48 hours prior to use. Dosages used for the wax emulsions vary from 0.1–0.5% for the unstable emulsions and 1.0–25% by weight of cement for the stable emulsions. The admixture levels used for the clay suspensions will depend on the cement fines content and percentage voids in the aggregate. Generally, suitable ranges of addition are 0.25–0.5% for bentonite suspensions and 1–20% for kaolin suspensions. Natural water soluble gums may be used at addition rates of 0.02–0.50%.

All liquid admixtures are added to the mix with the gauging water and may be dispensed by automatic dispensing equipment used for other admixtures; however, the specific and limited use of such materials usually does not justify the installation of special automatic dispensers, except for large projects such as dams, where the use of locally available crushed sands often results in severe bleeding of the mix.

6.7 Storage and Shelf Life

Clay dispersions and wax emulsions have a tendency to settle when stored for long periods. Therefore, bulk storage tanks should be equipped with a device for agitation of the admixture prior to discharge. Wax emulsions are also susceptible to loss of activity due to freezing. Lower temperatures increase the viscosity of these materials and may cause variation in the amount of admixture dispensed into the mix due to pipeline blockage. Shelf life is generally limited to 6–9 months.

6.8 Applications

A flocculating admixture is generally used for three purposes:

- Where the use of chemical admixtures to rectify bleeding problems is economical.
- Where the use of a rich mix to prevent high bleeding will be detrimental to the structure, e.g., mass concrete.
- Where low strength lean concrete mixes are used and when structural requirements are secondary to placing considerations.

Typical uses include reduction of the accumulation of water in concrete placed in deep forms, thereby preventing the formation of laitance on the surface of the concrete. Consequently, it is useful in mass concrete work because it reduces the excessive cleaning between successive lifts. It also reduces the voids formed under horizontal reinforcing bars. Therefore, the bond to steel is better and the potential corrosion problems are reduced. Flocculating admixtures are also used in concrete block manufacture, slip-form concrete and in lean concretes which use coarse sand.

6.9 Standards and Codes of Practice

No European and North American standards covering their use exists. General guidance on the evaluation, selection and use can be obtained from data contained in Ref. 60.

Test methods used for evaluation of the effectiveness of these admixtures are as follows: ASTM-C-243, Bleed Test method for determining bleeding rates and capacities, and ASTM-C-232, method for determining bleeding of concrete. Specific tests for determining the suitability of admixtures for use in pumped concrete are discussed in Sec. 5.

7.0 BACTERIAL, FUNGICIDAL AND INSECTICIDAL ADMIXTURES

7.1 Background and Definitions

Even durable concrete can, under certain conditions, suffer severe degradation by bacteria, fungi, and insects. The organisms contribute to concrete degradation primarily by establishing and maintaining large colonies on or within the concrete. Concrete containing such organisms usually suffers attack by one or more of the following factors:

(a) Corrosive chemicals released by their metabolism.

(b) Creation of an environment that promotes corrosion of steel.

(c) Creation of a large number of intrinsic channels due to penetration by insects.

(d) Formation of ungainly stains on the surface of concrete.

The primary attacking agent in bacterial degradation is nearly always an organic or mineral acid formed by the biochemical process promoted by the specific bacteria. The acids react with the cement paste and gradually dissolve it. Although the alkaline hydrates neutralize the initially formed acid, the fermentation or other bacterial metabolic activity, itself, continues as long as nutrients, bacteria, and moisture prevail. Prolonged exposure to such conditions results in the erosion of the surface of concrete. The floors and walls of restaurants, kitchens, school gymnasiums, shower rooms and dairies are prone to the growth of fungi. Evidence of the growth of these organisms is the dark stains, pungent smell or the outbreak of diseases known as *athlete's foot.*

The penetration of termites into walls and floors made of concrete is a common occurrence in most tropical countries. Porous concrete, particularly no-fines concrete which offers a suitable void system for their habitation, is quite prone to termite penetration. Good housekeeping measures such as the use of a variety of disinfectants are often ineffective because the rough texture of the concrete provides shelter for bacteria. In order to realize the benefit of daily disinfectant wash, it is necessary to incorporate an inherent toxic agent to the organisms in the concrete. This objective is often achieved by the use of potent antibacterial, fungicidal and insecticidal admixtures in the mix.

A survey of the literature shows that few investigators have been interested in the subject of the use of chemical admixtures to inhibit microbiological and insect attack. There is, therefore, a dearth of information relating to the effects of the chemicals used on other properties of concrete. Accordingly, no field practice, proprietary products, and standards covering their use exists.

7.2 Chemical Compositions

Bactericidal Admixtures. Materials which have been found most effective in imparting bactericidal properties include polyhalogenated phenols,[73] sodium benzoate, benzalkonium chloride[61] and copper compounds.[74] Addition rates range from 0.75–10% by weight of cement.[75] Other materials used as liquid admixtures for preventing bacterial growth include 2:4:5 sodium-o-phenyl phenol tetrahydrate (Dowicide-A)[76][77] and alkyldimethyl benzyl ammonium chloride (alkaquat).[78]

Fungicidal Admixtures. The generic types used to inhibit bacterial growth such as polyhalogenated phenols, copper acetoarsenite, and copper arsenite can also be used as fungicides. However, some are quite specific to either bacteria or fungi, so that killing one group promotes the proliferation of the other because of the elimination of competition for nutrients. Levels up to 10% have been used.

Termite-Proofing Admixtures. Emulsions of the chemical dieldrin when used at 0.5% by weight of cement is said to provide potent contact toxic effects toward termites.[79]

7.3 Method of Addition

It has been reported that a great rate of destruction of the microorganisms occurs both on the surface and within the matrix of the concrete when bactericidal admixtures are used.[75][76] However, the effects are reported to be transient and not always completely effective.[73] Effectiveness of the admixture is dependent on the degree of water solubility of the materials and the method of incorporation into the mix. Water soluble materials when added via the mix water, are said to be readily leached from the concrete and soon lose their effectiveness. For the polyhalogenated phenols good long term effects are obtained by treating the cement prior to incorporating into the mix.[75] Alternate methods of incorporation include the use in floor toppings or a *dust on* coat. However, their application by this method would be limited to floors subjected to light wear.

7.4 Effects on the Fresh and Hardened Properties of Concrete and Mortar

Bactericidal Admixtures. The hydration characteristics of cements treated with polyhalogenated phenols is similar to normal portland cements and compressive strength is unaffected. Long term performance history for the material is reported to be good and a number of floor surfaces treated with this admixture have resisted bacterial attack for ten years or more.[76] Notwithstanding its inhibitory properties, the concrete floor surface requires daily detergent wash to remove processing residues to ensure the retention of antiseptic properties.

Fungicidal Admixtures. The high water solubility of copper acetoarsenite and copper arsenite results in the ready leaching of the materials when used in concrete. The effects are, therefore, a temporary measure and strength reduction is significant, below acceptable limits. The consistency of the mix is increased while both initial and final set times are nearly halved compared to those of untreated concrete. Although these materials offer better performance and economic advantage than antibacterial cements, it is doubtful whether in actual practice the significant strength decrease could be tolerated.

Termite-Proofing Admixtures. The efficiency of the material is not significantly altered by weathering action and therefore, the toxic effect is enduring. Compressive strength values show negligible differences between treated and untreated concrete.[79]

8.0 SHOTCRETE ADMIXTURES

8.1 Background

Admixtures used in shotcrete usually fall into four categories: *(a)* accelerators, *(b)* air-entraining agents, *(c)* retarders, and *(d)* finely divided inert or hydraulically reactive solids. However, since the purpose of the use of admixtures in categories *(b)*, *(c)* and *(d)* is the same as that in regular concrete, their use in shotcrete, therefore, will not be discussed. Admixtures that are powerful accelerators of cement hydration are described in this section.

Admixtures that are used either in the wet or dry shotcrete process are required to comply with the following specifications.[80]

(a) Quick setting characteristics so that initial and final set occur within 3 and 12 minutes, respectively.

(b) Provide a capability to form maximum layer thickness by increasing the resistance to sloughing off.

(c) Reduce loss of material by rebound.

(d) Increase rate of strength development so that strength values of the order of 500–1000 psi are rapidly attained.

(e) Provide an ultimate strength (28 days) that is not less than 30% of the non accelerated mix.

8.2 Chemical Composition

The materials used are usually strong alkalis, and organic bases. Proprietary materials generally consist of various proportions of these ingredients and may be marketed in both liquid and powder form. In some admixtures, single materials (sodium aluminate) may be present as the sole active ingredient. More commonly, the main accelerating ingredient is combined with one or more of the following admixtures to obtain other desired modifications and are, therefore, multicomponent admixtures.[82]

- Wetting agents
- Thickening admixtures
- Stabilizing agents for liquids

Although $CaCl_2$ is used under certain conditions, the dosage is restricted to under 2% except when rapid set is required to stop leaks. Due to the restrictions imposed on the use of $CaCl_2$, in many applications where there is a potential for corrosion, its use in shotcrete has significantly diminished. Alkali hydroxides and other chemicals with strong basic characteristics have found widespread use. The alkaline character of the active ingredient renders the admixture highly caustic, which requires caution in handling. Low causticity materials which significantly reduce the potential for injury during application have now been introduced into the market. The compositions are closely guarded trade secrets and, therefore, little published information is available.

The main accelerator ingredient may consist of sodium aluminate, sodium and potassium hydroxide, or carbonates, triethanolamine, ferric sulfate[83] and sodium fluoride.[82][84] Sodium salts of hydroxycarboxylic acids such as gluconates and tartarates may be used as wetting agents. Thickening agents used are generally clays (bentonite), slag and silica fume. Polyhydroxy compounds are used to stabilize solutions of sodium aluminate.[82]

8.3 Mode of Action and Factors Influencing the Effects of the Admixture

Most of the admixtures used probably act by precipitating as insoluble hydroxides or other salts, a form of false set. Conduction calorimetric studies show that their main effect on early strength is due to the action on the C_3A fraction of the cement. The reaction of C_3A is intensified in the presence of these admixtures and a sharp peak occurs at an early age.

Two factors affect the reaction of both the wet and dry processes: *(a)* mix design, and *(b)* the ambient condition prevailing during the spraying of the concrete. Mix design factors include, cement type and content, water-cement ratio, cement/admixture compatibility and the presence of other admixtures. Cements with higher C_3A contents, such as Type I and III, give faster reactions than cement with low C_3A contents such as Types IV and V. More finely ground cement and high cement contents accelerate the reaction. Batch to batch variations in cement and admixture, change the compatibility of the mixture, result in lower early strength development and strength variation. Conventional admixtures used for pumping (in the wet mix process) often retard the cement accelerator reaction.

Other mix parameters that affect the reaction during the spraying of the concrete are: admixture dosage, mix and ambient temperature, W/C ratio, pre-hydration of the cement and a delay in addition of the admixture. High admixture dosage produces flash set resulting in a mix that is too dry to stay on the sprayed surface. Low dosages on the other hand, may result in delayed set time and the sloughing off of the mix. Consequently, in either case build up of layers may not be possible. Higher temperatures (> 30°C) accelerate set and produce dry mixes, increase rebound, and lower strength values. Lower temperatures (< 10°C) extend set time and increase sloughing off from the surface. Prehydration of the cement, due to the presence of moisture in the aggregate and a delay in the addition of the admixture, results in lower early strength values.

8.4 Effects on the Plastic and Hardened Properties of Concrete and Mortar

The method of placement makes shotcrete potentially more variable and more anisotropic than normal concrete. Consequently, the development of the physical and mechanical properties such as strength, shrinkage, permeability and durability is drastically different from those of concrete. The effects are particularly noticeable during the very early and later ages.

Consistency of the Mix. Depending on the dosage of the admixture, the mix may exhibit good cohesion or produce a dry gritty mix. High cement contents and optimum dosages (3–6%) usually produce cohesive mixes which enable the building of layers.

Initial and Final Set. At optimum dosage levels initial setting time may be reduced to 3–4 minutes while final set time can vary between 12–15 minutes. Higher dosages reduce the time even further.

Compressive Strength and Modulus of Elasticity. Strength values are usually lower (15–20%) than corresponding mixes containing no admixture for both wet and dry mix processes at optimum dosages of 2–4%. Drastic strength reduction occurs as the dosage exceeds 4%. The stipulated requirement that strength should not be reduced by more than 30% of the control concrete is not possible at dosages above 6%. However, under special conditions such as stoppage of water leakage, such reductions are acceptable. In general, factors that tend to improve early strength of concrete seem to have a detrimental effect on ultimate strength. The use of accelerators in shotcrete mixes using regulated set concrete usually results in strength reduction both at early and later ages.[100] In general, the relationship between compressive strength and modulus of elasticity is similar to that of regular concrete. As with regular concrete, if adequate curing is provided, values increase with age.

Tensile and Flexural Strengths. Direct tensile strength values are usually lower than what would be expected from compressive strength values. This probably reflects the effect of laminations and other defects in the shotcrete on tensile strength. Flexural strength values follow a similar relationship observed for regular concrete.

Bond Strength. High bond strength can be attained between layers of shotcrete and the rock surface for both wet and dry mix processes when admixtures are used. Bond strength increases initially with dosages up to 2%, and thereafter decreases with further addition.

Shrinkage. Higher values are obtained for mixes containing the admixture in comparison with the corresponding mixes with no admixture.

Shrinkage increases with higher admixture and water contents of the mix, for both wet and dry shotcrete.[84]

Durability. Most proprietary accelerating admixtures adversely affect the concrete's resistance to freezing and thawing.[105][106] More recently, the widespread use of silica fume has enabled the use of considerably lower dosages of accelerators and also contributed to the improvement of porosity values, thereby dramatically improving durability of such concretes.

Permeability. Since the admixtures improve spraying conditions and minimize rebound, it is argued that permeability should be improved. Actual tests however, show that the effect is marginal and the values obtained are similar to mixes with no admixture. Silica fume-containing mixes, however, show improved impermeability.

8.5 Addition Procedure

Addition rates used for the powder accelerator are generally in the range of 2–6% by weight of cement. Liquid accelerators are batched by volume ratios with the accelerator-water ratios ranging from 1:20 to 1:1. Various liquid accelerators have different concentration of solids, which should be taken into consideration in metering the admixture by volume ratios. Optimum concentrations are not used in all applications and where fast set and high early strength are to be attained, high dosages are used. However, specifications may stipulate the maximum strength reduction allowed for the accelerated mix and this, then, puts a limit to the amount of admixture.

Powder accelerating admixtures used in the dry mix process are usually added to the concrete or mortar using either an auger, corkscrew, or gear wheel type dispenser.[85] The powder is fed by gravity to the corkscrew helix and conveyed through a tube and then discharged into a hopper containing the mix. The rate of addition is adjusted by increasing or decreasing the rotational speed of the corkscrew. The admixture dispenser is usually positioned above the conveyor charging the shotcrete machine. This arrangement provides a relatively uniform distribution of the admixture in the incoming materials. The delivery rate of the admixture must be synchronized with the rate of material delivery past the dispenser so that desired cement accelerator mix proportions are achieved. When liquid admixtures are used in the dry process, they are injected from a pressurized tank into the water line at or near the nozzle. Proper proportioning by volume of water is obtained by adjusting the admixture feed control value.

At present, the only reliable method of dispensing powder shotcrete admixtures directly into the wet mix at a uniform rate at the nozzle is by using a log feeder. In this method, the powder is compressed to a log which, when placed in the feeder, is gradually ground off, then carried away in the air stream to the nozzle. The accelerator mixes with the other shotcrete ingredients at the nozzle in transit to the sprayed surface. The amount of admixture added is controlled by the rate of advance of the log in the feeder. The method of dispensing liquid admixtures in a wet mix is essentially the same as that used in the dry mix operation, except that admixture is injected into the air stream instead of the waterline.

8.6 Applications

The cost, lower ultimate strength, and safety hazards are often cited as reasons in seeking to limit the use of shotcrete accelerating admixtures. However, when quick setting characteristics are required for rapid build up of layers and early strength development for immediate support and to seal off water leakage are essential, the use of an accelerator is indispensable. Consequently, accelerators are generally used on all overhead work, on some vertical walls and in locations of high ground water flow. Their use in shotcrete prevents sagging and sloughing off the shotcrete and reduces rebound of the material. The use of silica fume in shotcrete mixes has widened the aggregate "envelope" that can be used in these mixes. The potential uses of the process in repair and protection applications is discussed in Ch. 13.

8.7 Storage and Shelf Life

Powder admixtures are moisture sensitive. They must, therefore, be stored in bags lined with plastic sheeting, in an elevated and dry location. Bags of the accelerator should be placed on pallets not closer than 5 cm to the ground surface. The material in ripped bags should be used immediately after the bags are damaged or should be discarded. Shelf life of the powder is limited to a period of 6–8 months under proper storage conditions. The activity usually begins to decrease significantly after 6 months.

8.8 Precautions, Hazards, and Safety Measures

The alkaline chemicals which constitute the main ingredients are caustic and require caution in handling. In order to minimize rebound, thorough blending of the ingredients should be done. The aggregate should be well coated with the cement in the dry mix process. Since shotcrete admixtures promote shrinkage it is essential that the sprayed surfaces be kept moist for at least seven days. Ambient temperature conditions should be maintained at a level so that air in contact with the shotcrete surface is above freezing at least for seven days.[86]

The caustic materials contained in the admixtures can cause reactions on exposed skin, ranging from mild irritation to severe burns. Most of the ingredients are classed as primary irritants. They cause dermatitis by direct action on the skin when allowed to act in sufficient concentrations for a length of time. With liquid admixtures burns can occur immediately. Because of the serious hazard to exposed skin and eyes, personal equipment is required for all those in the vicinity of the shotcrete machine and nozzle. These include long sleeved shirt or coveralls. In addition, prior to shooting, protective cream or lotion should be applied to skin areas likely to be exposed to the caustic chemicals. A suggested treatment is to wash exposed skin with water and rinse with vinegar followed by treatment with a protective cream. All exposures to the eye require the immediate attention of a physician; immediate action would be to flush the eye with copious amounts of water.[87]

8.9 Standards and Guides for Practice

ASTM-C-1141 refers to shotcrete. Some shotcrete specifications may require the accelerating admixtures to conform to ASTM-C-494, "Standard Specification for Chemical Admixtures" (such as rapid set). ASTM-C-494 is only partially applicable. The specifications for uniformity, packaging, storage, sampling and inspection stipulated for type C accelerating admixtures are still pertinent to these rapid set accelerators, but testing methods for set and strength are modified.

ACI Standard "Recommended Practice for Shotcreting" (ACI 506-66) describes the application of shotcrete for different types of construction. Although specific requirements for these types of accelerators used for fast setting properties are not mentioned, requirements for other admixtures and concrete ingredient are stipulated. Application procedures and equipment requirements are given for both the dry and wet mix processes. The testing of shotcrete is covered in some detail.

In general, the required performance criteria and product uniformity parameters stipulated in shotcrete specifications are as follows: *(a)* type and composition, *(b)* percentage active ingredient concentration, *(c)* chloride content, *(d)* maximum percentage of accelerator to be used, *(e)* compatibility with the cement to be used as defined by the requirements of initial and final set times, early and ultimate strengths, and *(f)* variation of dosage according to location, type of structure, or strength requirement.

Standard test for cement/admixture compatibility used in quality control of the product consists of the following methods.

Set Time. The method used is a modification of ASTM-C-266 test for "Time of Setting Hydraulic Cement by Gillmore Needles." The main modification is in the use of a special standard cup designed specifically for testing fast setting mixes. All the ingredients are mixed in the cup and the Needle test is also carried out in the same container. The method eliminates the need to transfer the paste, and disturbance of the mix is minimized. Careful control of ambient mix temperature and relative humidity is required. When powdered admixtures are used for both dry and wet processes, the consistency used is the same as that used for spraying a mix with no admixture, usually at a W/C ratio of 0.43. The W/C ratio of the wet mix is generally 20% higher. When liquid accelerators are used, however, there can be no standard W/C ratio as specified for the dry powder because of the variation in active ingredients concentration in proprietary materials. The amount of liquid admixture and water required to produce the proper consistency is determined by trial and error.

Compressive Strength. Strength values are usually determined in accordance with ASTM-C-109, except that the W/C ratio in the mortar is fixed at 0.40. In order to accomplish the molding of specimens before initial setting of the mortar takes place, the interval of time stated in ASTM-C-109 is not adhered to.

Rebound. The standard test for rebound consists of spraying the material on to a test board up to the required thickness. Material lost by rebound is collected on a plastic sheet at the bottom of the test panel. At the end of the test, the weights of the test board and rebound material are weighed. Average rebound is calculated as follows:

$$\text{Average rebound} = \frac{W}{W_r + W_w}$$

where: W_r = weight of material on plastic sheet

W_w = weight of material on the test board

Uniformity of the product in the field is monitored by two methods: *(a)* testing the physical and chemical characteristics with the purchase specification, and *(b)* by inspecting, sampling, and testing. Sampling of the placed concrete is generally done by coring from completed work at locations specified by the engineer or inspector.

9.0 ANTIWASHOUT ADMIXTURES

9.1 Background

Antiwashout admixtures (AWA's) are cohesion inducing materials that render concrete cohesive enough to allow limited exposure to the water with little loss of cement. The use of such admixtures allows placement of concrete under water without the use of conventional tremies.

9.2 Chemical Composition

The active ingredient in most AWA's is a water soluble cellulose ether or water soluble acrylic-type polymer. Auxiliary agents are often used to reduce the amount of polymer used in the concrete for cost reduction purposes. This agent reportedly reacts with the polymer in the AWA to increase the apparent molecular weight of the polymer, thereby improving its cohesion-inducing properties. Table 8 shows the results obtained from a study of concrete mixes containing the auxiliary agent glutaraldehyde combined with a polyacrylamide AWA. It can be seen that the auxiliary agent increases resistance to cement washout (as measured by transmittance), permitting a reduction of the polymer by 0.8% by weight without any adverse effect on strength.

9.3 Mode of Action

The action of admixtures is to increase the viscosity of water in the mix. This results in an increased thixotropy of the concrete and an improved resistance to segregation. When the concrete is allowed to free-fall through water, there is hardly any segregation. The magnitude of the effect produced is dependent on the admixture dosage and the molecular weight of the main component. It is frequently used in combination with a superplasticizer.[88]

Table 8. Results of Concrete Containing Polymer and Glutaraldehyde Auxiliary Agent

Amount of Polymer (% by wt., based on the cement content)	Amount of Glutaraldehyde (% by wt., based on the polymer content)	Transmittance	Slump (mm)	28 Day Strength(MPa) by Standard Specimen
0.6	-	92	130	34.5
	0.5	95	125	34.8
	1.0	97	125	35.0
0.8	-	95	180	33.5
	0.5	98	170	34.0
	1.0	100	160	34.2
1.5	-	99	225	33.2
	0.2	100	220	33.8
2.0	-	100	220	32.0
	0.1	100	215	32.5
3.0	-	100	145	29.0
	0.1	100	140	29.2

9.4 Dosage, Addition Procedure and Mix Design

Dosage of the admixture ranges from 1–1.5% by weight of the water in the mix. It is usually discharged into the mixer at the same time as the other materials. Minimum w/c ratios range from 0.36–0.40. Cement and fine aggregate contents are usually higher than corresponding mixes placed on land. Silica fume may be used in conjunction with a superplasticizer or conventional water reducers to reduce segregation. Often, it is difficult to adjust the mixture proportions to achieve desired design parameters for all properties of concrete. Consequently, the properties of colloidal underwater concrete are controlled by the addition of three chemical admixtures. The key to a non-dispersible concrete with self leveling characteristics is the successful optimization of the AWA with the superplasticizer used to increase the slump.

Studies on the effect of various combinations of water reducers and superplasticizers—conventional lignosulfonate and hydroxy carboxylic acid water reducers, and naphthalene formaldehyde sulfonate (NFS) and melamine formaldehyde sulfonate (MFS)—show that the best results are obtained with lignosulfonates and MFS. The NFS superplasticizers produced erratic results in flowability and cohesion.[89]-[91] The Tatterstal two point workability test and wash out test were used to evaluate the mix characteristics.

9.5 Effects on the Plastic and Hardened Properties of Concrete

The following effects are produced when the admixture is used in concrete: Cohesiveness, mobility and self-leveling characteristics are increased and the resistance to segregation is improved. These properties directly affect the steel reinforcement/concrete bond. The pH value and turbidity of the water is decreased with increased dosage. Turbidity and pH indicate the seepage of the hydrating cement in the area of concrete placement. Concretes containing cellulose ether-type AWA will have an extended set time. Those containing acrylic-type do not extend the set time except when combined with superplasticizers. Because of the high water retentivity these admixtures induce in concrete, there is hardly any bleeding. The ratio of compressive strength of specimens in water to the strength of specimens in air at 28 days increases with dosage. Strengths of cores show AWA concrete to be suitable material for in-situ structural concrete construction at considerable water depths.[92]

9.6 Applications

Typical application is in the production of cohesive underwater concrete to obtain dense structural repairs. Particular advantages over conventional concrete are realized both in terms of the quality of the repair produced and the reduction in placement cost associated with plant and diver manpower requirements.

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Batching and Dispensing of Admixtures

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1.0 INTRODUCTION

Most of the currently marketed admixtures are liquids added with the gauging water after the ingredients have been mixed together. Superplasticizers or high range water reducers which are added just prior to discharging of the mix containing the full volume of water, are exceptions to this general rule. Powdered admixtures are usually spread on the dry batch immediately prior to mixing. Calcium chloride, however, must be dissolved in water before addition to the mix. In North America and certain Scandinavian countries the severe winter conditions require the use of both water reducing and air-entraining admixtures in the same concrete mix. However, not all admixtures are compatible and the manufacturer's advice should be sought before two or more admixtures are used together. It is prudent to carry out mix trials with the actual materials that will be used on the job. For such trials, dosages up to three times normal should be included so that the potential problems resulting from overdosage can be appreciated.

This chapter presents information on the operational aspects pertaining to the use of admixtures in the field. It also offers guidance in the selection, use and control of uniformity of the product. Most of the issues discussed here apply equally to the three major fields of concrete construction, namely, site batched and placed concrete, ready-mixed concrete, and precast concrete.

2.0 MANUFACTURE

The quantity of an admixture used is small relative to other constituents of the mix but its effect, depending on the amount used, may be quite potent. Therefore, the method used to prepare the admixture is important. Most proprietary admixtures are ready to use liquids which require no further preparation at the location of use. Indeed, site preparation with these products is strongly discouraged by the manufacturer. Certain admixtures, however, are exceptions to this rule, and are described below:

- Admixtures supplied in concentrated form to minimize high freight costs that would otherwise be incurred in the transport of significant amounts of water.
- Flake calcium chloride that is dissolved in water at the plant by some concrete producers. Water soluble solids admixtures which require mixing at the job site or point of use.

Manufacture may involve making standard solutions (as in the case of calcium chloride and powder admixtures) or dilution to provide the manufacturer's recommended dosage to facilitate accurate dispersion.[1][2] Problems such as difficulty in mixing and sedimentation of insoluble or active ingredients may arise in the large scale manufacture of admixtures due to incorrect charging of the ingredients or a mismatch of mixer type with the viscosity of the product. All mixing of powdered admixture must be done in a mixing tank which is separate from the admixture storage tank from which the admixture is fed into the dispenser. The density of the admixture mixed in this manner should be checked daily or when new material is mixed, using hydrometers. The storage tanks should be equipped with agitators to keep the admixtures in suspension.[1]-[3]

3.0 PACKAGING AND DELIVERY

Admixtures are supplied in various forms of packaging depending on the amount contained and the ease of use required (Fig. 1).

Most proprietary admixtures are neutral or slightly alkaline solutions that are supplied in different containers according to the volume of concrete intended to be mixed. These are as follows:[2]

Figure 1. Different types of packages used in the delivery of admixtures. *(Courtesy K. Rear, W. R. Grace, USA)*

(a) Plastic containers made from low or high density polyethylene or polypropylene in five or twenty five liter capacity for small jobs.

(b) Two hundred and ten liter capacity lacquer-lined mild steel drums. Such drums should have a small opening available for fitting a tap, in addition to the normal filling bung. It is useful to have these drums in a cradle so that handling is made easy. Secondhand relined drums are quite commonly used for this purpose.

(c) One thousand liter portable tanks, made of mild or heavy duty polypropylene with a steel frame. The tanks can be delivered filled in a flat bed truck and are useful for medium sized precast and cast on site projects. A crane or a fork lift truck is usually used to handle these tanks on site.

(d). Cylindrical or rectangular shaped bulk storage tanks ranging in capacity from 2500–15000 liters, fitted with delivery and ventilation pipes, and an outlet pipe complete with a tap a few inches from the bottom, are commonly used. Although plastic tanks are sometimes used, utilization of those made with mild steel is more widespread. Clear marking of the tank is essential, and this is usually done with a label that cannot be altered which is placed in a conspicuous area such as near the access opening. Safety and handling aspects in a printed form should always be readily available, preferably in a plastic holder secured to the tank.

Delivery to fixed tanks are made from road tankers or occasionally 20-ton rail tankers. More commonly, admixtures are delivered by specialized vehicles containing several compartments with individually calibrated meters with printout facilities (Fig. 2). This method of delivery removes the necessity for inaccurate tank dipping or vehicle weighing before and after deliveries. It is required by law that such tankers should carry advice on hazards presented by accidental spillage of the materials being carried.

Typical powdered materials are waterproofing admixtures based on stearates or stearic acid, accelerators like calcium formate, some air entraining agents, latex materials, the spray dried solid forms of superplasticizer, corrosion inhibitors like sodium nitrite, water retaining flocculating agents, expansion producing admixtures, and some caustic materials used as shotcrete admixtures. Most of these materials are often deliquescent or hygroscopic and require storage conditions which exclude moisture and carbon dioxide. They are, therefore, usually packed in either multi-ply paper sacks or small fibrite kegs.

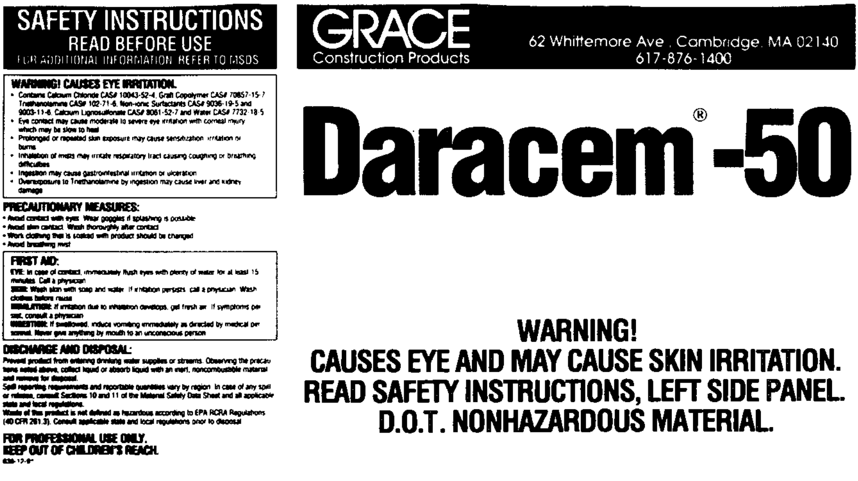
Figure 2. Specialized admixture delivery vehicle. *(Courtesy K. Rear, W. R. Grace, USA)*

3.1 Labels

Since admixtures are potent modifiers of the concrete's characteristics, it is imperative to minimize potential mistakes. Thus, it is important that all containers in which admixtures are delivered or stored should be clearly labeled and marked in such a way that the information cannot be altered. The label should contain the standard information given below:[2][3]

- Manufacturer's and distributors name, address and telephone number.
- The relevant standards (ASTM, BS, CSA) number.
- Brand name of the product, reference number and/or letter.
- Designated type as given by the relevant standards or principal and secondary functions, e.g., accelerating, water reducing or water reducing/air entraining admixture.

- Basic information for use, and precautions regarding the handling of the admixture.
- The chloride content of the admixture. This should be expressed as a percentage (of anhydrous chloride ion) of cement at the recommended dosage.
- Data relating to shelf life or special storage requirements.
- Manufacturer's recommended dosage or dosages and the maximum amount not to be exceeded.
- An example of a typical label is shown in Fig. 3.



SAFETY INSTRUCTIONS
READ BEFORE USE
FOR ADDITIONAL INFORMATION REFER TO MSDS

WARNING! CAUSES EYE IRRITATION.

- Contains Calcium Chloride CAS# 10043-52-4, Graft Copolymer CAS# 70857-15-7 Triethanolamine CAS# 102-71-6, Non-ionic Surfactants CAS# 9036-19-5 and 9003-11-6, Calcium Lignosulfonate CAS# 8061-52-7 and Water CAS# 7732-18-5
- Eye contact may cause moderate to severe eye irritation with corneal injury which may be slow to heal
- Prolonged or repeated skin exposure may cause sensitization, irritation or burns
- Inhalation of mists may irritate respiratory tract causing coughing or breathing difficulties
- Ingestion may cause gastrointestinal irritation or ulceration
- Overexposure to Triethanolamine by ingestion may cause liver and kidney damage

PRECAUTIONARY MEASURES:

- Avoid contact with eyes. Wear goggles if splashing is possible
- Avoid skin contact. Wash thoroughly after contact
- Work clothing that is soaked with product should be changed
- Avoid breathing mist

FIRST AID:

EYE: In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Call a physician

SKIN: Wash skin with soap and water. If irritation persists, call a physician. Wash clothes before reuse

INHALATION: If irritation due to inhalation develops, get fresh air. If symptoms persist, consult a physician

INGESTION: If swallowed, induce vomiting immediately as directed by medical personnel. Never give anything by mouth to an unconscious person

DISCHARGE AND DISPOSAL:

Prevent product from entering drinking water supplies or streams. Observing the precautions noted above, collect liquid or absorb liquid with an inert, noncombustible material and remove for disposal.

Spill reporting requirements and reportable quantities vary by region. In case of any spill or release, consult Sections 10 and 11 of the Material Safety Data Sheet and all applicable state and local regulations.

Waste of this product is not defined as hazardous according to EPA RCRA Regulations (40 CFR 261.3). Consult applicable state and local regulations prior to disposal

FOR PROFESSIONAL USE ONLY.
KEEP OUT OF CHILDREN'S REACH.

[illegible]

GRACE
Construction Products

62 Whittemore Ave., Cambridge, MA 02140
617-876-1400

Daracem®-50

WARNING!
CAUSES EYE AND MAY CAUSE SKIN IRRITATION.
READ SAFETY INSTRUCTIONS, LEFT SIDE PANEL.
D.O.T. NONHAZARDOUS MATERIAL.

Figure 3. A typical label for admixtures. *(Courtesy K.Rear, W.R. Grace, USA)*

3.2 Storage

Three items are important in the storage of admixtures namely, the ease of identification, humidity and temperature at which they are stored. To avoid confusion between different admixtures, drums should be delivered clearly labeled as to the contents; identification can be made easier by a colorant which has no influence on the concrete. Powdered admixtures are more sensitive to moisture and carbon dioxide than are portland cements. The materials should, therefore, be packed in waterproofed bags and always stored in areas free of high relative humidity and temperature extremes to avoid condensation.

Most of the liquid admixtures are aqueous solutions which freeze at -3°C. They, therefore, require protection against freezing. Some, like emulsions, require greater care in storage to prevent freezing and the manufacturer's instructions should be carefully followed. Typical data for minimum storage temperatures for the various types of admixtures currently marketed are presented in Table 1. In the UK, winter conditions are mild and the majority of the materials can be stored in drums in unheated enclosed buildings without freezing. North American winters, however, are much more severe, and proper provision should be made to prevent freezing of liquid admixtures. Although bulk storage outdoors in lagged steel or plastic tanks have been found satisfactory in the milder climate of the UK and some coastal and southern parts of North America, in Canada and the Northern States they should be inside an enclosed, heated building. Protection must be afforded to the whole system, including storage areas, lines to the dispenser and lines to the mixer.[2]

Table 1. Minimum Storage Temperatures for Admixtures

Category	Type	Approximate minimum storage temperature (°C)
Water-reducing	Lignosulfonates	-3 to 0
Hydroxycarboxylic acid		-5 to 0
Hydroxylated polymer		-5 to 0
Superplasticizers		-3 to 0
Air-entraining	Neutralized wood resins	-3 to 0
Fatty acid soaps		
Alkyl-aryl sulfonates		
Waterproofers	Fatty acid emulsions	1
Wax emulsions		
Accelerators	Calcium chloride solution	-10 to -5

Courtesy, Chemical Admixtures for Concrete, M.R Rixom and N.P.Mailvaganam with permission

Although most of the frozen admixtures mentioned in Table 1 may be used in concrete after thawing and thorough mixing, some emulsions cannot be reconstituted on thawing.[3] Thawing of frozen admixtures is usually done by gradually raising the material's temperature to at least 10°C above their freezing temperature and maintaining this temperature for a period of time. The contents of the drum or tank should be agitated, either manually or using a low pressure air flow, to produce a homogeneous solution or emulsion. It should be emphasized that frozen admixtures require both thawing and remixing prior to use. The use of admixtures which have been thawed with no remixing may result in a number of problems including severe retardation of concrete, bleeding and segregation, and heavy air entrainment. Dispenser lines may also be clogged because of the separation of the admixture into a supernatant water layer and thick lower liquid that occurs on thawing.

Solid admixtures are not normally affected by winter conditions, but should be stored in areas free from dampness, condensation or rain, preferably in an elevated location. Materials in ripped bags should be used as soon as possible after the bags are damaged or should be discarded.

Although elevated temperatures, even those prevailing in hot weather countries, do not markedly change the shelf life or effectiveness of the majority of the admixtures, some, because of their chemical make up are more prone to bacterial and fungal attack than others. The following basic admixture raw materials which can support fungal and bacterial growth are vulnerable to such attack; impure lignosulfonates, hydroxycarboxylic acids, hydroxylated polymers and fatty acid based materials. Since bacterial and fungal activity is usually accelerated at elevated temperatures, the use of bactericidal and fungicidal agents is important to prevent deterioration of admixtures under hot weather conditions. Materials such as formaldehyde or sodium -*o*- phenyl phenol tetrahydrate are normally added to prevent this form of attack.

Other admixtures prone to damage by the high temperatures that prevail in hot weather countries include emulsified products, such as waxes, fatty acids and waterproofers. The emulsion breaks down at elevated temperatures due to coagulation of the suspended particles and most often it is difficult to reconstitute the material on lowering the temperature and remixing. The use of such materials is generally discouraged in hot climates. However, when their use is necessary, proper care should be exercised in the storage and use of the products and advice should be sought from individual manufacturers.[2]

4.0 DISPENSING OF ADMIXTURES

4.1 Time and Sequence of Addition

The incorporation of admixtures into a concrete batch involves control of the rate of discharge, timing in the batching sequence and the amount of material used. In North America and other cold weather countries, where the use of two admixtures is the norm, this is important because of the dire consequences that can result from an incorrect addition sequence, e.g., the difference between adding the material in the initial gauging water and adding it after a premixing period can be two or three times the normal retardation time. When two or more admixtures are to be used in the mix, they should be incorporated in the mix, at different times during the mixing.

The compatibility of the admixtures intended to be used in the same concrete batch, when discharged in the same water phase, should be determined and a procedure for controlling the time and rate of addition to the concrete batch should be established and closely followed. It should be emphasized that the mixing of admixtures prior to introduction into the mix is strongly discouraged because of the possible reaction between the mixed admixtures, which very often results in nullifying of the desired effects these admixtures were expected to produce individually. This applies particularly in situations where rapid repetitive mixing occurs and it is often not possible to adhere closely to these recommendations. Table 2 summarizes the preferred points of admixture addition in the mixing cycle to obtain the best results.[2]

4.2 Dispensing Equipment

In view of the small amount involved, accurate and reliable dispensing is essential for the proper use of chemical admixtures in concrete mixes. A means must be provided for reliable and accurate batching of the admixtures into the concrete batch. Uniform dispersion of the admixture is essential and dosage should be reproducible so that the quantities are controlled with very little variation. The type of dispenser must be relevant to size of the project and determined by the volume of concrete, batch size and type of admixture itself. The greatest demand is for the medium dosage range water reducers, but the use of low dosage products such as air entraining agents will require equipment that is suited for measuring and controlling small dosages. Small amounts should be diluted at the point of use. Suitable admixture batching systems are usually supplied by the admixture manufacturer and are generally of two types:

- Liquid batching systems for materials introduced in the liquid form.
- Dry batching systems for materials which are powders.

Table 2. Time and Sequence of Addition in the Mixing Cycle for Different Admixture Types

Admixture Type	Point of addition	Notes
(a) All water-reducing admixtures (except superplasticizers used for flowing concrete production) particularly when a retarding effect is required.	After initial mixing period of up to 30 s of aggregates, cement and part of the gauging water. Should be dissolved in a proportion of the remainder of the gauging water.	Pre-mixing with moist aggregate is often sufficient to partially hydrate the cement.
(b) Air-entraining agents	Dissolved in gauging water which can be added directly.	These materials are not particularly sensitive to the point of addition
(c) Accelerators (except powders) and		
(d) Emulsified water-proofers		the main purpose is to obtain the maximum dispersion through the mix
(e) Powdered waterproofers	Pre-mixed with dry mix ingredients before addition	In order to aid the dispersion of this type
(f) Powdered accelerators	of mix it is advisable to of the gauging water.	sprinkle the admixture over the mix during
the		dry cycle.
(g) Superplasticizer for flowing concrete	After the mixing cycle just prior to placing.	-------

Courtesy Chemical Admixtures for Concrete M.R Rixom and N.P.Mailvaganam with permission

Liquid Dispensing Systems. Currently used dispensing systems include simple pumps, timers, visual volumetric displacement systems and weight batching. Essentially a liquid dispensing system consists of equipment for moving the liquid from the feed tank to volumetric containers (usually by pneumatic or electric pumps) a batching or dispensing device, controls and appropriate interlocking devices. A secondary circuit is usually provided to come into play in the event of a failure of the primary control. Visual volumetric containers in the form of a calibrated cylindrical sight-glass for visual checking of the required quantity should also be provided for all liquid systems. With certain water reducing and air entraining admixtures, it may be necessary to incorporate an antifoaming device to ensure accuracy.

Measuring devices are either positive displacement devices or timer controlled systems. The former includes flowmeters and measuring containers equipped with floats or probes. Flowmeters may be equipped with pulse emitting equipment which operate at a preset electrical counter on the control unit located near the batching console. Such meters are usually geared in a manner which facilitates variable admixture dosage. Figure 4 shows a typical displacement flowmeter operated by pneumatic power, while Fig. 5 shows a control unit on which the required dosage can be preset.

A measuring container operates on the principle whereby the linear movement of a float in a container of given cross section meters out a volume of solution required for the batch. Usually the floats are connected to a potentiometer or pulsating switches which operate electrical preset counters.[2] A typical unit is shown in Fig. 6 where it can be seen that the measuring device consists of a graduated steel bottle containing a movable electrode, which in this case is connected to a dial calibrated in terms of cement content. The admixture is pumped into the graduated bottle until it touches the upper electrode when the pump is automatically switched off and the material is allowed to discharge into the water pipe.

Timer controlled systems are simple, low cost systems which involve timing of flow through an orifice. Most include a sight glass or other means of checking the amount batched. Figures 7 shows a timer controlled unit installed in a readymix concrete plant. They have been successfully used with high volume dilution admixtures.[1][4]-[7] However, due to a number of variables that can introduce error into the measurement, such as changes in viscosity of the admixture or in the power supply, their use is generally discouraged.[8] The systems are permitted only for calcium chloride in the NRMCA Check List.

Most dispensing systems are custom-made to meet the method of control or degree of automation required for the particular operation. Commonly available dispensing systems and controls can, therefore, be discussed under three main groups: fully automated, semi-automated, or manual systems.

Figure 4. Typical positive displacement flowmeter used for variable admixture dosage. *(Courtesy M. A. Drolet, Euclid, Canada.)*

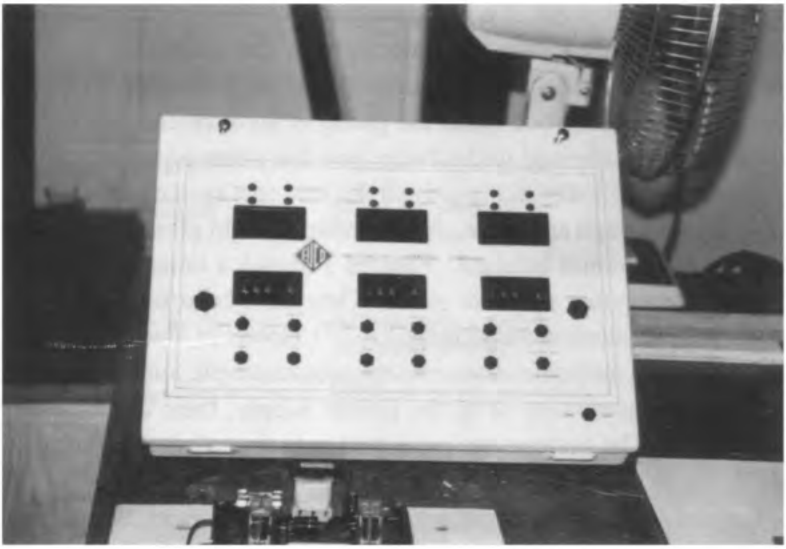


Figure 5. Unit used for the control of liquid admixture dosage in dispensing system. *(Courtesy M. A. Drolet , Euclid, Canada.)*

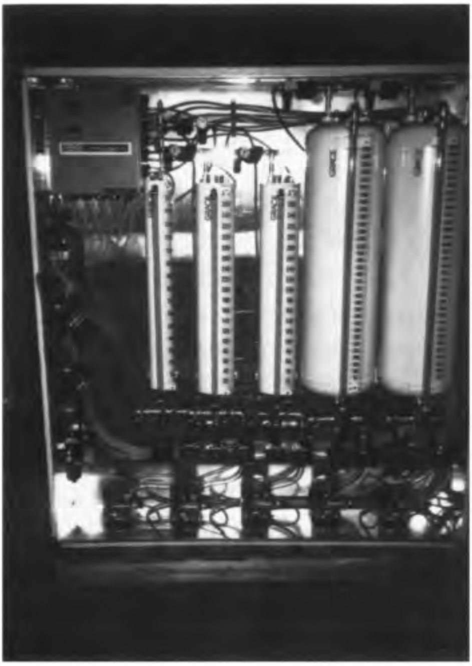


Figure 6. Electrically operated dispensing equipment. *(Courtesy K. Rear, W. R. Grace, USA.)*

Figure 7. Controlled unit installed in ready-mix concrete plant. *(Courtesy L. Ramo, Stoneway Concrete, Seattle, WA.)*

Automated Dispensers. A fully automatic or pneumatic dispenser based on either electric or pneumatic systems has good accuracy and can cope with more than one type of admixture with facilities for flushing. It is, therefore, the ideal method of adding liquid admixtures to a concrete. One form of dispenser feeds the admixture by an electronically driven pump controlled by a timing device, and can be fitted with a sensing unit for automatic cutoff. This type of dispenser is shown installed in a ready-mixed concrete plant in Fig. 8. The control release can be operated automatically so that when the batching console is used in the normal way, a signal is picked up by the dispenser relay and the material is automatically fed into the mix. Precasting operations usually employ an electrical dispenser while ready-mixed batching plants, where a high rate of production and fast accurate measurement is essential, may use the pneumatic type. These systems include the required combination of automated individual volumetric devices, but they should also have the following features :[9][10]

(i) A single starting mechanism or separate starting mechanisms for admixtures not batched at the same time as other ingredients.

(ii) A mechanism for signaling empty and resetting to start by volumetric devices.

(iii) A device that prevents the discharge of any ingredient until all individual batches have been cleared of the previous batch and returned to zero within tolerance.

Semi-Automated Dispensers. These systems can operate either electrically or pneumatically and they contain the necessary volumetric devices, the controls of which are either semiautomatic, interlocked, or automatic or a combination of these (Fig. 9). With this type of equipment the level of admixture is allowed to rise in the sight glass by the operation of a switch or valves until a correct level is reached. The valve is then opened to allow dispensing of the admixture into the water pipe or mixer. Although this type of dispenser is widely used, some precautionary action is required in the installation and operation of the system:

- the arrangement of the piping system in the dispensing equipment requires careful attention to ensure that variable amounts of material are not trapped in the lines;
- that the valves will not leak and the amount of material measured is actually discharged into each batch.[4][10]

Figure 8. Electrically operated fully automatic dispensers. *(Courtesy M. A. Drolet, Euclid, Canada.)*

Figure 9. A pneumatically operated portable semi-automatic dispenser. *(Courtesy M. A. Drolet, Euclid, Canada.)*

Manual. These types of dispensing equipment are used in small scale operations where admixtures are only occasionally used. Reliability of the system is dependent on the accuracy exercised by the operator who is responsible for visual assessment of the correct level of dosage. For small and occasional additions, hand-dispensing equipment may be used to measure reasonably accurate quantities. A hand-operated plunger can be used to dispense water reducers and air entraining agents for normal work but for intermittent use, a mechanical dispenser is the best.

- *Hand pump.* It is normally constructed to fit a 210 liter drum bung hole. Two types are available: one is simple which will require hand dispensers of the types described below to measure the actual quantity; the other is a type in which one stroke of the pump delivers a set volume. It can be used for adding the admixture directly to the concrete mix.[2]
- *Hand dispensers.* Containers of standard and correct volume may be used in small applications or special mixes. It is important that a dispenser of the correct size for one mix be used rather than a measuring cylinder or other partly filled vessel.

Weight batching of admixtures using beam and dial scales, with an indicator in the batching system to register the discharge of the material, is occasionally used to measure the addition of admixtures. The disadvantages of the system include the necessity for conversion of the admixture dosage from volume to weight, and the necessity to dilute admixture solutions to obtain a sufficient quantity for accurate batching. The method has been found suitable for air-entraining admixtures.

The complexity and cost of the dispenser system used is largely dictated by the size of the operation. The basic requirements of all methods, however, are that they function at the temperature ranges at which normal concreting is permitted, have an insensitivity to changes in viscosity for the admixture, and an accuracy of ± 3%.[4]-[10] All components should be constructed with materials which will not be corroded by the admixture being used and of proven low failure rate to ensure reliability in the long term. A clear indication should be given on the dispenser as to the range throughout which it will effectively operate within the specified limits. The equipment should also comply with Plant Manufacturer's Bureau (CPMB) standards and provide a device for routine diversion of a measured dosage into a small container for verification of the batch quantity.

To facilitate maintenance of the equipment and prevent the liquid admixture thickening within the dispensing system when the batch plant is not in operation, means should be afforded for washing out the complete system. All measuring devices must be kept in serviceable condition, zeroed daily, and calibrated monthly. It is desirable that the supplier of the dispenser make available detailed advice on regular maintenance. Specific requirements pertaining to dispensing systems are detailed in BS 5328, ASTM Publication C-94, NRMCA Check List, CPMB Standards and the National Bureau of Standards (NBS) Handbook.

Dispensing Systems for Solid Admixtures. Solid admixtures such as calcium formate or some waterproofers are measured by weight. Since relatively small quantities of such admixtures are used, a greater degree of measurement control is required. Therefore, it is wise to blend them with finely divided inert or pozzolanic material such as fine sand, pulverized fly ash or ground blast furnace slag. This not only facilitates more accurate weighing but also prevents flotation of the powder on the mix water, thus ensuring better dispersion in the mix. In the use of powdered admixtures, care must be taken to prevent the adherence of the powder to the sides of the mixer or the formation of clumps. These problems can be avoided if the powder admixture is not dispensed with the mixing water but, is added after the fine aggregate in the mixing sequence.[2]

A suitable measuring device for powders is the automatic pigment scale. Most of the units commercially available consist of a part that operates volumetrically (e.g., screw, shaking gutter) and a suitable metering scale. Space is essential in positioning the metering unit and powder admixture containers as closely as possible to the mixer or raw material supply lines. Care must be taken to ensure that the powder that enters the concrete mixer is free flowing.[11] These automatic scales are quite expensive.

5.0 CRITERIA FOR SELECTION

The purchase of admixtures is based on specifications that stipulate the required properties, permit evaluation of the uniformity of the admixture from batch to batch, and exclude adverse effects. The following information should be provided by the admixture manufacturer or supplier; composition of the admixture in terms of the generic type of its main constituents, incompatibility with other admixtures or special cements, typical dosage, detrimental effects of overdosage or underdosage, chloride content, and whether air is entrained at the recommended dosage.

Requirements for admixtures should be based on performance tests detailed in the relevant standard specifications. Data should be provided by the admixture supplier on the results of laboratory acceptance tests, including mix proportions of the concrete materials, dosage of the admixture, slump or compacting factor value obtained, set times, air content and compressive strength. In addition, the effects of admixtures on other concrete properties should also be supplied by the admixture supplier.

Specifications, however, deal primarily with the influence of admixtures on standard properties of fresh and hardened concrete such as set time extension and compressive strength, respectively. Potential users may be interested in other properties of the concrete, particularly flowability, placing and finishing qualities, and early strength development. Such secondary modifications may, in some instances, be of greater importance in selection of the admixture and dosage needed for the particular application. Testing for compliance to national standard specifications is, therefore, essentially a screening procedure in the selection process. Suitable admixtures should then be tested in concrete mixtures made with job site materials under actual operating conditions, so that a proper measurement of the desired engineering properties is obtained. The dosage that may be necessary to enhance a particular secondary effect, as well as the cost of the concrete containing the admixture, can be established from the results of these concrete mix trials.

6.0 QUALITY CONTROL

Admixture uniformity plays a pivotal role in minimizing the variation of the concrete produced. The degree of control of the uniformity of the concrete will depend on the criticality of the structure being built, but any substantial use of admixtures in operations which produce concrete continuously should be accompanied by routine sampling and testing of the admixture to determine within-lot variation of the product, and also to provide data showing that lot is the same as that previously supplied. Such routine control of uniformity will be based on physical and chemical index tests, e.g., solids and ash content, specific gravity of the solutions at 20°C and infrared spectroscopy of active constituents. The trace obtained from infrared spectroscopy is particularly useful in this regard since it serves as a finger print of the material. Uniformity of the admixture batches supplied during construction can be readily determined by matching the trace of the sample supplied during purchasing negotiations to those obtained from the job site. Although such tests are not definitive of the quality of the product, they are done mainly to assure uniformity of the product being supplied.

7.0 PRECAUTIONS

Specific effects produced in concrete by admixtures are dependent on a number of factors such as cement composition, aggregate characteristics, the presence of other admixtures and ambient conditions. Therefore, manufacturer's instructions should be carefully followed in the storage and use of admixtures. All liquids, particularly emulsion types, should be protected from exposure to drastic temperatures. Care should be exercised to ensure that the admixture is properly and uniformly dispensed and that the functioning of dispensing equipment is thorough and consistent. Since the effects produced may vary with the point of addition in the mixing cycle, a standard mixing sequence should be established and admixtures must not be added during transportation, placing or compaction.

The full potential of admixtures in both economy and desired engineering objectives is often realized only by changes in the proportioning of the concrete mix otherwise employed. Therefore, it is important that laboratory and field trials be carried out to select the appropriate admixture type and dosage to be used. The effects obtained with the admixture using job materials under job site conditions should be determined. This is particularly important when special types of cement are specified, when more than one admixture is to be used, or when the mixing and placing is carried out at ambient temperature conditions well above or below generally recommended concreting temperatures.[1]

8.0 SAFETY AND HYGIENIC ASPECTS IN THE HANDLING OF ADMIXTURES

The national organizations for health and safety of most countries mandate the supply of information necessary to ensure the health and safety of personnel handling admixtures. Such information is usually contained in the hazards data sheet required to accompany shipments of admixtures. The information required includes the following:[2]

- Nature of the hazard, e.g., caustic, inflammable, etc.
- Stipulated protective clothing, e.g., gloves, goggles, boots, etc.
- Toxicity and required first aid in the event of ingestion, prolonged exposure, skin or eye contact.
- Action to be taken in the event of spillage, e.g., type of fire extinguisher if flammable, washing of slippery floors, etc.

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Admixture Formulations

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1.0 INTRODUCTION

There has been continued interest in research and development of admixtures. There is, therefore, a need for information on the advances made in research as well as on the developments in the formulation of novel admixtures. Although several reviews have appeared pertaining to the advances in research on admixtures, there is no publication that has reviewed the advances made in the formulations of admixtures in recent years. The objective of this chapter is to highlight information on the patents related to concrete admixtures derived mainly from the *Chemical Abstracts* published in the years 1985 to 1992.

2.0 PATENT LITERATURE

A survey of the patent literature on admixtures reveals that annually a substantial number of new formulations are reported. In 1976 a book on "Cement and Mortar Additives," containing 220 patents, included a list of novel admixture formulations.[1] Another publication in 1980 covered the formulations for the period 1977–1980, listing 257 patents on cement and mortar additives.[2] Ramachandran, covering the patent literature for the years 1976–81, listed a total of 577 admixture formulations[3] and 488 for the years 1985–1989.[3a]

Continued interest in the development of new formulations is evident from the number of patents taken in the years 1985–1992. Table 1 gives the number of patents taken in each year on different types of admixtures. The year refers to the year in which the patents were abstracted in the *Chemical Abstracts.* It is obvious that under almost every category the largest number of patents appeared in the year 1989. The increase in the patents pertaining to the miscellaneous and polyfunctional admixtures is particularly significant. Renewed interest in the development of superplasticizers can be seen from the number in 1992. It is also clear from the table that not much development has occurred in the formulation of new air-entraining (AE) or retarding agents. The information for the years 1985–88 was derived from *Cements Research Progress,* published annually by the American Ceramic Society. In spite of a large number reported, only a few of the formulations are expected to find large scale practical application. It is, however, instructive to follow the trend in the development of novel admixture formulations, some of which are claimed to be superior to those being used presently. Discussed below are a few selected formulations covering the period 1985–1992. A brief description of the formulations can be found in *Chemical Abstracts (CA).* The Cements Research Progress provides annually a list of patents on admixtures in Ch. 6 entitled "Admixtures."

Table 1. Yearly Statistics on Patented Formulations

Year	Accelerators	Water Reducers	Superplasticizers	Retarders	AE	Polymer Modifiers	Multi-Function Admix
1985	7	15	14	2	1	1	4
1986	4	12	4	-	2	29	13
1987	9	30	7	-	11	27	15
1988	3	22	26	1	11	49	21
1989	37	24	38	8	4	15	116
1990	5	6	9	3	3	5	26
1991	12	5	6	1	-	4	25
1992	22	17	38	5	-	4	63

It is difficult to select patents on admixtures from the chemical abstracts titles because many patents do not indicate in their titles that the use of admixtures is essential for the successful application of the claim. If the selection is based only on titles then the number of admixtures will be lower, as evident from the statistics for the years 1990 and 1991. Hence, although the numbers in the table may not be accurate, the table gives important information on the formulation of various types of admixtures.

Classification of patented admixtures into various categories is not always easy. In some instances one material may belong to more than one category. Diversified claims and lack of detailed information may result in some sort of compromise in categorization. The admixtures have been divided for convenience into seven categories as follows.

1. Accelerators
2. Water Reducers
3. Superplasticizers
4. Retarders
5. Air Entraining Agents
6. Polymer-Modified Systems
7. Multifunctional Admixtures

3.0 ACCELERATORS

The formulations on *Accelerators* include synthetic compounds as well as those derived from wastes and by-products. The formulation may be a single substance or a combination of compounds. Many types of organic and inorganic compounds have been proposed that either contain chloride or are chloride-free.

Many types of accelerating admixtures have been proposed for accelerating setting and hardening of concrete. A synergistic effect occurs with a mixture of triethanolamine and calcium formate.[4] Other formulations include a mixture of thiocyanates, thiosulfates, nitrates and water soluble alkanolamines.[5][6] In some other formulations a mixture of metal aluminates, hydroxides and carbonates and ethanolamine, aluminates and alkali metal aluminates or metal tetraborates are proposed.[7]-[9] Significant strength benefits result from the use of a potassium-based salt containing potassium pyrophosphate, aluminate and carbonate.[10] An accelerating agent imparting high workability comprises a high molecular weight polymer or copolymer with groups such as vinyl acetate, acrylic acid, alkyl acrylate or styrene.[11]

There is continued interest to develop a formulation that accelerates the hardening of concrete and also retards or inhibits corrosion of steel. The formulations include a mixture of calcium chloride, sodium nitrite, gypsum and calcium lignosulfonate,[12] a triply bonded diol (e.g., 2 butyne-1, 4-diol),[13] bromide compounds,[14] iron salts as corrosion inhibitors and alkali-aggregate expansion reducers,[15] a complex mixture of Na-silicate, NaOH, $NaNO_3$, $NaNO_2$, Na-lignosulfonate, triethanolamine and Bu_3PO_4,[16] aqueous solutions of monosaccharides with CH_2OH groups and Zn ions[17]-[18] and a mixture of hydroxycarboxylic acid and saccharide with a styrene butadiene copolymer latex as well as a high fatty acid salt (sodium stearate).[19][20]

Using a waste liquor containing rhodonate and thiosulfate from the desulfurization of coal distillation, an accelerator was obtained that increased the one day strength by nearly 300%.[21] An admixture containing a mixture of sodium thiocyanate and sodium sulfate was found to increase the early strength of concrete as efficiently as calcium chloride.[22] An accelerator formulation without toxic effects and that could be used at low temperatures consisted of amidosulfonic acid salt admixed with Ca-thiocyanate and calcium nitrite or slaked lime and triethanolamine.[23][24]

In the years 1990–91, accelerators that were formulated, not only developed higher initial strengths but also provided quick setting, antifreezing and underground applications. They included polycarboxylate polymer,[25] basic magnesium carbonate,[26] metallurgical slag of high fineness + anhydrite,[27][28] a mixture of Ca aluminate, sulfates of Al, Na and or K,[29] alum + lime + alkali metal aluminate + alkali metal carbonate + gypsum,[30] triisopropanolamine,[31] potassium pyrosulfate,[32] isobutylene-maleic anhydride copolymer,[33] calcium sodium aluminate + sodium alkali sulfate,[34] aluminum sulfate + aluminum oxide,[35] Ca haloaluminate + $CaSO_4$ + sulfate of mono or trivalent metals,[36] alkali metal aluminate or carbonate + aluminum sulfate[37] and microcapsulated water absorbing polymers in which setting is controlled by the release of the additive.[38]

Although a number of accelerating admixtures have been formulated, many of them promote high-early strengths but cause low long-term strengths. Some formulations published in 1992 are enumerated below: potassium magnesium silicate or sodium magnesium silicate + calcium sulfate;[39] anhydrite, Na_2CO_3, hydroxyethyl cellulose (plasticizer);[40] slaked lime, a siliceous compound and Na naphthalene sulfonic acid;[41] fluoroaluminate, Na gluconate and sodium carbonate;[42] alkali metal carbonate, organic acid and alkali metal sulfate;[43] calcium fluoroaluminate with inorganic sulfates;[44] polycarboxylate + monomethyl ether + Ca poly-methacrylate + accelerator;[45] acrylate + methacrylate;[46] naphthalene based-superplasticizer + Na_2CO_3;[47] alkali metal carbonate + $2Na_2O\ 5Al_2O_3$ + gypsum;[48] Fe oxide + kasilite + K_2SO_4;[50] calcium sodium aluminate + sodium sulfate + sodium aluminate + alkali carbonate + gypsum;[51] diethylene glycol + Na-thiosulfate;[52] trihydroxy benzoic acid + disodium dihydroxy benzene disulfonate + reactive silica;[53] pre-sintered alunite + calcium aluminate + inorganic sulfate + reactive silica;[54] pentaerythritol + Ca containing organic compound.[55]

4.0 WATER REDUCERS

Water reducers/plasticizers comprise those that reduce water requirements by normal amounts as well as possess normal dispersing and plasticizing abilities. Improvements in many physical properties of concrete and mortar are obtained by using these admixtures. Most water reducers are organic, water soluble compounds. It has been estimated that in about 50% of concrete produced in the USA a water reducer is used.

Lignin-based products continue to receive attention. Examples are: a formulation containing Na and Ca-chromolignosulfonate salts[56] a granular material containing hormite and lignosulfonate,[57] a mixture of Na-lignosulfonate and 1, 3, dimethylol-4, 5-dihydroxyimidazolidone,[58] polymerized lignosulfonate with water soluble peroxide dispersant,[59] lignosulfonate and nonionic surfactant with tallow fatty acid-propylene oxide[60] and desulfurized sodium solution, Ca-lignosulfonate, sodium gluconate and triethanolamine.[61] Lignosulfonic acid graft polymers prepared from lignosulfonic acid or salts with acrylic or vinyl monomers have been found to have dispersing and slump loss reducing properties.[62]

Many formulations based on acrylate and methacrylate polymers may be used for slump retention, improved workability and strength development. Examples are: polymers of alkoxylated monomers and copolymerizable acid functional monomers.[63][64] Some were polymers of maleic acid or anhydride that were copolymerized with a variety of monomers and blended with other materials.[65]-[72] Some maleic acid water reducers contained isobutylene,[72a]-[72c] and styrene copolymers.[73][74]

Copolymers containing ethylene, pentene or isopropene-2 methyl butene-pentene have also been described.[75][76]

Other copolymers have also been synthesized for use as water reducers. They include: acetone-formaldehyde-sodium sulfite,[77] 1:1 1-allyloxy-2, 3 dihydroxy propane-maleic anhydride,[78] copolymer containing 4 - 6 carbon olefin and maleic anhydride[79] and a composition containing saturated beta dicarboxylic acid and C_6 olefin.[80]

Several waste materials are used for developing water reducers. They include: digested product of cellulosics,[81] sulfite-yeast mash based product,[82] wastes from fish oil processing,[83] corn cobs, straw and sunflower heads treated with sulfuric acid and sodium hydroxide,[84] and residues from the manufacture of dibutyl phthalate.[85] A good plasticizer was obtained using the alkaline wastes from caprolactam manufacture, lime and sodium sulfate.[86]

Other novel combinations included magnesium methacrylate, dihydroxyethyl methacrylate, methylene bis-acrylamide, ammonium persulfate and dimethylamino-propionitrile,[87] a mixture containing sulfonated phenol, boric acid, potassium carbonate and ozocerite emulsion,[88] ethylene oxide-ethylene imine propylene oxide copolymer,[89] salts of di and polycarboxylic acids polymerized with various olefins and unsaturated non-cyclic and alicyclic hydrocarbons.[90]-[92]

In the years 1990–91 the water reducers formulated, were claimed not only to disperse the cement particles but some of them also increased the water resistance, fluidity and strength. The formulations included, the compound prepared by hydrolysis of polysaccharide or oxalic acid,[93] dicyclo-pentadiene derived acrylate,[94] acrylic resins,[95] condensation product with Na-carbazol disulfonate + calcium chloride,[96] maleic anhydride(I)-styrene copolymers and alkoxylated alcohols or phenols,[97] water soluble cellulose ether derivative containing hydroxyethyl substituents and 1,3 alkoxy 2-hydroxy propyl groups,[98] styrene-maleic acid copolymer + poly(styrene-sulfonate) or sulfonated polymer mixture,[99] polycarboxylic acid containing 2 - 4 carboxyl groups and polyoxyethylene glycol[100] and non-air entraining type lignosulfonate using membrane of polysulfone or polyolefin.[101]

Several types of water reducers have been reported in 1992 and they are as follows: a product formed by the reaction of lignosulfonate and alkali salt mixtures,[102] a grout containing a mixture of cellulose ether, aluminum and water reducing agent,[103] Na lignosulfonate-based material with monohydric alcohols,[104] mother liquor from pentaerythritol manufacture or a product obtained by treating hydrozylates from wood with NaOH or lime at 40°C,[105] sulfonated polystyrene,[106] water soluble copolymers by hydrolyzing sulfonated styrene-(meth) acrylate ester copolymers,[107] admixture combination prepared from $C_{2\text{-}8}$ olefin-ethylenic unsaturated anhydride copolymers and their salts,[108] sodium formate + low molecular weight di-Me polymethylene glycol ether + Na_2SO_4[109] and salts of polymer containing sulfonic acid and carboxylic acid groups + polyoxyethylene alkyl phenyl ether + defoaming agent.[110]

5.0 SUPERPLASTICIZERS

Superplasticizers, also called *high range water reducers,* are claimed to reduce water requirements by an amount much higher than is possible with normal water reducers and also have very high liquefying or plasticizing action. Many formulations are based on sulfonated melamine or naphthalene formaldehyde. Some formulations contain additional materials. Generally, incorporation of these admixtures promotes strengths, flowability and durability characteristics in concrete.

Continued interest is evident in the development of formulations to improve the slump retention of superplasticized concrete. Examples are naphthalene sulfonic acid-isocyanuric acid condensates,[111] micropellets containing unsaturated dicarboxylic acid anhydride,[112] copolymer of styrene and maleic acid graft polymerized with a conventional lignin or naphthalene formaldehyde condensate,[113] oxidized formaldehyde-methyl naphthalene sulfonic acid/naphthalene sulfonic acid copolymer,[114] copolymer of OH-containing oligo(meth)acrylate monomer,[115] copolymer of ethylene-maleic anhydride and CM cellulose,[116] a mixture of polyvinyl alcohol and ß-sulfonated naphthalene formaldehyde[117] and a copolymer (meth) acrylic acid or its alkali metal or earth salts and hydroxy alkyl esters of ethylenic unsaturated acids.[118] Superplasticizers containing copolymers such as methacrylic acid-polyethylene glycol, Me ether methacrylate copolymer Na salt, ethylene oxide-propylene oxide copolymer stearate, etc.,[119] sulfonated naphthalene formaldehyde containing a water absorbing organic gel,[120] and a copolymer of polystyrene sulfonate with water soluble salt of lower olefin maleic anhydride[121] have also been proposed.

Other formulations were claimed to improve the flowability characteristics of concrete. They included: naphthalene sulfonic acid containing polyoxyethylene type compound,[122] sulfonic acid-naphthalene carboxylic acid copolymer,[123] a superplasticizer containing C_4 - C_6 olefin-ethylenic unsaturated dicarboxylic acid copolymer,[124] novel polymeric backbones such as poly(diethylamino-methyl) methacrylate,[125] sulfonated dicyclopentadienes,[126] sulfonated styrene oligomers,[127] sodium naphthalene formalin condensate containing Na gluconate,[128] copolymer of acrylic acid, methacrylic acid and their alkali or alkaline earth salts and hydroxy $C_{2\text{-}3}$ alkyl acrylate or methacrylate,[129] polystyrene sulfonated salts containing partially alkylated $C_{2\text{-}12}$ alkyl groups,[130] and dispersant polymers with molecular weights 550–300,000 and containing carboxyl, and trialkylammonium groups.[131] Very high slump concrete that does not need vibrating was made with a formulation containing ethyl hydroxy ethyl cellulose, defoamer, a highly condensed triazine compound, and a melamine-based superplasticizer.[132]

Several patents were claimed to impart superior strength and durability to concrete. They included: melamine + naphthalene formaldehyde sulfonates added to alkenyl sulfonates,[133] lignosulfonates in combination with naphthalene sulfonate condensates,[134][135] amino-containing substances of melamine, treated with formaldehyde and sulfite salts,[136][137] sulfonated naphthalene formaldehyde with dioctyl sodium sulfosuccinate,[138] a reaction product of triethylene tetramine with a monoester of maleic acid and maleic anhydride with sodium sulfite,[139] sulfonated copolymers of styrene and alpha methyl styrene and optionally gluconic acid salts,[140] condensate of melamine formaldehyde and alkali metal bisulfite[141] and a highly stable sulfonated melamine formaldehyde condensate prepared by a four-stage process.[142][143]

Some patents referred to materials that are used as dispersants in concrete containing silica fume. They comprised fatty acid + nonionic or anionic surfactant[144] a dispersing agent with EDTA[145] and a dispersant with inert ultrafine particles.[146] A few of the formulations for high-strength concrete included: a mixture of Na lignosulfonate, Na gluconate, beta naphthalene and melamine sulfonic acid salts to produce concrete of strength 152 MPa,[147] and further strength development by utilizing the same admixtures but with added silica dust.[148]

In the years 1990–91 continued interest was shown in the development of formulations to control slump loss. Others increased the fluidity and strength of concrete. Examples are as follows: azo type superplasticizer,[149] indene carboxylic acid copolymer,[150] product from isobutylene-maleic anhydride copolymer and laurylamine,[151] alkali, alkali earth, ammonium or amine salts of HCHO condensation copolymers with

CO_2H^- and OH^- containing aromatic hydrocarbons,[152] copolymer of acrylamide and vinylimidazole or their derivatives,[153] alkoxylated H_2CO^- or epichlorohydrin-cross linked, sulfonated or sulfomethylated lignin,[154] copolymers from $C_{5\text{-}10}$ hydrocarbons and unsaturated carboxylic acids or their anhydrides,[155] α, β unsaturated carboxylic acid and/or its salt, $C_{1\text{-}4}$ alkyl (meth)acrylate and optionally other unsaturated monomers,[156] NH_4, NH_2 or alkali metal salt of copolymer of an indene-based component and unsaturated carboxylic acid anhydride,[157] cross-linked acrylic polymer,[158] sulfonated styrene-maleic acid copolymer, poly(acrylic acid), and olefin-maleic acid copolymer,[159] sugar-free lignosulfonate,[160] copolymer of acrylamide + vinyl imidazole + terpolymer of acrylamide, acryamidomethyl propane sulfonic acid salt and vinlylimidazole,[161] and dienesulfonic acid copolymer with mol wt less than 50,000.[162]

In 1992 several patented formulations referred to the synthesis of superplasticizers. They include: lignosulfonate-based admixture produced by heating lignosulfonate, followed by mixing it with alkaline salts;[162a] alkaline earth NH_4 or organic amine salt condensate of formalin and sulfonated neutral oil from coal tar;[162b] condensation product by reacting $(CH_2)_n\ CR_1R_2SO_2O$ where n = 1–5, $R_1R_2 = H$ or alkyl group with sulfites and aldehydes in the presence of alkali;[162c] copolymers of $CH_2{:}CR_1CONHR_2SO_3$ X or methacrylic acid or its salts;[162d] molasses from cane sugar treated with Ca terpionate and NaOH and HCHO;[162e] condensation product of phenol, phenol sulfonates, aniline, amino-naphthalene, melamine, etc.;[162f] copolymers of N-substituted alpha and beta unsaturated monocarboxylic acids with methacrylic acid or its salt and methyl methacrylate by redox polymerization using peroxysulfate, sulfite, etc.;[162g] addition of C_2H_4-2-ethyl acrylate-vinyl acetate copolymer emulsions to naphthalene sulfonate-based superplasticizer.[162h]

Many patents have been reported in 1992 describing how slump loss can be prevented in superplasticized concrete. Some of them are enumerated below: cross-linked polymers methacrylic acid-diglycidyl phthalate copolymer;[163] Na-lignosulfonate-based plasticizers;[164] methyl methacrylate-Na-2-acrylamide, a methyl propanesulfonate;[165] an aromatic compound having hydrophilic group (OH, carbonyl, amino, or sulfone groups);[166] $C_{10\text{-}16}$ fatty acid alkyl ester sulfonate salts;167] hydroxyethyl cellulose modified with alkaline solutions;[168] sulfonated polystyrene Na salt + 2 acrylamide 2 methyl propane sulfonic acid Na salt-Me methacrylate copolymer;[169] sulfated copolymers of aliphatic dienes and other copoylmerizable monomers;[170] melamine sulfonic acid HCHO condensate

- isobutylene maleic anhydride copolymer Cu complex;[171] indene-coumarone-maleic anhydride copolymer Na salt of naphthalene sulfonic acid HCHO copolymer and Na lignosulfonate;[172] formaldehyde-phenol sulfonate-aniline sulfonate condensate;[173] modified lignosulfonate concentrated by ultrafiltration using a membrane of polysulfone or polyolefin and saponified copolymer of sulfonated styrene-maleic acid naphthalene-based superplasticizer;[174] tannin-grafted with vinyl monomer selected from 2-acrylamide 2-methyl propane-sulfonic acid and acrylamide;[175] and hexaethylene glycol alkyl methylene ether-maleic acid butyl tetra ethylene-tetra propylene glycol monoester.[176]

6.0 RETARDERS

Admixtures which are proposed primarily for retarding of hydration, setting and hardening characteristics of mortar or concrete are treated in this section. Most admixture combinations in this category are based on lignosulfonates, sugars, hydroxycarboxylic acids and their salts and other organic compounds. They are also used in combination with other admixtures such as accelerators, water reducers and superplasticizers.

A patent refers to a retarder containing humic acid and sulfonic acid groups[177] and to another containing amino acids or their alkali metal salts or alkaline earth metal salts that imparted good fluidity and strength characteristics to concrete.[178] Urea has been suggested as a good retarder in another recent patent.[179] Lignosulfonates have a retarding action. In one formulation, an alkalized sulfite liquor was mixed with ethylene oxide-propylene oxide copolymer to extend the setting time of cements by 2½ to 5 hrs.[180] In cementing well applications, Ca lignosulfonate in combination with potassium pentaborate and alkanolamine titanium chelates produced a good retarding action.[181] Extended set retarders are produced by a mixture of phenol carboxylates with an alkali such as NaOH or saccharides. The setting times vary between 2 and 10 days.[182][183]

Other retarders include phenol polymer pretreated with formaldehyde and monomethyl urea,[184] hydroxymated polyacrylamide homopolymer or copolymer (0.01%)[185] and waste syrups from pentaerythritol.[186]

Very few formulations were related to the development of retarders in the years 1990 - 91. Examples are: cryolite + chiolite + MgF_2 + NaF + CaF_2,[187] vinyl acetate + polyoxyethylene-polyoxypropylene block copolymer, hydroxyethyl cellulose + NH_4 salt of polyoxyalkyl sulfate + Na acetate,[188] cellulose + NaOH + Na chloroacetate,[189] and paraffin.[190] In 1992, only five admixture formulations were related to retarding agents. They included a mixture of stearic acid + sucrose + diethylene glycol + cellulose ether,[191] a granular polymer that absorbed water and released slowly,[192] Na salt of gluconic acid + glucose + clay,[193] wet spraying admixture containing organic or inorganic phosphoric acids and their salts[194] and polyhydroxy acids/polycarboxylic acids and hydroxycarboxylic acid-anionic surfactant with hydrolyzable tannins or lactones.[195]

7.0 AIR ENTRAINING AGENTS

Air entraining agents in combination with other compounds provide several beneficial effects to concrete such as high frost resistance. Most air-entraining agents are based on animal or vegetable oils and their fatty acids, natural wood resins or wetting agents.

An admixture containing a water reducing agent and an amphoteric surfactant exhibited improved air entrainment and other properties.[196] A chloride free air entraining agent has been described in another patent.[197] It contained lignosulfonate, naphthalene sulfonate, thiocyanate and triethanolamine. A protein-based air entraining agent was suggested for use in lightweight concrete and water floatable cement structures.[198]

A few formulations were claimed to decrease water demand, improve workability, increase air content and freeze-thaw resistance of concrete. They included lignosulfonic acid + castor-ethylene oxide,[199] phenolic wood chemicals and syrup,[200] and polyoxyethylene alkyl sulfuric acid and copolymer with dicarboxylic acid salts.[201] Another formulation contained an amidocarboxylic acid surfactant, maleic anhydride, NaOH and sulfonated naphthalene.[202] Recent formulations include NaC_3-alkylbenzene sulfonate + Na salts of sulfonated ethoxylated C_{12} fatty alcohols + condensates of Na lignosulfonate with mono-methylophenol,[203] ethoxylated nonyl phenol + Na-isooctyl benzene sulfonate + Na-p-aminobenzene sulfonate[204] and esters derived from polyoxyethylene polyaliphatic acid esters, polyethylene glycol fatty acid esters, etc.[205]

Compared to other admixtures only a few patents referred to the development of air-entraining admixtures in the years 1990–92. This is because the existing admixtures are sufficiently effective in providing adequate bubble size and spacing in concrete. An air-entraining agent of long stability contained vinsol resin + a phenolic compound,[206] and another contained a fatty ester of particle size 0.05–1.0 μm + C_{1-10} alcohol[207] and another formulation was essentially a coconut acid diethanolamide produced by reacting alkyl ester of coconut acid with diethanolamine.[208] Improved frost resistance of concrete has been claimed with the use of pore forming chemicals such as those obtained by methylyzing and saponification with alkali metal hydroxides.[209]

8.0 POLYMER-MODIFIED SYSTEM

Addition of water soluble polymers or emulsified polymer to concrete is beneficial with respect to its several properties such as better workability, decreased water absorption, improved tensile, flexural, shear, impact and bond strengths and increased durability. Many of these formulations contain polyvinyl acetate, polyvinylidine chloride-polvinyl chloride copolymer, styrene-butadiene copolymer, polyacrylate copolymer, epoxy, etc.

Excellent adhesion properties were claimed for concrete obtained with the following: modified polyvinyl alcohols,[210][211] vinylidene chloride resin latex[211a] and others.[212]-[214]

High compressive and flexural strengths are obtained with the following formulations: water soluble poly (diethyl aminomethyl methacrylate) polymer,[215] polyacrylate based compositions,[216] unsaturated polyester resin, melamine cyanurate cobalt naphthenate and cumene hydroperoxide,[217] indene-styrene resin, coal tar plasticizer,[218] a composition containing urea resin, tetraethoxysilane and formaldehyde[219] and a mixture containing furan epoxy resin, diethylene glycol, triethanolamine, silane, silicone and phosphoric acid.[220]

Several patents, including some of the above, are based on vinyl acetate or acrylate/or methacrylate copolymers. Four patents were based on styrene-butadiene copolymers.[221]-[224] Epoxy resins were used in 5 formulations.[225]-[229] Four patents were based on polyisocyanates and urethane copolymer.[230]-[233] Others were unsaturated polyester resin,[234] polyacrylamide,[235] carbamide resin[236] and polyethylene polyamine.[237]

Improvement in the broad range of properties in mortar or concrete is claimed when certain polymers are added. Examples are: Suppression of water absorption or waterproofing properties,[238]-[241] underwater application,[242] control of bleeding,[243][244] slump loss controlling agents,[245]-[249] improvement in workability,[250]-[252] improvements in curing time,[253][254] better frost resistance,[255] elasticity,[256] durability,[257] chemical resistance,[258][259] air entrainment,[260] decreased rebound,[261] superior oil well and geothermal cementing compositions,[262] repair of damaged concrete,[263] carbonation inhibition[264] and fire retarding and sound proofing compositions.[265]

In the years 1990–91, some polymer-based admixture formulations were developed which provided benefits such as dispersion, control of slump loss, better adhesion, reduced carbonation and lower chloride penetration. Following were some of the formulations: acrylic acid polymer dispersant or carboxylic acid polymer grout,[266] quaternized N-containing water soluble copolymers (mol wt 500–200,000),[267] emulsion obtained by polymerization of esters of alpha, beta-ethylenically unsaturated 5-carboxylic acids and $C_{1\text{-}8}$ alcohols,[268] polymer emulsions (polyvinyl acetate, ethylene-vinyl acetate copolymer, acrylic polymer) and rubber latexes,[269] acrylic polymer,[270] fine silica particles + polymer latex such as Bu acrylate, ethyl acrylate, methyl acrylate, etc.,[271] copolymers of (meth) acrylic acid and (meth) acrylate esters and $C_{1\text{-}8}$ alcohols,[272] and acrylic polymer-epoxy resin.[273]

There has been considerable activity in 1992 in the development of various polymer-based admixtures as evidenced by the number of patents. Some examples of those reported in 1992 are: strength increase by the use of polymer latex such as ethylene vinyl acetate or acrylic ester containing a water reducer, silica fume and slag;[274] ammoniacal solution of methacrylic acid-methyl methacrylate copolymer;[275] synthetic latex, an alkanolamine and a set retarder that promotes water repellency and adhesion;[276] ethylene-vinyl acetate copolymer, styrene-butadiene rubber latex and vinylidene polymer emulsion that provides high flexural strength;[277] self leveling composition containing 1-alkyl vinyl ester dispersant.[278]

9.0 MISCELLANEOUS AND POLYFUNCTIONAL ADMIXTURES

Formulations with two or more compounds in which each compound may play a specific role, or a single admixture which does not fall under any of the above categories, are included under this group. They are based on organic, inorganic or organo-inorganic compounds and many of them are obtained as by-products from the industries. They are claimed to possess many advantages when used in mortars and concrete. They include, prevention of shrinkage and cracking, improvements in stability and plasticity, sedimentless concrete, better strengths, reduced bleeding, prevention of slump loss and cracks, increased resistance to water, better flowability, air entrainment, water reduction, water repellency, efflorescence prevention, improved bending and tensile strengths, and increased durability.

Some admixture formulations such as the chloride-free admixture containing inorganic salts can be used at temperatures -7 to + 4°C.[279] Using urea as the major constituent an antifreezing formulation was developed.[280] Another formulation included NH_4SCN, $(NH_4)_2S_2O_3$, NaSCN and/or $Na_2S_2O_3$.[281]

Several formulations have been developed for underwater applications. Prevention of cracking and heat build up could be achieved with the following formulations: blast furnace slag, cellulose thickeners,[282]-[284] compositions based on polyacrylamide,[285] blend of sulfonated polyvinyl alcohol and cellulose ether,[286] polyethylene oxide and/or polyacrylamide and a cationic water soluble resin,[287] N, N-dimethyl acrylamide polymer,[288] methyl cellulose for calcium aluminate-gypsum system,[289] a combination of carboxymethyl cellulose, cellulose ether and sodium silicate,[290] polyacrylamide, Me methacrylate-Na acrylate polymer,[291] cellulose ether + water soluble acrylic polymer + plasticizer[292] and a copolymer prepared from diacetone acrylamide, acrylamide, alkali metal or ammonium acrylate.[293]

Certain formulations are suggested for smooth finishing of concrete. An example is lignosulfonate containing methyl cellulose polymer or other hydroxy-based polymer.[294] An admixture which can be used in high temperature oil well drilling contained hydroxyethyl cellulose.[295]

Several other types of admixtures have been formulated including those for water proofing, preventing efflorescence and carbonation, reducing drying shrinkage, preventing segregation, producing buoyant concrete, controlling alkali-aggregate expansion, etc. Some examples follow: The formulations to control alkali-aggregate expansion are porous particles containing mineral oil or a surfactant[296] and Ca or Li-based clinoptilolite.[297] The compound 2,2 dimethyl propane, 1,3 -diol has been suggested as a shrinkage reducing agent.[298] A combination of Li(OH) and activated silica has been proposed for preventing efflorescence.[299] Many formulations have been claimed to increase the strength of concrete and they include, maleic anhydride copolymer mixed with sulfonated naphthalene or melamine formaldehyde, lignosulfonate, carboxylate, styrene sulfonate, etc.,[300] polypropylene glycol lauryl ether + 70% reaction product of polyethylene polypropylene 2, ethyl hexyl ether with toluene di isocyanate,[301] and a mixture of $NaNO_2$, Na_2SO_4/K_2SO_4 + HCOONa + $Ca(COOH)_2$ + Ca lignosulfonate.[302] A slump increasing compound consisted of poly 4-vinyl N-benzyl trimethyl ammonium chloride.[303] A mixture of thiocyanate, thiosulfate and water soluble polymer or methyl cellulose can used as a corrosion resistant accelerating admixture.[304] A composition containing ground lime, plasticizer (polyvinyl alcohol + lignosulfonic acid, alkyl sulfonated polyphenols or melamine) is claimed to be a good expanding plugging additive for grouting.[305]

In the years 1990–91, several multifunctional admixtures were developed with varied functions. They were as follows: increased corrosion resistance using quick lime and mineral oil,[306] waterproofness with polyethylene glycol esters of $C_{8\text{-}22}$ fatty acids,[306a] starch esters and polyacrylamide,[307] fatty acids, rosin acids and their salts + retarding agent and a polymer,[308] gypsum + calcium nitrite + ferric sulfate;[309] laitance prevention with quaternary ammonium-containing cationic or amphoteric resin;[310] increased strength and freeze-thaw resistance with ammonium thiocyanate or alkali thiocyanate;[311] silica micropowder + fly ash + zirconium oxide + MgO + alkali metal or earth metal salt of stearic acid + set accelerator + water reducing agent + polymer stabilizer,[312] silica fume,[313] crosslinked polymers + polystyrene sulfonate,[314] the a olefins + olefin fiber,[315] hydropropylmethyl cellulose + amine + melamine formaldehyde,[316] anhydrite + silica fume,[317] ceramic waste + blast furnace slag + limestone + barium chloride or sodium chloride,[318] high quality cement paste,[319] sulfonated polyphenolate, carbonates, hydrocarbonates or silicates of alkali metals and/or grinding additive, hydroxyacid salts, boric acid and esters of silicic acid,[320] ultrafine blast furnace slag + aluminum sulfate,[321] silica fume:[322] corrosion inhibitor admixtures included, amidosulfonate and amino alcohol[323] and graft polymer plasticizer comprising polyether backbone and polymer side chain formed by polymerization of ethylenically unsaturated monomer and alkali metal nitrite;[324] for articles with better extruding properties use of cellulose ethers with hydroxyalkyl cellulose ether was advocated;[325]-[327] slow setting grouting or fast setting grouting compositions such as fly ash and water glass;[328][329] low shrinkage/bleeding agent included 2-propenoic acid, esters, polymers with isobutylene and maleic acid and styrene;[330] for low temperature application, alkali aluminate + alkali carbonate + calcium aluminate + aluminum sulfate;[331] for resistance to salt attack, amine derivative + hydrolyzable organosilane,[332] silicone oil + trimethyl siloxy-terminated dimethyl polysiloxane-silica mixture,[333] aluminum hydroxide-based additive;[334]

activator for slags or fly ash comprised fluorosilicate with sodium hydroxide,[335] KOH + K_2CO_3 + NaOH + Na_2CO_3 + citric acid;[336] and solidification additive for radioactive wastes was high cation absorptivity Si compounds containing siloxane and silanol groups.[337]

A few additives have also been described in the patent literature in 1992 for counteracting alkali-aggregate expansion reaction. They included: zinc compounds especially ZnO,[338] alkyl-alkoxy silane;[339] cation exchangers.[340] Patented admixture formulations reported in 1992 for underwater concreting included chlorinated paraffin, surfactant and bentonite;[341] Ca-fluoroaluminate containing inorganic salts, hardening accelerators and cellulose;[342] and a combination of calcium aluminate glass, anhydrite, Na gluconate, Me cellulose, air entrainer and a water reducing agent.[343]

Attempts have been made to develop formulations that accelerate hardening of concrete, and also act as corrosion inhibitors. The patented formulations reported in 1992 include: a mixture of calcium chloride, sodium nitrite, gypsum and calcium lignosulfonate,[344] triply bonded diol (e.g., 2 butyne-1, 4-diol),[345] iron salts,[346] a complex mixture of Na-silicate, NaOH, $NaNO_3$, Na-lignosulfonate, triethanolamine and Bu_3PO_4,[347] aqueous solutions of monosaccharides with CH_2OH groups and Zn ions,[348][349] a mixture of hydroxycarboxylic acid and saccharide with a styrene butadiene copolymer latex as well a high fatty acid salt,[350][351] and a mixture thiocyanate, thiosulfate, and a water soluble polymer or methyl cellulose.[352] Other examples include: combination of $C_{15\text{-}17}$ fatty acid with cerisin;[353] amino acids;[354] a mixture of $NaNO_2$ + nitroglycerine + potassium ferricyanide[355] and 2-hydroxy phosphono acetic acid.[356]

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18

Admixtures For Oilwell Cements

John Bensted

1.0 INTRODUCTION

Before considering admixtures for oilwell cements, it is necessary to appreciate the conditions under which oilwell cements are used.

Oilwell cements are primarily employed in the exploration for and the production of oil and gas. They are mostly utilized for sealing the annular space (annulus) between the borehole walls and the steel casing (out of which oil and/or gas eventually flows to be collected and separated as appropriate at the surface), so as to isolate the pressured or weak zones found during drilling. The oilwell cement needs to have the following properties so that it can function as an effective seal in the annulus:

(i) Low permeability.

(ii) Form a satisfactory bond with both the rock at the borehole walls and the metal casing.

(iii) Keep these properties not only under the downhole temperature and pressure conditions, but also when the metal casing undergoes vibrations caused by continued drilling activity.

(iv) Protect the casing against aggressive wellbore fluids.

(v) Protect the casing against collapse by rock creeping in on the wellbore.

In order to accomplish these desired functions, it is essential that the oilwell cement slurries meet the following requirements:

1. Staying pumpable for enough time to allow cement placement under the particular well conditions.
2. Be stable suspensions.
3. Once in place to harden rapidly.
4. To retain high strength and low permeability for the lifetime of the wells, which in productive reservoirs may be 15–20 years or more.

Individual well conditions may thus require the utilization of oilwell cement slurries with densities ranging from ~ 1.0 to 2.4 kg/liter (~ 8–20 lb/US gallon), pumping times from 2 to 6 hours, temperatures ranging from freezing to ~ 200°C (~ 400°F) and pressures up to 140 MPa (20,000 lb/in^2). Tailoring oilwell cement slurries to the particular circumstances of given wells normally requires the judicious use of additives.

It is important to note that in the oil and gas industry, unlike the construction industry, all additions to cement and cement slurries are referred to as *additives*—there is no differentiation between additives (the larger additions) and *admixtures* (the smaller additions, normally below about 5% by weight of cement). The advantage of the single term *additive* here is that certain materials may be used over a wide range of addition levels and would hence be classified as admixtures in one situation and additives in another. So the term *additive* is more convenient to employ in the oil and gas industry, even though it may not satisfy the admixture purist! In this chapter, the term *additive* is used throughout to conform to its industrial usage with oilwell cements.

In most parts of the world, oilwell cements are produced to American Petroleum Institute (API) specifications.[1] At one time, nine different Classes (A-H and J) were defined in terms of well depth,[2] but now[3] the depth requirements have been withdrawn and Class J cement (a dicalcium silicate-silica cement) has been deleted from the specification since it is no longer used in North America, but does still have currency in the national oilwell cement standards of Argentina, India, and Indonesia.[1] The reason for the omission of well depth requirements in the current API oilwell cement standard is that the depths refer to average conditions determined by the API, like downhole temperature, from well data collected mostly from the South Western United States and Gulf of Mexico regions. These data have been employed as the conditions of API testing, such as the standard operating schedules for thickening time testing.[2][3] Thickening time is a setting time under defined simulated downhole conditions, which is measured in an appropriate consistometer.[2]-[4] The API schedules have been designed to simulate the pumping of cement slurries through the wellbore until they reach defined bottom hole pressures and circulating temperatures.[5] These are currently being modified somewhat.[6] The reality is that holes of the same depth in different geographical and geological locations frequently show different bottom hole temperatures that depend upon the actual geothermal temperature gradient in the particular well. Hence, in these cases, the standard API schedules may not be suitable and specific schedules for the area concerned will then need to be devised. There are no mandatory standards as such those governing the use of additives in oilwell cements.

From all this it can readily be realized that cement-additive combinations need to be precisely tailored in order to achieve a good well cementing job.

Firstly, consider the oilwell cement. The normal manufacturing process usually requires at least some modification for producing good quality oilwell cements, particularly those of Class G and Class H, the basic categories.[7] Oilwell cements usually have to be of low reactivity for giving a suitable placement time, whereas construction cements normally need to be of higher reactivity for achieving desired compressive strength development at early ages. Oilwell cements need to have a high level of consistency of response to the effects of given concentrations of additives, which means that they must be made to a high batch-to-batch consistency. This is accomplished by minimizing variations in raw materials, proportioning and processing, which means that quarrying raw materials, raw feed preparation, kiln fuel, burning conditions (including avoidance of a reducing atmosphere),[8] clinker cooling, gypsum quality, clinker-gypsum grinding, silo storage and transportation must be addressed in this respect. A "good housekeeping policy" must be maintained by the manufacturer at the cement works, which involves more stringent quality control than for construction cements.

For a consistent oilwell cement of low hydraulic reactivity that gives a good additive response, the following criteria should be observed:

(a) Reactive phases such as tricalcium silicate (alite), tricalcium aluminate (aluminate) and free lime must be minimized.

(b) SO_3 content and fineness (specific surface area) must not normally be too high.

(c) Reducing conditions in the kiln must be avoided.

(d) Clinker-gypsum grinding temperatures as well as cement storage temperatures must not be too high, so that some residual dihydrate gypsum $CaSO_42H_2O$ (preferably ~ 1% by weight of cement) remains and does not end up fully dehydrated to the hemihydrate $CaSO_40.5H_2O$/soluble anhydrite stages.[9]

(e) All unnecessary exposure to the elements must be avoided.

Secondly, the additives need to be considered. These are normally recommended and supplied by the cement service companies. During usage, oilwell cements are commonly mixed with appropriate additives in various proportions, so as to give a suitable cement slurry performance for the specific well conditions. As well depths, pressures, and temperatures have risen, improvements have been made with different additives to produce both the required cement slurry properties and also to extend the range of the oilwell cements. The increasing propensity to drill and cement deviated and horizontal wells has necessitated a greater appreciation of the interactions between cements and additives. These wells are drilled so as to facilitate and maximize gas and/or oil extraction from particular reservoirs or for environmental reasons to overcome unsightly installations in areas of natural beauty. Deviated and horizontal wells are successfully cemented with slurries of Class G or Class H cements, wherein any tendencies to bleed or settle are prevented and any annular eccentricity[10] of the metal casing in the borehole is minimized. Such slurries may contain suitable anti-settlement agents which, in addition, are normally good fluid loss controllers, especially at high deviations from the vertical. These will be discussed more fully later. Also, there must be judicious usage of additives for cementing slim-hole wells.[11] Various texts describe the well cementing processes.[12]-[18]

Additives, such as retarders for example, can have a considerable influence upon the cement hydration chemistry, where their effects may not be simply physical but also chemical. The science of additives in well cementing environments has been less extensively studied than that of the oilwell cements. Accordingly, the different types of additives for use with oilwell cements have been set out and their functions as well as their influences (where known) upon the hydration chemistry discussed in some detail.

A further important point concerns the preferences where possible for the use of solid additives instead of liquid additives (additives in aqueous solution). In the North Sea, for example, liquid additives are preferred, whereas in the United States (particularly along the Gulf Coast) solid additives are preferred. There are, of course, various pros and cons associated with the use of both types of additives.

Liquid additives have the advantages of taking up less rig space, since no blending plant is required, and are also convenient to use—they are normally premixed with water before mixing with the cement. However, there are some disadvantages in their utilization. Overdosage or underdosage is easily done with liquid dispensers. The liquid dispensers readily become dirty on rigsites and at times it can be difficult to read the levels of additive being dispensed. Some liquid additives like lignosufonate solutions sometimes have a shorter shelf life than their solid equivalents. This problem normally only arises after a period of several months in storage.

Solid additives have advantages in being easy to dose correctly and, as mentioned above, some may have a longer shelf life. There are certain disadvantages in their employment. The bulk facilities required for mixing solid additives with the cement take up much valuable space and the logistical considerations can cause difficulties on site. (In some new frontier areas of oil and gas exploration suitable blending facilities may not be available). Also, blending in the additive(s) homogeneously with the cement can be difficult—usually three or four movements of cement containing the additives is considered sufficient. Inhomogeneity in a sensitive cement slurry may have a serious effect upon thickening time and waiting-on-cement (WOC) time.

2.0 CLASSIFICATION OF OILWELL CEMENT ADDITIVES

For convenience, oilwell cement additives can be classified into different categories; fifteen categories have been considered here. In a number of instances, the classification is arbitrary because the additive is multifunctional, for example, lignosulfonates are retarders, dispersants, and to some degree fluid loss controllers; SMFC and SNFC dispersants may also retard, accelerate slightly or be neutral to the rate of cement hydration, depending upon their precise composition; HEC and CMHEC fluid loss controllers are also retarders.[8]

2.1 Retarders

Retarders are employed for increasing the thickening times of oilwell cement slurries, and permit longer pumping times and better flow properties. Normal practice is to employ the basic oilwell cements of Class G or H and to add a retarder in the cement slurry formulation sufficient to cope with the particular well conditions. The principal criterion for the employment of a specific type of retarder is well temperature. Cements of Classes D, E and F, where retarders are incorporated during manufacture, are seldom utilized nowadays. The most commonly used retarders are calcium and sodium lignosulfonates, that are usually satisfactory up to 95°C, which often corresponds to a well depth of ca. 12,000–14,000 ft (3660–4270 m). For use at higher temperatures they must either be modified in a suitable manner or used in conjunction with other additives, where retarding performance is enhanced by a synergistic effect. The performance of lignosulfonates can be improved per se by a number of means—refining, modifying or oxidizing. Owing to their variable quality, different results for retardation by different lignosulfonates with a series of oilwell cements can be encountered in practice.[19]

Lignosulfonates are cheap by-product materials readily obtainable from the paper pulp industry. They are impure substances of variable composition, whose complete structures are not precisely known. The lignosulfonate structures are polymeric, being based upon phenylpropane units having -OH, $-CO_2H$, $-OCH_3$ and $-SO_3H$ groupings. Lignosulfonates have typical average molecular weights of around 20,000–30,000 in a typical distribution range of about 300–100,000. They are not linear polymers, but take the form of spherical microgels with charges that predominate on the outside of the spheroids; the internal carboxyl and sulfonate groups are non-ionized. Normally, lignosulfonates on average tend only to be 20–30% ionized. Optimum retardation arises at a molecular weight of about 1000. Higher levels of polymerization tend to have a reduced retardation. Lignosulfonates often have sugar impurities at levels of 1–30% by weight; these are mostly pentoses, with few hexoses usually being present. Sugar impurities affect the retardation of lignosulfonates by providing additional retardation. The variable sugar content does mean that this extra retardation is more variable. Hence, in many modified lignosulfonates, the sugar content is minimized, so that products of relatively greater consistency in retardation can be given. Bacteria can feed on this sugar content and in so doing can cause the degradation of the lignosulfonates to products like vanillin; this results in the loss of the key properties like retardation. Thus, lignosulfonates are either treated with antibacterial formulations, or suitably modified so as to minimize the sugar content and then treated with suitable bactericide, so that active shelf life can be extended indefinitely. Lignosulfonates tend to last longer when stored in powdered form. This occurs because solutions tend to polymerize further with time, and this reduces the retardibility.

Sources of lignosulfonates vary considerably. In Europe the principal source is the spruce fir, in North America the maple and in the Far East the bamboo. The parent lignins will differ according to the type of wood, the different types of soils, and the different seasons of the year. The lignins will alter as a response to temperature changes in the external atmosphere. Sulfonation of the lignins causes further changes, because the process is incomplete. The nature and extent of sulfonation influence both the aqueous solubility of the lignosulfonate produced and the type of bonding to the surfaces of the cement particles, which in turn influences its retardability.

The aqueous solubility is important because the greater the solubility is, the better the retardation of cement thickening. This is influenced not only by the degree of sulfonation and polymerization, but also by the choice of cation (sodium or calcium, usually). Sodium lignosulfonates generally tend to maintain their solubility at low temperatures (below -10°C) and thus, unlike calcium lignosulfonates, avoid sedimentation under cold conditions. Also sodium lignosulfonates have a greater extent of ionization in solution than their calcium counterparts. As a result, solutions of higher concentrations of calcium lignosulfonates are often needed to attain the same effect obtained by employing the same dosage of the corresponding sodium lignosulfonates. However, calcium lignosulfonates ought to be cheaper than sodium lignosulfonates which should offset the higher concentrations that might be needed to give a particular level of retardation.

Lignosulfonate quality, thus, depends upon the seven basic S-factors: sources, soils, seasons, sugars, sulfonation, solubility, and shelf life.

Polyhydroxy organic acids of sugar origin are often employed as retarders for temperatures, such as, calcium or sodium gluconate, calcium or sodium glucoheptonate or glucodeltalactone. They are powerful retarders and only small dosages are necessary, otherwise, overdosing can easily arise and thickening can be unduly extended. Phosphonates can give good high temperature retardation at only one-tenth the concentration of sugars and are regularly used in Russia and other CIS countries.

Carboxymethylhydroxyethylcellulose (CMHEC) can be utilized in concentrations of 0.1 to 1.5% by weight of cement as a combined high temperature retarder (up to at least 140°C) and fluid loss controller. However, CMHEC increases the viscosity of the cement slurry, so for employment at high temperatures it is often essential to add dispersant or small quantities of water to ensure that the slurry is pumpable. It can be utilized to retard salt-containing systems when other retarders cannot always be effectively employed. Hydroxyethylcellulose (HEC) retards cement hydration up to about 95°C but is mainly used as a fluid loss controller (see later).

Other retarders include sugars and citric acid, where retardation is highly sensitive to retarder addition. Sodium chloride (common salt) NaCl retards cement slurries when present in concentrations above ~ 20%, but decreases compressive strength. Such retardation is a manifestation of the common ion effect. For cementing through salt sections, the cement slurries are commonly salt saturated, but lower salt concentrations may suffice for freshwater-sensitive shales and bentonitic sands.

It was thought until fairly recently that retarders of portland cement hydration, which commonly contain -OH, $-CO_2H$ groups or both, acted by adsorption onto the surfaces of the cement particles to give monolayers that physically impeded the hydration process. Investigation of the hydrated cement systems with retarders has indicated that, while hydration of the alite and belite phases is indeed retarded, the hydration of the aluminate and ferrite phases to form ettringite is actually increased significantly. More heat is often released at the beginning of hydration than in the absence of the retarder. Poor correlation exists between retardation and the sorption of organic compounds onto unhydrated cement, where water competes effectively with the sorbate. Thus, the concept of an all-embracing monolayer physically thwarting hydration cannot be accepted. Where adsorption does arise, as with lignosulfonates, there is undoubtedly a selective element involved in the operation, which has the effect of accelerating early aluminate and ferrite hydration reactions.[22]

Sometimes with retarders S-curve formation takes place. Here, when the concentration of retarder increases, the thickening time starts to decrease instead of rising in the expected way. At greater retarder concentrations the thickening time then changes back to its normal practice of increasing once more. When plotted graphically, an S-shaped curve is obtained, hence the name. S-curve formation can be found with various retarders like lignosulfonates, sugars and phosphonates and can be explained on the basis that when the dosage of retarder is raised in the highly alkaline cement-water medium, there is a gradual trend towards more polymerization. This releases more calcium hydroxide through condensation reaction and effectively interferes with the retardation process to give correspondingly less retardation of thickening. More retarder gives a diminished overall likelihood to polymerize, causing proportionally better retardation behavior. S-curve behavior is favored by proportionately high levels of free lime CaO, strontia SrO, and magnesia MgO in the cement clinker component and is usually lowered, minimized, or avoided if these parameters can be minimized.[20]

A threshold of unexpectedly long thickening time at ~ 70–90°C is frequently experienced by oilwell cement slurries with commonly employed retarders, which is in contrast to the normal exponential type dependence of thickening time upon increases in retarder concentration. The cause of the threshold effect was attributed to a surge in hydraulic reactivity of the ferrite phase.[21] The hydration products thus formed, mostly ettringite (AFt phase) $C_3(A,F)\bullet 3CaSO_4\bullet 31\text{-}32H_2O$, are deposited on the hydrating clinker surfaces and impede, in particular, the alite hydration to calcium silicate hydrate C-S-H, the initiation of which is the prime cause of cement thickening. Hence thickening time is extended and not diminished. As the temperature rises above ~ 90°C the increased hydraulic potential of the cement manifests itself. There is no longer an increased surge in ferrite phase hydration to obstruct C-S-H formation, so the alite hydration rate rises again, culminating in lower thickening times once more. The existence of the threshold effect in many hydrating oilwell cements has important implications in oilwell cement slurry designs and placement operations.

In shallower wells, where the hydration products calcium silicate hydrate C-S-H and ettringite are produced during hydration, a possible reaction mechanism for retardation takes place thus. When the clinker silicate phases (primarily alite) begin to hydrate, the calcium ions react preferentially to form ettringite, instead of assisting with the initial formation of C-S-H. This causes the transient formation of amorphous hydrated silica at the clinker silicate surfaces, which, especially those of alite, are still reacting, but are not initially forming C-S-H in amounts comparable with those being produced in the absence of retarders like sugar and their derivatives and lignosulfonates. Scanning electron microscopy shows no evidence for the existence of "skin" barriers. Indeed, a protective barrier is unlikely, since more, not less, ettringite is produced during early hydration. The retarder might locally reduce the pH in the neighborhood of the exposed alite particles. Hence, calcium ions at the alite surfaces would migrate to the aluminate, and (to a lesser degree) the ferrite phase surfaces, and preferentially react to form ettringite. There would thus be a relative deficiency of calcium ions at the alite surfaces, as a result of which C-S-H formation would be impeded there. Because it is the formation of the C-S-H that is the main cause of thickening and hardening, the effect of a reduced C-S-H formation rate is to retard the thickening and hardening of the cement slurries.

When considering retardation and retarders, one must be precise about what is meant by these terms. *Retardation* refers to the observed delaying effects upon the thickening and early hardening of cement slurries, and *retarders* are the agents which bring these effects about. Retardation does not imply a retardation of total chemical reaction. Indeed, reactivity is commonly greater in the presence of the retarder. It is common during retardation for alite and belite hydration to be reduced, while both aluminate and ferrite hydration are raised.

The retardation mechanism of sodium chloride is somewhat different from that described above and is related to the common ion effect. The large concentrations of sodium and chloride ions in the slurry impede the reaction of calcium ions at the silicate surfaces, resulting in a lower rate of formation of C-S-H and, hence, a longer thickening and hardening process.

Borax $Na_2B_4O_7 10H_2O$ and other borate retarders are not often utilized as retarders per se but as aids for use with other retarders, especially in high temperature slurries. Borates are less powerful retarders at high temperature than at low temperatures, and exert a synergistic effect on other retarders like lignosulfonates of different types, whereby better retardation is given than for either of the two types of individual retarders. This synergistic effect seems to be related to some type of complexation involving hydrogen bonding between the borate and the organic retarder, which raises the overall effective thermal stability of the retarding system, but the detailed mechanism of this synergy is not yet known. Borax is the most commonly encountered retarder aid, although other water-soluble borates have periodically been utilized. Potassium dichromate has also been employed as a retarder aid in the CIS (the former USSR).[17]

Within the CIS, numerous other materials have also been used as retarders.[17] These include sulfite lye, spent sulfite-yeast liquor (SUL), sulfite alcohol liquor (SAL), tartaric acid (TA), commercial cream of tartar (CCT), pyrogallol, wood chemical polyphenols, sodium tannate, potassium dichromate (see also above), hydrolyzed pentosanes (L-6), dextrin (starch gum), oxidized cellulose, hypan copolymer, wine yeast (WY), fruit processing wastes, etc. Many of the spent liquors are of very variable composition and do not give consistent batch-to-batch performance with given oilwell cements.

2.2 Accelerators

Acceleration is utilized for lowering thickening times and increasing early compressive strength when cementing surface casing and conductor strings below ~40°C. This permits a 500 psi (3.5 MPa) compressive strength threshold, which is commonly accepted as a suitable minimum for bonding and supporting pipe, to be achieved in as little as 4 hours. Accelerators are sometimes also used in extended cement slurries (see later) to give adequate thickening times.

The most widely used accelerator is calcium chloride $CaCl_2$ in 2–4% quantities by weight of cement. Calcium chloride is hygroscopic and can be used in anhydrous or hydrate (77% $CaCl_2$) forms. It reduces the viscosity of oilwell cement slurries by also acting as a dispersant. Although now banned as an accelerator in construction with steel reinforcement, calcium chloride is not known to pose any corrosion problems with metal casing, because of the lack of oxygen downhole.

Sodium chloride $NaCl$ also accelerates in dosages ~ 1–4% by weight of cement, but is not normally included as an accelerator as such. Large dosages (usually over 20%) retard. As the oilwell cement slurry thickens, it is expanded a little by the sodium chloride, and this tends to give improved bonding with shale formations. Potassium chloride KCl and ammonium chloride NH_4Cl can also accelerate thickening and function in a similar manner to sodium chloride in this respect, but are rarely employed. Aluminium chloride accelerates cement slurry thickening in dosages ~ 4–10%, but can decrease the fluidity of the slurry, and is not normally considered to be a suitable accelerator. All four of these chlorides are less effective accelerators of cement thickening and hardening than calcium chloride, and are not usually employed as such. These chlorides are not known to cause problems, per se, by corrosion of metal casing downhole where the lack of oxygen inhibits normal chloride corrosion.

Sodium silicate Na_2SiO_3 can be employed as an accelerator in ~ 2–4% quantities by weight of cement, but is mainly used as an extender (see later). If used as an accelerator, it is normally dry blended, because, in comparison with calcium chloride, it is slower to thicken but rapid in early compressive strength development. For reliable acceleration, it is essential that the polymeric metasilicate ion $(SiO_3)_n^{2n-}$ remains in solution, before reacting with the Ca^{2+} ions, otherwise premature gelling is likely to arise. For optimum solubility and hence better acceleration, the Na_2:SiO_2 ratio of the sodium silicate should not be less than about 1.0. Suitable salts may be added to accelerate the cement thickening more, so that the sodium silicate can be used primarily to increase the hardening of the cement, if this be appropriate. Potassium and ammonium silicates are normally insufficiently water-soluble to be good accelerators for oilwell cements.

Seawater also accelerates cement hydration by virtue of including significant concentrations (up to 25,000 parts per million) of chlorides. Seawater is commonly employed for logistical reasons on offshore rigs for mixing cement slurries and its acceleration needs to be taken into account when designing the cementing formulations. Seawater is normally reasonably consistent in composition well away from shorelines. However, for rigs just offshore, the seawater may not always be consistent because of dilution by fresh river water, or in equatorial rain forest climates by varying quantities of dissolved lignins and tannins, which can themselves retard the cement slurries.

Calcium sulfate hemihydrate (plaster of Paris) $CaSO_40.5H_2O$ is described as a cement accelerator. Acceleration takes place as long as the hemihydrate remains unreacted to form gypsum $CaSO_42H_2O$, since hemihydrate has a greater solubility than gypsum. The greater numbers of dissolved sulfate ions promote increased formation of both ettringite and the calcium silicate hydrate C-S-H. Acceleration is unreliable with hemihydrate since the effect falls off as gypsum is produced. Thickening times may be as low as 5 minutes with certain high hemihydrate-portland cement blends, which is totally unrealistic. Mixing of excessive quantities with portland oilwell cements (such as above 12%) can cause severe stiffening problems during pumping and placement.

Sodium aluminate $NaAlO_2$ also accelerates hydration. However, its hydration is often difficult to control compared with other accelerators and, if used downhole, needs to be very carefully employed.

The mechanism of acceleration of cement hydration has not been known with any precise certainty. Formation of hydration products such as C-S-H and calcium hydroxide is accelerated at the prescribed dosages and some morphological changes in the hydrates take place, probably as a result of specific changes in the ionic character of the solution phase. The acceleration presumably takes place as a result of increased penetration of

OH^- ions in the cement paste, causing more calcium hydroxide precipitation and corresponding reaction at the calcium silicate (particularly alite) surfaces, producing C-S-H at an increased rate. There is no universal mechanism of acceleration.[23] The effects of salts upon cement hydration, where different concentrations may accelerate, neutralize, or retard hydration in particular instances, has been interpreted in terms of changing the respective ionic strengths of the solution phases.[24][25] Acceleration of thickening time is based primarily upon acceleration of C-S-H formation. Sometimes aluminate and ferrite hydration are also accelerated, but since their acceleration also arises in many retarded systems, they are clearly not rate-determining here from the accelerative viewpoint.

2.3 Strength Retrogression Inhibitors

Portland cements suffer from strength retrogression at temperatures above ~ 110–120°C. Instead of the normal increase in compressive strength with time, loss in strength and impermeability arise due to the formation of large crystals of α-dicalcium silicate hydrate $Ca_2(HSiO_4)OH$.

Strength retrogression is counteracted by the addition of active silica from silica sand or flour, which will react with lime released by the change in crystallinity of the calcium silicate hydrate binders that causes the observed loss in strength. Additions of, say ~ 35% silica flour SiO_2 tend to prevent the formation of α-dicalcium silicate hydrate at these temperatures and give a CaO/SiO_2 ratio of 0.8, that is favorable for the formation of tobermorite $Ca_6(H_2Si_6O_{18})4H_2O$, a good strong binder of high impermeability which has a smaller crystal size. It is this change in chemical reaction that overcomes the problem of strength retrogression.

Sometimes natural pozzolans or pulverized fly ash have been used to prevent strength retrogression, but have generally been less effective than silica flour and are not commonly employed for this purpose in well cementing.

Silica sand is a coarser material than silica flour (generally ~ 75–210 µm particle sizes compared with less than 75 µm for silica flour) and may have certain advantages with its lower reactivity when high slurry viscosity is a problem downhole. For the completion of high temperature wells which contain highly saline brines, silica flour are preferred if logistically possible. High sodium chloride concentrations reduce the solubility of silica. Thus, when coarser silica sand is employed because of the low surface area, less silica is actually available for hydrothermal reaction. Hence, silica-deficient phases of high permeability and low compressive strength can be formed under such conditions, like α-dicalcium silicate hydrate $Ca_2(HSiO_4)OH$, afwillite $Ca_3(HSiO_4)_2\ 2H_2O$, calciochondrodite $Ca_5(SiO_4)_2(OH)_2$ and kilchoanite $Ca_6(SiO_4)Si_3O_{10}$.[26][27]

In high temperature oilwell cement slurries, silica sand and flour do have some effect upon the actual thickening time obtained. Since silica flour is more finely divided than silica sand, and thus potentially more chemically reactive, it might be assumed that the thickening time of a slurry would be lower with silica flour than with silica sand. In reality this is not necessarily so—the relative thickening times may be reversed, because of the effects in particular slurries of given additives like retarders upon the reacting systems.[28]

2.4 Fluid Loss Controllers (Filtration Control Additives)

Cement slurries can lose water by filtration into adjacent permeable zones in a static or dynamic fashion. If sufficient water is lost, the cement either gives rise to non-strengthening filter cake type deposits or else it may flash set. Fluid loss controllers are utilized for maintaining a reasonably constant water-to-solids ratio in cement slurries downhole by controlling the rate of water loss to the permeable formations. A laboratory fluid loss test is given in API RP 10B, the recommended practice for the testing of well cements. Fluid loss control is normally more difficult for extended oilwell cement slurries, because of their higher water/cement ratios.

Polymers such as polyacrylamide and polyethyleneamines have been widely employed as fluid loss controllers. Polyacrylamide (acrylamide/acrylic acid copolymers), which can be prehydrated, can normally be utilized downhole at up to 60°C bottom hole circulating temperature; above that, chemical changes take place which cause extensive retardation of thickening and, in consequence, lower compressive strengths. Chemical modification of polyacrylamide can give better higher temperature performance. Polyethyleneamines appear to behave synergistically with melamine and naphthalene sulfonates, and lignosulfonate retarders, but must be carefully used. This is necessary because the effects of temperature, pressure and mixing time vary between the different types of polymer in this category; in addition problems of free water and interference with compressive strength development that sometimes arise need to be avoided.

Among cellulosic derivatives, both carboxymethylhydroxyethyl-cellulose (CMHEC) and hydroxyethylcellulose (HEC) have been employed as fluid loss controllers. Both CMHEC and HEC retard the cement slurry and increase viscosity slightly, but HEC does not normally retard as much as CMHEC. The limit to their use is the maximum quantity that can be added to a slurry to increase viscosity slightly while remaining mixable and pumpable. At elevated temperatures, as with most viscosifiers, solution viscosity is decreased.

Latex is sometimes utilized, but shows high foaming during mixing with the cement slurry and is expensive.

Dispersants like melamine- and naphthalene-sulfonate superplasticizers also help to prevent water loss. These superplasticizers will slightly accelerate, be neutral, or slightly retard cement thickening depending upon their particular composition, and may also be utilized to lower the viscosity of CMHEC or HEC if the mixes are not suitably pumpable.

Fluid loss controllers appear to function by forming a film on the surface of the formation which impedes the movement of cement slurry water into the formation. Particulate systems have also been employed to control fluid loss by entering the filter cake and lodging between the cement particles, which improves the impermeability of the filter cake, thus reducing the fluid loss. Such particulate fluid loss controllers have included bentonite, carbonate powder, asphaltines, thermoplastic resins and latices such as those of vinylidene chloride (to 50°C), polyvinylacetate (to 50°C) and styrene-butadiene (to 176°C).[12]

2.5 Lost Circulation Controllers

Lost circulation is the total or partial loss of drilling fluid or oilwell cement to high permeability zones, cavernous formations, and natural or induced fractures during the drilling or completion of a well.[12] Lost circulation controllers are additives that form a low permeability bridge across the opening that is accepting fluid. Lost circulation is normally treated at the drilling mud stage by pumping the lost circulation controller with the drilling mud, or sometimes by adding nitrogen to the mud system. It is no longer conventional practice to add such materials to cement slurries, especially for primary cementing jobs, due to logistical difficulties in pumping such slurries into position with the downhole cementing equipment. Should any lost circulation still occur after treatment of the drilling mud, then either a lightweight or a thixotropic cement slurry is usually employed (Sec. 2.11). Indeed, the effectiveness of lost circulation controllers in oilwell cement slurries is limited to minor or partial losses in highly permeable formations and not for solving total lost circulation in naturally fractured or cavernous formations. Foamed cement has been suggested as the only truly effective solution.[12]

Essential requisites for lost circulation (or bridging) materials are the size and shape of their grains and their rigidity and density. A bridging material is deemed suitable for an isolation work if its grain size is not less than one-third of the maximum size of the pores or fractures to be clogged or bridged. Special materials are used to wall off, or plug in, large size fractures.[17]

Lost circulation controllers may be blocking granules such as walnut shells. Other materials like gilsonite, crushed coal (including anthracite) and perlite (expanded or semi-expanded) are occasionally employed. They are chemically inert angular materials which can bridge the fissures. The lost circulation controller must have a suitable particle size distribution so as to form an adequate bridge.[12] Alternatively, lamellated materials like cellophane flakes, which give flake-type mats, can be utilized. Cellophane flakes are thin and tough and maintain their strength when wetted with water. Their matting action is due to their having a higher surface area for sealing action per unit weight of flakes. Fibrous materials, such as nylon fibers, are effective in drilling fluids for sealing off large openings by forming interlocking mats, but cannot normally be used in oilwell cementing because of their high propensity to plug surface and downhole cementing equipment. Synthetic fibers such as nylon do not per se affect cement properties.[12] However, some other fibrous materials contain organic material like lignins and tannins that can seriously retard the thickening of the cement slurries.

In general, fibrous materials produce satisfactory results in bridging small crevices in sandy and gravelly rocks with a grain size (diameter) of up to 25 mm. Lamellated materials are employed for clogging crevices and pores of 2–3 mm across. Granular materials bridge pores and fissures most effectively in beds composed of gravelly rocks with a grain size of 25–30 mm.[17]

The most common lost circulation controllers currently employed in the North Sea are, for instance, walnut shells, mica, shredded paper, and calcium carbonate of different particle sizes, while in Asia, coconut shells and sugar cane are frequently utilized.

2.6 Gas Migration Controllers

Gas migration can be a serious problem for effecting a secure cement sheath. When cement has been pumped into position in the annulus and is in the process of setting and hardening, it is in a state of neither being truly solid nor truly liquid. Gas migration arises by percolation through the cement in this "transition" state and flows if the hydrostatic pressure in the cement column falls below the pore pressure of a gas zone through which the well cementing is being carried out.

Gas migration can be combatted by various means.[12][13] Polymeric additive systems, which can swell and block the pores to prevent water movement within the hardening cement slurry, can stop or at least minimize gas migration. Such systems contain suitable fluid loss controller, retarder, and dispersant that can effectively block the pores. Control of gas migration can also be achieved by in-situ generation of hydrogen gas bubbles from finely-ground aluminium pellets. Alternatively, microsilica can be employed. This is supplied as an aqueous slurry or as the dry product, depending upon gas pressure and weight of cement. The microsilica is normally used in concentrations of 10–50% by weight of cement (as a 50% aqueous slurry). It is very finely divided and is a very effective pore blocker.

2.7 Weighting Agents (Heavyweight Additives)

Weighting agents are used to increase oilwell cement slurry densities in deep or overpressured wells, wherein high hydrostatic pressures govern unstable wellbores, high pore pressures and deformable or plastic formations. Drilling mud densities need to be at least 18 lb/US gallon (2.16 kg/liter) for these conditions. Hence, to maintain control of such wells and prevent blowout, oilwell cement slurries of equal or higher density are necessary, so that effective cementing can be secured.[12][13]

The basic requirements for weighting agents are that they should have s.g.'s within the range of 4.2–5.0 for most purposes, have a low water requirement, minimal effects upon compressive strength of the hardened cement and pumping time for the slurry, and possess a uniform particle size range from batch to batch, which is similar to the cement particle size range to avoid segregation or bleeding from larger particles and increased slurry viscosity from smaller particles during pumping into position in the annulus. Also, they should be chemically inert and not interfere with well logging, the recording of one or more physical parameters of the geological formations as a function of depth in the boreholes. Use of weighting agents should ordinarily achieve cement slurry densities of up to 20 lb/US gallon (2.40 kg/liter).

The principal weighting agents are haematite α-Fe_2O_3, barite $BaSO_4$ and ilmenite $FeTiO_3$. Some sources of barite and ilmenite may contain small traces of radioactivity, which can interfere with well logging. Each potential source of supply should, thus, be checked so that only nonradioactive sources are utilized for well cementing. Various weighting agents are given in Table 1.

Table 1. Specific Gravities of Oilwell Cement Weighting Agents

Weighting Agent	Formula	Typical s.g.
Barite	$BaSO_4$	4.2
Hausmannite	Mn_3O_4	4.3
Iron base spent catalyst (IBSC)	Fe_2O_3	4.5
Ilmenite	$FeTiO_3$	4.7
Haematite	α-Fe_2O_3	5.0
Magnetite	Fe_3O_4	5.2
Ferrosilicon	Fe_x-Si_y	6.5
Specularite (specular iron)	Fe_3O_4	6.6
Ferrophosphorus	Fe_a-P_b	5.4-7.8
Galena	PbS	7.5
Iron arsenite	$FeAsO_3$	8.0

Barite is not commonly used now as a heavyweight agent for well cementing, because it has a significant water requirement for wetting its particles and tends to reduce compressive strength development somewhat. Sometimes it contains a barium carbonate $BaCO_3$ impurity that can accelerate cement thickening, which would require additional retardation as compensation.

Finely divided hausmannite is increasingly being used in heavyweight cement slurries because of its good anti-settlement properties. It has a negligible effect upon thickening time and compressive strength development.

Iron base spent catalyst (IBSC), which is obtained from a petroleum residual conversion process, has similar characteristics to haematite (see below) as a weighting agent.[29]

Ilmenite possesses a very small surface area and does not require additional water for slurry mixing. Like hausmannite, it has negligible influence upon thickening time and compressive strength development. However, its coarser particles have a tendency to settle out relatively easily; alternation of the slurry viscosity can overcome this settling.

Haematite is the most widely utilized weighting agent worldwide. It barely affects the cement slurry properties and has a very low water requirement. Sometimes, its small particle size can create problems at high concentrations when the slurry viscosity increases appreciably—judicious use of dispersant can counteract this effect.

Magnetite is often used in the CIS. It has little effect on the cement slurry properties and its water requirement is even lower than that of haematite.

Ferrosilicon, specularite (a crystalline variant of haematite with a metallic luster), and ferrophosphorus can be utilized to produce cement slurry densities above 20 lb/US gallon (2.40 kg/liter) where required. Ferrosilicon needs to be employed with caution as it sometimes has significant water requirement. Ferrophosphorus is available over a wide density range and needs to be carefully checked for s.g. before usage. Even at the lower density of 5.4, it can produce stable heavyweight slurries at 22 lb/US gallon (2.6 kg/liter).[30] These weighting agents, apart from ferrosilicon in some instances, have only a minimal effect upon cement properties.

For rare occasions when very heavy slurries, ~ 25 lb/US gallon (~ 3.0 kg/liter), have been required in the CIS, iron arsenite has been employed. No mention of its possible toxicity or effects upon cement properties like possible retardation of thickening and hardening have been given.

Galena is occasionally utilized as a weighting agent. However, there is some concern that its sulfide content may contribute to well corrosion problems.

Dispersants should only be used with weighting agents where absolutely necessary to achieve slurry pumpability, otherwise, free water and, hence, segregation of the slurry could ensue. Depending upon the actual slurry density required and the particular weighting agent employed, concentrations of weighting agents can vary from ~ 10% to 100% or more by weight of cement. Condensed silica fume (microsilica) is sometimes employed as a bedding in small concentrations (~ 5–10% by weight of cement) to stabilize heavyweight cement slurries.

Another way of achieving a high density slurry is to use silica sand (s.g., 2.23) in a densified slurry, where the water content is reduced with the aid of a dispersant to increase the slurry density. Slurry densities of up to 18 lb/US gallon (2.16 kg/liter) can be achieved in this way.

2.8 Extenders (Lightweight Additives)

The main function of extenders is to reduce cement slurry density. This lowers the hydrostatic pressure, which in turn minimizes the breakdown of weak rock formations and, thus, the occurrence of lost circulation caused by such breakdown. Extenders basically function by reducing the mobility of water as more water is added to lower the weight of the slurry. A list of extenders is given in Table 2.

Table 2. Extenders Used in Well Cementing

Extender	s.g.	Approx Minimum (lb/US gallon)	Slurry Density (kg/liter)
Bentonite	2.65	11	1.32
Attapulgite	2.89	12	1.44
Pozzolans	2.0 - 2.6	13	1.44
Ground granulated blastfurnace slag	2.4 - 2.6	13	1.56
Sodium silicate	2.64	11	1.32
Diatomite	2.1 - 2.2	11	1.32
Gilsonite	1.07	12	1.44
Crushed coal	1.3	12	1.44
Expanded perlite	2.2 - 2.4	12	1.44
Microspheres	0.65 - 0.85	8	0.96
Nitrogen	-	6	0.72

Bentonite clay (often referred to simply as *gel)* is the most commonly employed lightweight extender.

Bentonite can absorb water and swell. It can hold several times its own weight of water, hence, the slurry volume and the mix water requirements are increased, whereas overall slurry weight is decreased. Amounts of bentonite ranging from 2% to 20% by weight of cement can be used. For each 1% added, the water can be increased by approximately 5.3% and slurry densities of 12–13 lb/US gallon (1.44–1.56 kg/liter) can be attained, yielding a further 60% of slurry volume. Higher levels of bentonite can be utilized, but only if dispersants are employed for lowering the viscosities of these high gel slurries. Sodium chloride is also sometimes used in these slurries. Bentonite, to some degree, limits fluid loss in slurries and can be utilized to prevent free water (free fluid) from developing. Strength retrogression is enhanced by bentonite at temperatures above 110°C, when formation of low strength hydrogarnet phases can arise. Bentonite can be utilized as either dry-blended or prehydrated. Two percent bentonite by weight of cement prehydrated in fresh water will usually absorb as much water as 8% dry-blended, although the slurry yield point is much higher. Dry mixed bentonite does not always hydrate so satisfactorily, because of partial inhibition of calcium ions in the cement slurry. With prehydration, the period of prehydration must not be too long. Allowing the bentonite to prehydrate for 24 hours or more before adding the oilwell cement may actually increase the separation of free water from the slurry and is best avoided. The minimum prehydration time is normally 2–3 hours.

Evaluation of beneficiated bentonites in the laboratory and comparison with untreated natural Wyoming bentonites for lightweight extension of Class G oilwell cement slurries showed that these bentonites can replace Wyoming bentonites in preblended G + 8% BWOC bentonite-cement slurries for lightweight extension at 13.5 lb/US gallon (1.62 kg/liter) in freshwater or in 18% salt water. However, mature blends of G + 8% bentonite in 18% (by weight of water) salt water produced appreciable increases in thickening time and free fluid together with lower plastic viscosities and yield points, indicative of aeration of the cement component by moisture from the bentonite. Such results emphasized that rig storage of bentonite-cement blends can substantially alter field performance and that storage time must be allowed for in slurry design, if successful cementing jobs are to be achieved. It is also possible to employ beneficiated bentonites prehydrated in seawater for lightweight cement slurry extension with additional salt added prior to mixing. However, since yield points and gel strengths are low and operating free water values relatively high, better slurry properties are obtained with prehydration in freshwater. Dispersants can be employed if necessary in freshwater-prehydrated bentonite-cement slurries extended in freshwater to optimize rheological properties and operating free water values. Because bentonite quality is variable, each bentonite consignment (whether beneficiated or untreated Wyoming) must be individually assessed for lightweight slurry formulation, so that successful cementing can be achieved. Judicious selection of materials and quality control procedures should ensure that there is no loss in technical performance in employing beneficiated bentonites.[31]

The effect of calcium chloride on prehydrated bentonite-cement formulations has shown that calcium chloride is not an efficient accelerator when used in conjunction with prehydrated bentonite extended slurries at 13.5 lb/US gallon (1.62 kg/liter). If calcium chloride is included in such formulations, it must be added after prehydration, otherwise an extremely unstable slurry will result. It does not matter when the calcium chloride is added after prehydration, as similar results for particular cementing tests were obtained when calcium chloride was added 4 hours, 1 hour or immediately before cement addition to the slurry. The optimum addition level of calcium chloride was 3% by weight of cement. It is preferable to hydrate the calcium chloride prior to mixing rather than preblending with the cement. This is for logistical reasons and also because calcium chloride is itself deliquescent.[32]

Pozzolans function by tying up calcium and alkali metal hydroxides; in so doing they lower the mobility of water and raise the viscosity of the slurry. They can also be utilized in the form of pozzolanic oilwell cements. Both natural and synthetic types are used (s.g. in range ~ 2.0–2.60). Approximately 2% bentonite is sometimes added to cement-pozzolan mixes to initiate the actual lightweight extension. The amount of pozzolan blended will vary according to the cementing requirements. Mixes which are 50/50 by volume are commonly used. The pozzolan combines gradually with the calcium hydroxide and alkali metal hydroxides to form normal cementitious hydration products such as C-S-H. A pozzolan-containing cement can be convenient to employ because it contains only about 50% oilwell cement, but yields the same volume as a neat oilwell cement and gives a lightweight slurry at the same time. Like bentonite, pozzolans can produce slurry densities of ca. 13 lb/US gallon (1.56 kg/liter). Granulated blast furnace slag is less frequently used than the synthetic pozzolan pulverized fly ash because it is commonly considered to be a less effective water reducer than fly ash. Microsilica has been proposed for the extension, since it does not show the rapid shrinkage effect at the higher water-cement ratios used in extended cement systems. Its pozzolanic activity varies considerably and too much uncombined iron left over from the ferrosilicon process may be included. Rice husk ash is sometimes used for extended systems but often suffers from poor indigenous ashing and consequent poor and variable pozzolanicity.

Sodium silicate is often utilized for lightweight extension in small quantities which assists handling and storage. Two to three percent sodium silicate has a similar yield to 10% bentonite. The sodium silicate reacts with calcium ions from the oilwell cement or from calcium chloride to form a calcium silicate hydrate gel. This effectively ties up large quantities of the slurry mix water without the occurrence of significant free fluid, which can be contrasted with the bentonite or attapulgite where water is absorbed by the clay mineral. Sodium silicate can be used for extension in freshwater or seawater; however, the premixing of this chemical extender in freshwater should best be preceded by the addition of a little calcium chloride.[12][14]

Nitrogen is sometimes employed ahead of the cement slurry downhole to help reduce the bottom hole hydrostatic pressure during cementing operations. It is normally introduced into the drilling mud stream in advance of the cement slurry, or with the hole loaded with mud and circulation established, circulation is stopped and a "slug" of nitrogen is introduced before cementing.[13] This has the effect of producing a very lightweight slurry, particularly when foamers are present.

Other lightweight extenders used include microspheres, ceramic beads and glass beads. Microspheres are usually derived from pozzolanic float ash which is separated off from heavier material in float ponds at steel mills or from specially selected fly ash spheres at power stations. Slurries of 8–12 lb/US gallon (0.96–1.44 kg/liter) can be produced. Ceramic and glass beads may be employed, but are normally more expensive than microspheres. However, glass beads made from sodium borosilicate cannot be employed for most high pressure cementing jobs. Extenders such as microspheres are often utilized with API Class C rapid-hardening cement, so that the compressive strength can be maintained, while the slurry weight is lowered.

Diatomite (diatomaceous earth) is a naturally occurring mineral consisting of hydrated silica. The water requirement is very high. Diatomite is composed of many tiny air-filled cells. When employed in lightweight extension, it can give slurry weights as low as 11 lb/US gallon (1.32 kg/liter). Diatomite does not usually increase slurry viscosity when present in large amounts, unlike bentonite and attagulgite. However, this depends upon how much water is used. It can be employed for high temperature extension above 230°C. Its prime disadvantages are unpredictable strength retrogression and expense.

Gilsonite is a natural asphaltite consisting of high molecular weight hydrocarbons. Gilsonite has some disadvantages: oil-soluble, starts melting at ~ 195°C and high cost. Its main employment has been in downhole situations where some level of lost circulation control is also needed. Around 2–6% bentonite is added to prevent the gilsonite from floating out of the slurry mix. An advantage of gilsonite is that it does not absorb water under pressure. Hence, the hardened lightweight cement is stronger than for other comparable hardened oilwell cements with other lightweight extenders.

Crushed coal (including anthracite) can be used like gilsonite for lightweight extension and lost circulation control. However, additions of bentonite to prevent flotation are not normally needed. Crushed coal may be suitable for high temperature applications like steam injection wells.

Expanded perlite is a siliceous volcanic glass. It contains many tiny independent air voids that are separated by very thick cell walls, which do not fill up with water like those of diatomite. Expanded perlite presents handling problems and is expensive. It actually has two water requirements, one for the surface and another for the downhole pressures, since the structure breaks down under pressure. This behavior permits the slurry mix water to enter the broken down cells and thus raises the viscosity and density of the slurry. Around 2–6% bentonite is required to stop the flotation of perlite in the mix, like for gilsonite.

Attapulgite, or *salt-gel,* used to be employed as an alternative to bentonite when seawater was used, or in saturated salt slurries. Attapulgite hydrates differently from bentonite in that its clusters of fibrous needles become dispersed in water.[14] Mechanical shearing needs to be utilized to achieve this—simple paddle agitation is inadequate. Attapulgite, however, gives no fluid loss control, unlike bentonite; that is due to its having an open needle type of structure, while fully hydrated bentonite has flat sealing plates. Due to the similarity of attapulgite fibers to asbestos fibres, which present a potential health risk, various countries have banned attapulgite from cementing operations. However, not all forms of attapulgite are fibrous, some are granular. These granular forms are still available for lightweight extension in some locations, but are rarely used in practice nowadays.

2.9 Dispersants (Friction Reducers, Thinners or Turbulence Inducers)

Dispersants are substances which improve the flow properties of the cement slurry by breaking up cement agglomerates and freeing the water, thus giving slurries of lower viscosity and permitting turbulent flow conditions to be achieved at lower pump pressures.

Dispersants include superplasticizers like sulfonated melamine formaldehyde condensate (SMFC) and sulfonated naphthalene formaldehyde condensate (SNFC), together with lignosulfonates, sodium chloride (salt), hydroxylated polysaccharides, polyacrylamides and organic acids. Some of these materials, like the lignosulfonates and organic acids, also retard the cement slurries and are generally used at higher temperatures, particularly lignosulfonate-organic acid blends. Of the organic acids, citric acid is often favored for dispersion of cement slurries in saltwater environments. Superplasticizers are excellent dispersants and may slightly retard, be neutral, or slightly accelerate, depending upon their precise composition.

The way dispersants work has been discussed.[12][33] Dispersion of the cement particles involves a modification of the electrostatic interactions at the surfaces to produce charged particles which undergo mutual repulsion. During early hydration, when water is added to the cement, calcium ions from the silicate, aluminate and ferrite phases dissolve in the water and become sorbed during the production of hydration products such as calcium silicate hydrate (C-S-H) at the cement particle surfaces. The sorption of calcium ions from solution and, with this, the ionization of the surface molecules give rise to electrical charges at the cement-water interface. Dispersants such as superplasticizers are anionic; their adsorption from solution onto the positively charged particle sites inverts the positive to a negative charge causing repulsive forces which make the aggregated particles break down into their individual particles. When saturation of the positive surface adsorption sites has been achieved, a state of optimum dispersion exists. There must be not overdosage, since this destroys the microstructure produced by the electrostatic interaction. The cement particles are then no longer self supporting and, hence, the slurry shows a loss in homogeneity and the occurrence of free water (bleeding or settlement) problems.

2.10 Salt for Saline Environments

When it is necessary to cement through salt strata, cement slurries for this purpose are utilized which contain either very high or very low quantities of salt (sodium chloride). Very high means around 18% sodium chloride by weight of water in cementing formulations and very low can be from zero to several % by weight of cement. Details of the techniques used have been described.[12][13]

2.11 Thixotropic Agents

Thixotropic agents induce thixotropic behavior in cement slurries downhole after placement, where there is a need to seal off lost circulation zones or to achieve a good annular fill across incompetent zones to prevent fallback. The cement slurries thicken up rapidly to form rigid gel structures once pumping has stopped. These rigid gel structures are self supporting and lower the hydrostatic pressure to the formation as gel strength increases, thus preventing fallback of the cement column. Lost circulation is addressed by the velocity of the leading edge decreasing when the cement slurry enters the lost circulation (or thief) zone, since the increased resistance to flow plugs the zone. Hence, when the cement slurry thickens up, the zone is effectively consolidated.[12]

The most common thixotropic aid is calcium sulfate hemihydrate $CaSO_4\ 0.5H_2O$. When mixed with an oilwell cement like Class A, G or H, the slurry becomes quick thickening and thixotropic. It develops a high gel strength rapidly when motion ceases. The thixotropic reaction is based upon rehydration to the less soluble dihydrate (gypsum).

$$CaSO_4\ 0.5H_2O + 1.5H_2O \rightarrow CaSO_4\ 2H_2O$$

The false setting properties shown by this reaction allow the thixotropic mix to block most channels accepting the slurry once flow has stopped. The hemihydrate needs to be sufficiently coarse so that the mix can be pumped during 80% of its thickening time, which is greatly affected both by temperature and by the presence of retarding or accelerating additives. Temperature rise significantly lowers the thickening time. Calcium sulfate hemihydrate cannot normally be employed downhole at temperatures above 80°C, because it will not then thicken suitably. Compressive strengths developed by the hydrating hemihydrate are somewhat low compared with those of ordinary portland cements, ~20 MPa at 28°C when fully hardened, but can be raised by addition of portland cement. When mixed with portland cements (optimum additions are normally 8–12% by weight of cement), both thixotropic and expansive properties are developed. These are caused mainly by the formation of gypsum with some arising from the formation of ettringite from the aluminate and ferrite phases. Calcium sulfate hemihydrate actually accelerates portland cement hydration, but is unreliable (as mentioned beforehand under accelerators). Severe stiffening can occur if excessive quantities are mixed with portland cements.

Alternative thixotropic systems in oilwell cements include mixtures of soluble sulfates like iron (II) sulfate and aluminium sulfate[34] that generate gypsum in-situ and give rise to ettringite formation, and the use of proprietary organic-based mixtures. These include the use of water soluble cross-linkable polymers like HEC, CMHEC, polyvinyl alcohol and sulfonated acrylamide polymers with suitable chelating agents of titanium or zirconium.[35]

2.12 Defoamers and Deaerators

Defoamers and deaerators can be distinguished in well cementing. Defoamers are added in small amounts of about 0.2% by weight of cement, either in solid or liquid (solution) form, to remove foaming that arises during the mixing of cement slurries. However, defoamers do not normally remove all air entrained within the slurry. Excessive foaming causes pump cavitation and loss of suction head during cementing, and makes calculations of slurry volume in the mix tub impossible, thus causing the slurry density to read low on a mud balance or densitometer. This can result in a higher density slurry than is needed for the particular cementing operation. The main cause of foaming is the employment of additives in cement slurries like the salts of organic acids. Defoamers lower surface tension and need to be insoluble in water to be effective. Examples of defoamers include dodecyl (lauryl) alcohol, polypropylene glycols, and lower sulfonate oils.

Deaerators are utilized for removing entrained air from cement slurries, where appropriate, in small quantities similar to defoamers. Slurry weights may be changed by as much as 4–5% by entrained air. Adjusting the slurry weight to compensate for entrained air can sometimes be achieved by adding more water, but this could produce too a fluid mix. Alternatively, a pressure balance could be used which can eliminate entrained air by subjecting the slurry to about 250 psi (1.7 MPa) pressure. Air entrainment, like foaming, mainly arises through the use of additives such as salts or organic acids in cement slurries, particularly lignosulfonates and other retarders. Examples of deaerators include dibutylphthalate, tributylphosphate and silicone polymers like polydimethylsiloxane. Tributylphosphate can cause nausea and is preferably not employed.

2.13 Foamers

As discussed in Sec. 2.12, cementing formulations normally need some use, however small, of a defoamer, since the presence of foam is detrimental. However, when ultralightweight cement slurries with densities as low as 6 lb/US gallon (0.72 kg/liter) are required, appropriate foaming agents are employed to assist in generating and stabilizing the foamed cement slurry formed in a highly alkaline environment at high down hole temperatures and pressures. In foamed slurries gaseous nitrogen is incorporated directly into the slurry at injection rates of 200–15000 scf/minute (6–245 m^3/minute), depending upon depth, temperature and pressure, as a foam density control agent, in order to produce an effective ultralightweight system. Importantly, the effects of other additives present in the foamed cement slurry are generally similar to their corresponding effects in neat non-foamed cement slurry. Foamed cement slurries are utilized mainly for primary cementing of weak formations, and also for overcoming lost circulation in cavernous vugs, for squeeze cementing of depleted zones, for zonal isolation and for heat insulation.[12] Cationic and anionic surfactants can both be used as foamers in small quantities.

2.14 Coloring Materials

Coloring materials are periodically used to color cement slurries in order to see whether they return to the surface or not during cementing operations. Such materials include mica, which is normally satisfactory for subsea returns, calcium carbide CaC_2 (as a slug) which is often preferable for determining circulation volume both on land and offshore wells due to its distinctive black color in cement slurries, and dyestuffs or pigments. Dyestuffs so used include fluorescein, methylene blue and phenolphthalein, while pigments include yellow or red iron oxide, all at concentrations of about 0.1% by weight of cement. However, it should be borne in mind that sometimes the effects of drilling mud contamination and/or dilution may cause the dyestuffs to become ineffectual by dimming or clouding their colors.[13]

2.15 Radioactive Tracers

Radioactive tracers are sometimes added to oilwell cement slurries as markers, which can be detected by logging devices. Location of cement tops, location plus disposition of squeeze cement (used in remedial work), and tracing lost circulation and fracturing are examples of their application. Radioisotopes used in cement include ^{46}Sc, ^{131}I and ^{192}Ir, which have respective half-lives of 84, 8 and 74 days. ^{131}I is not recommended for squeeze cementing. By the proper selection of radioactive tracer, the time required to get back into the well for a survey can be programmed.[13]

For environmental reasons, radioactive isotopes cannot be utilized indiscriminately and their usage should be controlled and licensed by the appropriate national regulatory agencies.

3.0 SPECIAL OILWELL CEMENTS AND ADDITIVE USAGE

A number of special oilwell cements are considered from the viewpoint of additive usage.

3.1 Dicalcium Silicate - Silica (Class J) Cement

This high temperature cement utilizes similar additives to portland oilwell cements under comparable conditions, since thickening and hardening here are also basically manifestations of a calcium silicate hydrate formation. For instance, sugar-lignin derivatives give good retardation at 0.1% addition level and calcium chloride is (if required) an excellent accelerator at 2% addition.[36]

3.2 Calcium Aluminate (High Alumina) Cement

Calcium aluminate cements are employed at high temperatures (up to 1000°C or more) in fireflood and geothermal wells and at low temperatures (around 0 to -10°C) for cementing through permafrost in Arctic environments.[12][13][37]

At high temperatures calcium aluminate cement shows considerable resistance to the great temperature fluctuations commonly experienced in fireflood and geothermal wells, due primarily to the absence of calcium hydroxide as a hydration product. The loss in compressive strength that arises at 900–1100°C needs to be accommodated, so that the minimum compressive strength attained can maintain the integrity of the well.[37] The quantity of added water should be the minimum required to achieve a pumpable slurry and may require the use of dispersants. Extenders enable calcium aluminate cement to be utilized effectively at very high temperatures. For optimum performance with extenders, calcium aluminate cement should be at least 50% of the solids content. Suitable extenders include crushed aluminosilicate firebrick, calcined bauxite, certain fly ashes, diatomaceous earth, and perlite. Such extenders must be stable at high temperatures, must not decompose, nor must they show anomalous thermal expansions or inversions. Silica sand should not be utilized above 300°C, because thermal expansion of quartz is relatively high above this temperature and thermal cycling could eventually disrupt the hardened cement.[12][13]

At low temperatures, calcium aluminate cement is diluted with pulverized fly ash to function as a filler (normally in 50/50 quantities), which lowers the heat of hydration generated in order to minimize any damage to the permafrost, when cementing surface and conductor casings in a permafrost environment. Calcium aluminate cements can thicken and harden appreciably around 0°C, by formation primarily of CAH_{10}.[37] Suitable accelerators can be utilized if the thickening time is too long under these conditions.

It is important to remember that additives can sometimes behave differently with calcium aluminate cement than with portland cements, including portland oilwell cements. For instance, superplasticizing dispersants for portland oilwell cements, like the sulfonated melamine and naphthalene formaldehyde condensates, behave merely as plasticizing dispersants for calcium aluminate cement. They do not appear to affect either the hydration process for calcium aluminate cement or the hydrates produced, but conversion to C_3AH_6 appears to be somewhat accelerated. True superplasticizing dispersants for calcium aluminate cement have not yet been produced. Although calcium chloride accelerates portland oilwell cement hydration, it is actually a retarder for calcium aluminate cement hydration. Lithium salts, such as the chloride LiCl, are effective accelerators for calcium aluminate cement—the carbonate Li_2CO_3 is often too efficient and may produce a flash set. When LiCl is used as an accelerator in small quantities, CAH_{10}, C_2AH_8 and C_4AH_{13} are found as transient hydration products prior to conversion to C_3AH_6. C_4AH_{13} is not normally found in abundant quantities in calcium aluminate cement hydration, but is observed here due to changes in the solubility relationships giving a higher lime to alumina ratio which favors the formation of significant amounts of C_4AH_{13}. Sodium hexametaphosphate accelerates above ~20°C but retards hydration below this temperature. Lignosulfonates and citric acid retard calcium aluminate cement hydration.[37][38]

The effects of accelerating and retarding additives can be understood on the basis of calcium aluminate cement hydration occurring by precipitation of the hydrates in the liquid phase. Foreign cations that accelerate the setting like Li^+ and also Co^{2+} and Ni^{2+}, do so by heterogeneous nucleation. This acceleration can be explained in terms of release of Ca^{2+} ions by precipitation of $Al(OH)_3$ or aluminate salt into the solution phase. Li^+ may have other effects to explain its dramatic efficiency. Lime-rich products like CAH_{10} and C_4AH_{13} are formed here because the Ca/Al ratio in solution is much higher in the presence of LiCl, as mentioned above. However, the corresponding role of the anions is not yet clearly understood. The added chloride salts barely alter the total heat of hydration measured with a microcalorimeter. Retardation of setting can be attributed to chelation of Ca^{2+} ions in solution with the retarder.[37][38]

3.3 Sorel (Magnesium Oxychloride) Cement

Pure Sorel cement is not employed in well cementing because of the significant aqueous solubility of the magnesium chloride hydroxide hydrates formed upon hardening.[39] However, modified Sorel cements containing carbonates can be utilized, because the magnesium carbonate chloride hydroxide hydrates and carbonate hydroxide hydrate formed have a far greater resistance to water.

One particular development, used as a specialist oilwell cement, is *acid-soluble magnesia cement (ASMC)*. This consists of a stoichiometric mixture of magnesium and calcium oxides, carbonates and sulfates, which is hydrated in chloride-containing waters (brines). The cement mix is described as reacting by polymerization to form a magnesium-hydroxy-sulfate-chloride-polyhydrate of high compressive strength.[40] This cement has been employed in production zones and for water injection zones of wells to reduce brine losses during completion and workover (repair) operations. Its acid solubility minimizes potential formation damage.

Additives are often utilized with ASMC. Retardation is less easily controlled than for portland oilwell cements and much retarder has to be used. For example, up to 100°C, 4–12% borax may be required to retard thickening sufficiently to give a workable thickening time of 3–4 hours compared with around 0.2–0.3% for a conventional Class G or Class H oilwell cement. Thickening time can be further modified as appropriate with suitable accelerators. Similar dispersants (e.g., SMFC, SNFC), weighting agents (barite, haematite etc.), lightweight additives (microspheres etc.) and fluid loss controllers (polymeric systems) can often be used as for conventional Class G or Class H oilwell cements, but the amounts required may differ significantly.

3.4 Drilling Mud-to-Cement Conversion

In more recent times, a number of wells have been cemented by adding ground granulated blast furnace slag to the drilling mud and activating the slag with alkali (sodium hydroxide, carbonate silicate etc.) to cement the mud and obviate the need for its external disposal and for the specific use of oilwell cements.[41]-[43] Additives like retarders and dispersants can be added to the mix to control the thickening time and rate of gain of compressive strength as appropriate. However, it has been considered that the use of blastfurnace slag for such oil field applications should be carefully evaluated on a per case basis and that further research needs to be done before the technique can be more widely recommended.[44] Clearly, more work needs to be undertaken in order to assess accurately just how wide the true potential is for drilling mud-to-cement conversion.

4.0 CONCLUSIONS

This brief overview has characterized the main types of additives employed in cementing with oilwell cement systems. Mechanistic information has been given, where known, in order to throw more light on the complexities of interaction with the cement hydration process. It has been shown that various additives, particularly accelerators and retarders, but also to some extent others like dispersants and fluid loss controllers themselves exert a significant effect upon the hydration reactions of the hydraulic components of the cements considered.

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