Modern Cement Factory
Courtesy : Grasim Industries Cement Division

1

C H A P T E R

Cement

General

The history of cementing material is as old as the history of engineering construction. Some kind of cementing materials were used by Egyptians, Romans and Indians in their ancient constructions. It is believed that the early Egyptians mostly used cementing materials, obtained by burning gypsum. Not much light has been thrown on cementing material, used in the construction of the cities of Harappa and Mohenjadaro.

An analysis of mortar from the Great Pyramid showed that it contained 81.5 per cent calcium sulphate and only 9.5 per cent carbonate. The early Greeks and Romans used cementing materials obtained by burning limestones. The remarkable hardness of the mortar used in early Roman brickworks, some of which still exist, is presenting sufficient evidence of the perfection which the art of cementing material had attained in ancient times. The superiority of Roman mortar has been attributed to thoroughness of mixing and long continued ramming.

The Greeks and Romans later became aware of the fact that certain volcanic ash and tuff, when

mixed with lime and sand yielded mortar possessing superior strength and better durability in fresh or salt water. Roman builders used volcanic tuff found near Pozzuoli village near Mount Vesuvius in Italy. This volcanic tuff or ash mostly siliceous in nature thus acquired the name Pozzolana. Later on, the name Pozzolana was applied to any other material, natural or artificial, having nearly the same composition as that of volcanic tuff or ash found at Pozzuoli. The Romans, in the absence of natural volcanic ash, used powered tiles or pottery as pozzolana. In India. powered brick named *surkhi* has been used in mortar. The Indian practice of through mixing and long continued ramming of lime mortar with or without the addition of *Surkhi* yielded strong and impervious mortar which confirmed the secret of superiority of Roman mortar.

It is learnt that the Romans added blood, milk and lard to their mortar and concrete to achieve better workability. Haemoglobin is a powerful air-entraining agent and plasticizer, which perhaps is yet another reason for the durability of Roman structures. Probably they did not know about the durability aspect but used them as workability agents. The cementing material made by Romans using lime and natural or artificial Pozzolana retained its position as the chief building material for all work, particularly, for hydraulic construction. Belidor, a principal authority in hydraulic construction, recommended an intimate mixture of tiles, stone chips, and scales from a black-smith's forge, carefully ground, washed free from coal and dirt, dried and sifted and then mixed with fresh slaked lime for making good concrete.

When we come to more recent times, the most important advance in the knowledge of cements, the forerunner to the discoveries and manufacture of all modern cements is undoubtedly the investigations carried out by John Smeaton. When he was called upon to rebuild the Eddystone Light-house in 1756, he made extensive enquiries into the state of art existing in those days and also conducted experiments with a view to find out the best material to withstand the severe action of sea water. Finally, he concluded that lime-stones which contained considerable proportion of clayey matter yielded better lime possessing superior hydraulic properties. In spite of the success of Smeaton's experiments, the use of hydraulic lime made little progress, and the old practice of mixture of lime and pozzolana remained popular for a long period. In 1976 hydraulic cement was made by calcining nodules of argillaceous lime-stones. In about 1800 the product thus obtained was called Roman cement. This type of cement was in use till about 1850 after which this was outdated by portland cement.

Early History of Modern Cement

The investigations of L.J. Vicat led him to prepare an artificial hydraulic lime by calcining an intimate mixture of limestone and clay. This process may be regarded as the leading knowledge to the manufacture of Portland cement. James Frost also patented a cement of this kind in 1811 and established a factory in London district.

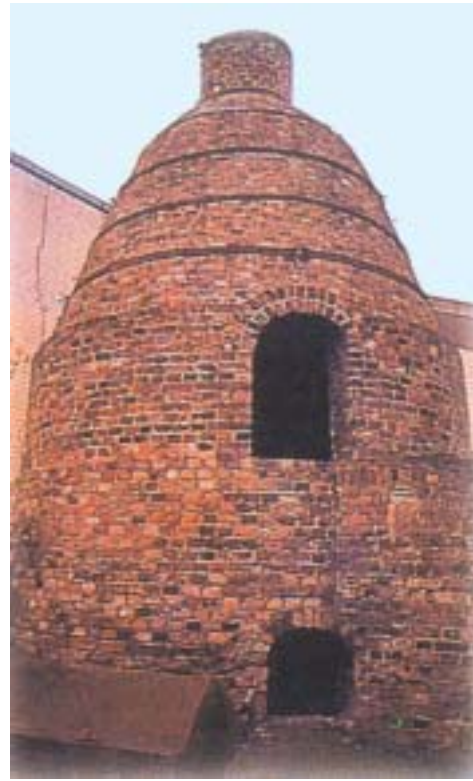Joseph Aspdin's first cement works, around 1823, at Kirkgate in Wakefield, UK.
Courtesy : Ambuja Technical Literature

The story of the invention of Portland cement is, however, attributed to Joseph Aspdin, a Leeds builder and bricklayer, even though similar procedures had been adopted by other inventors. Joseph Aspdin took the patent of portland cement on 21st October 1824. The fancy name of portland was given owing to the resemblance of this hardened cement to the natural stone occurring at Portland in England. In his process Aspdin mixed and ground hard limestones and finely divided clay into the form of slurry and calcined it in a furnace similar to a lime kiln till the CO_2 was expelled. The mixture so calcined was then ground to a fine powder. Perhaps, a temperature lower than the clinkering temperature was used by Aspdin. Later in 1845 Isaac Charles Johnson burnt a mixture of clay and chalk till the clinkering stage to make better cement and established factories in 1851.

In the early period, cement was used for making mortar only. Later the use of cement was extended for making concrete. As the use of Portland cement was increased for making concrete, engineers called for consistently higher standard material for use in major works. Association of Engineers, Consumers and Cement Manufacturers have been established to specify standards for cement. The German standard specification for Portland cement was drawn in 1877. The British standard specification was first drawn up in 1904. The first ASTM specification was issued in 1904.

Oldest surviving kiln, northeast Kent, UK, (1847AD).
Courtesy : Ambuja Technical Literature

In India, Portland cement was first manufactured in 1904 near Madras, by the South India Industrial Ltd. But this venture failed. Between 1912 and 1913, the Indian Cement Co. Ltd., was established at Porbander (Gujarat) and by 1914 this Company was able to deliver about 1000 tons of Portland cement. By 1918 three factories were established. Together they were able to produce about 85000 tons of cement per year. During the First Five-Year Plan (1951-1956) cement production in India rose from 2.69 million tons to 4.60 million tons. By 1969 the total production of cement in India was 13.2 million tons and India was then occupying the 9th place in the world, with the USSR producing 89.4 million tonnes and the USA producing 70.5 million tonnes[1.1]. Table 1.1 shows the Growth of Cement Industry through Plans.

Prior to the manufacture of Portland cement in India, it was imported from UK and only a few reinforced concrete structures were built with imported cement. A three storeyed structure built at Byculla, Bombay is one of the oldest RCC structures using Portland cement in India. A concrete masonry building on Mount Road at Madras (1903), the har-ki-pahari bridge at Haridwar (1908) and the Cotton Depot Bombay, then one of the largest of its kind in the world (1922) are some of the oldest concrete structures in India.[1.2]

Table 1.1. Growth of Cement Industry through Plans

Five Year Plan	At the end of the Year	Capacity (*)	%age Growth	Production (*)	%age Growth Cement	GDP Growth
Pre Plan	50-51	3.28		2.20		
I Plan	55-56	5.02		4.60		
II Plan	60-61	9.30	13.12	7.97	11.62	7.1
III Plan	65-66	12.00	5.23	10.97	6.60	3.4
There were Annual Plans for 1966-67, 67-68 and 68-69						
IV Plan	73.74	19.76	10.49	14.66	5.97	4.6
V Plan	78-79	22.58	2.70	19.42	5.78	5.5
VI Plan	84-85	42.00	13.22	30.13	9.18	3.8
VII Plan	89-90	61.55	7.94	45.41	8.55	6.9
Annual	90-91	64.36	0.90	48.90	1.49	5.4
Plans	91-92	66.56	3.42	53.61	9.63	5.3
VIII Plan	92-93	70.19	5.45	54.08	0.88	4.1
	93-94	76.88	9.53	57.96	7.17	6.0
	94-95	83.69	8.86	62.35	7.57	7.2
	95-96	97.25	16.20	69.57	11.58	7.1
	96-97	105.25	8.23	76.22	9.56	6.8
IX Plan	97-98	109.30	3.85	83.16	9.10	5.2

(*) Includes mini cement plants

Source: Indian Cement Industry Emerging Trends — P. Parthsarathy and S.M. Chakravarthy

Table 1.2. Per Capita Cement Consumption of Selected Countries of the World (1982, 1994 and 1997)

Country	Per Capita Cement Consumption (Kg.)		
	1982	1994	1997
USA	256	328	347
China	92	333	388
Taiwan	590	1285	966
Japan	617	642	622
Malaysia	290	512	831
Thailand	132	491	595
Argentina	198	184	145 (1996)
Brazil	201	165	240
Venezuela	356	222	169 (1996)
Turkey	251	436	511
World	188	241	252 (1995)

India 78 kg (1996), 82 kg (1997)

The perusal of table 1.2 shows that per capita cement consumption in India is much less than world average. Considerable infrastructural development is needed to build modern India. Production of more cement, knowledge and economical utilisation of cement is the need of the day.

The early scientific study of cements did not reveal much about the chemical reactions that take place at the time burning. A deeper study of the fact that the clayey constituents of limestone are responsible for the hydraulic properties in lime (as established by John Smeaton) was not taken for further research. It may be mentioned that among the earlier cement technologists, Vicat, Le Chatelier and Michaelis were the pioneers in the theoretical and practical field.

Systematic work on the composition and chemical reaction of Portland cement was first begun in the United States. The study on setting was undertaken by the Bureau of Standards and since 1926 much work on the study of Portland cement was also conducted by the Portland Cement Association, U.K. By this time, the manufacture and use of Portland cement had spread to many countries. Scientific work on cements and fundamental contributions to the chemistry of Portland cements were carried out in Germany, Italy, France, Sweden, Canada and USSR, in addition to Britain and USA. In Great Britain with the establishment of Building Research Station in 1921 a systematic research programme was undertaken and many major contributions have been made. Early literatures on the development and use of Portland cements may be found in the Building Science Abstracts published by Building Research Station U.K. since 1928, "Documentation Bibliographique" issued quarterly since 1948 in France and "Handbuch der Zement Literature" in Germany.

Manufacture of Portland Cement

The raw materials required for manufacture of Portland cement are calcareous materials, such as limestone or chalk, and argillaceous material such as shale or clay. Cement factories are established where these raw materials are available in plenty. Cement factories have come up in many regions in India, eliminating the inconvenience of long distance transportation of raw and finished materials.

The process of manufacture of cement consists of grinding the raw materials, mixing them intimately in certain proportions depending upon their purity and composition and burning them in a kiln at a temperature of about 1300 to 1500°C, at which temperature, the material sinters and partially fuses to form nodular shaped clinker. The clinker is cooled and ground to fine powder with addition of about 3 to 5% of gypsum. The product formed by using this procedure is Portland cement.
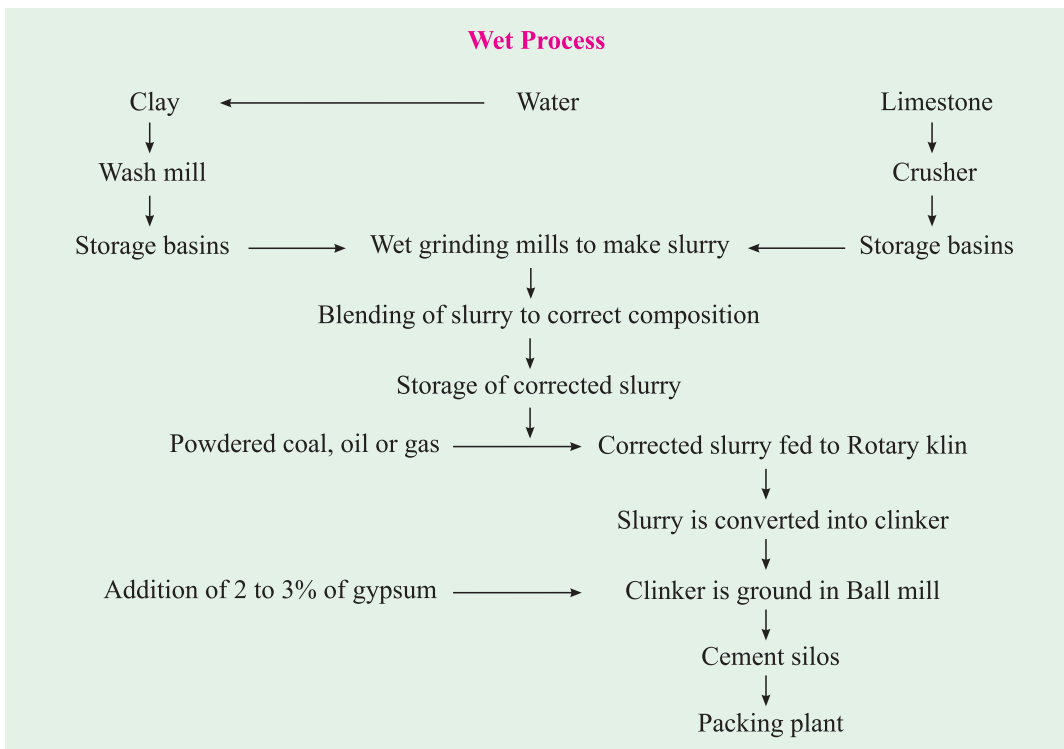
There are two processes known as "wet" and "dry" processes depending upon whether the mixing and grinding of raw materials is done in wet or dry conditions. With a little change in the above process we have the semi-dry process also where the raw materials are ground dry and then mixed with about 10-14 per cent of water and further burnt to clinkering temperature.

For many years the wet process remained popular because of the possibility of more accurate control in the mixing of raw materials. The techniques of intimate mixing of raw materials in powder form was not available then. Later, the dry process gained momentum with the modern development of the technique of dry mixing of powdered materials using compressed air. The dry process requires much less fuel as the materials are already in a dry state, whereas in the wet process the slurry contains about 35 to 50 per cent water. To dry

the slurry we thus require more fuel. In India most of the cement factories used the wet process. Recently a number of factories have been commissioned to employ the dry process method. Within next few years most of the cement factories will adopt dry process system.

In the wet process, the limestone brought from the quarries is first crushed to smaller fragments. Then it is taken to a ball or tube mill where it is mixed with clay or shale as the case may be and ground to a fine consistency of slurry with the addition of water. The slurry is a liquid of creamy consistency with water content of about 35 to 50 per cent, wherein particles, crushed to the fineness of Indian Standard Sieve number 9, are held in suspension. The slurry is pumped to slurry tanks or basins where it is kept in an agitated condition by means of rotating arms with chains or blowing compressed air from the bottom to prevent settling of limestone and clay particles. The composition of the slurry is tested to give the required chemical composition and corrected periodically in the tube mill and also in the slurry tank by blending slurry from different storage tanks. Finally, the corrected slurry is stored in the final storage tanks and kept in a homogeneous condition by the agitation of slurry.

The corrected slurry is sprayed on to the upper end of a rotary kiln against hot heavy hanging chains. The rotary kiln is an important component of a cement factory. It is a thick steel cylinder of diameter anything from 3 metres to 8 metres, lined with refractory materials, mounted on roller bearings and capable of rotating about its own axis at a specified speed. The length of the rotary kiln may vary anything from 30 metres to 200 metres. The slurry on being sprayed against a hot surface of flexible chain loses moisture and becomes flakes. These flakes peel off and fall on the floor. The rotation of the rotary kiln causes the flakes to move from the upper end towards the lower end of the kiln subjecting itself to higher and higher temperature. The kiln is fired from the lower end. The fuel is either powered coal, oil or natural gass. By the time the material rolls down to the lower end of the rotary kiln, the dry material
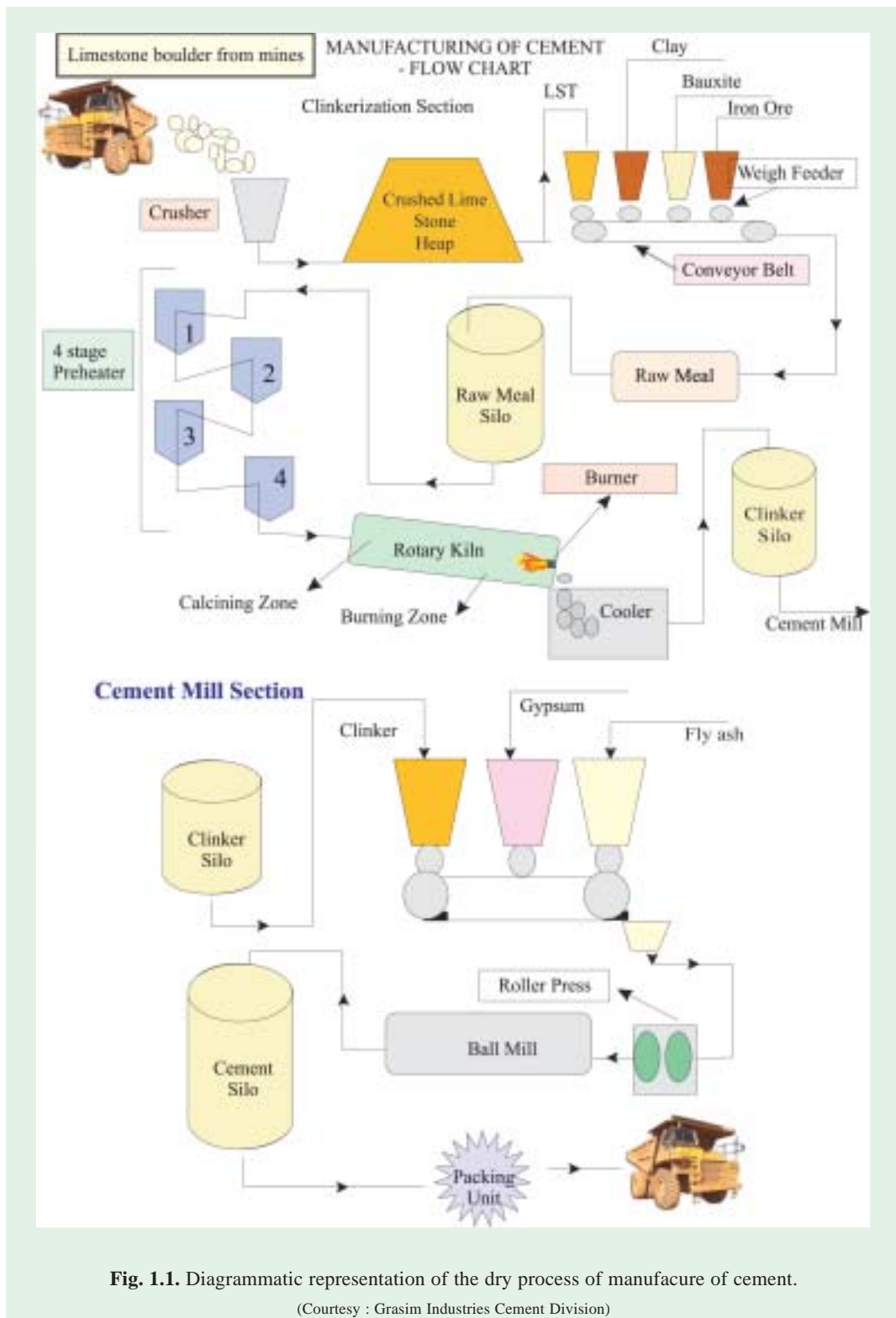

Wet Process

Clay ← Water   Limestone

Clay → Wash mill → Storage basins → Wet grinding mills to make slurry ← Storage basins ← Crusher ← Limestone

Wet grinding mills to make slurry → Blending of slurry to correct composition → Storage of corrected slurry

Powdered coal, oil or gas → Corrected slurry fed to Rotary klin → Slurry is converted into clinker

Addition of 2 to 3% of gypsum → Clinker is ground in Ball mill → Cement silos → Packing plant

Fig. 1.1. Diagrammatic representation of the dry process of manufacure of cement.
(Courtesy : Grasim Industries Cement Division)

A view of Limestone quarry, *raw material preparation :* The prime raw material limestone after blasting in mines is broken into big boulders. Then it is transported by dumpers, tippers to limestone crusher where it is crushed to 15 to 20 mm size.

◄

STACKER FOR CRUSHED LIMESTONE

RECLAIMER FOR CRUSHED LIMESTONE

After crushing, the crushed limestone is piled longitudinally by an equipment called stacker. The stacker deposits limestone longitudinally in the form of a pile. The pile is normally 250 to 300 m long and 8-10 m height. The reclaimer cuts the pile vertically, simultaneously from top to bottom to ensure homogenization of limestone.

Reclaimer for homogenization of crushed limestone.

undergoes a series of chemical reactions until finally, in the hottest part of the kiln, where the temperature is in the order of 1500°C, about 20 to 30 per cent of the materials get fused. Lime, silica and alumina get recombined. The fused mass turns into nodular form of size 3 mm to 20 mm known as clinker. The clinker drops into a rotary cooler where it is cooled under controlled conditions The clinker is stored in silos or bins. The clinker weighs about 1100 to 1300 gms per litre. The litre weight of clinker indicates the quality of clinker.

The cooled clinker is then ground in a ball mill with the addition of 3 to 5 per cent of gypsum in order to prevent flash-setting of the cement. A ball mill consists of several compartments charged with progressively smaller hardened steel balls. The particles crushed to the required fineness are separated by currents of air and taken to storage silos from where the cement is bagged or filled into barrels for bulk supply to dams or other large work sites.

In the modern process of grinding, the particle size distribution of cement particles are maintained in such a way as to give desirable grading pattern. Just as the good grading of aggregates is essential for making good concrete, it is now recognised that good grading pattern of the cement particles is also important.

The Fig. 1.1 shows the flow diagram of dry process of manufacture of cement.

Dry Process

In the dry and semi-dry process the raw materials are crushed dry and fed in correct proportions into a grinding mill where they are dried and reduced to a very fine powder. The dry powder called the raw meal is then further blended and corrected for its right composition and mixed by means of compressed air. The aerated powder tends to behave almost like liquid and in about one hour of aeration a uniform mixture is obtained.

The blended meal is further sieved and fed into a rotating disc called granulator. A quantity of water about 12 per cent by wright is added to make the blended meal into pellets. This is done to permit air flow for exchange of heat for further chemical reactions and conversion of the same into clinker further in the rotary kiln.

The equipments used in the dry process kiln is comparatively smaller. The process is quite economical. The total consumption of coal in this method is only about 100 kg when compared to the requirement of about 350 kg for producing a ton of cement in the wet process. During March 1998, in India, there were 173 large plants operating, out of which 49 plants used wet process, 115 plants used dry process and 9 plants used semi-dry process.

Since the time of partial liberalisation of cement industry in India (1982), there has been an upgradation in the quality of cement. Many cement companies upgraded their plants both in respect of capacity and quality. Many of the recent plants employed the best equipments, such as cross belt analyser manufactured by Gamma-Metrics of USA to find the composition of limestone at the conveyor belts, high pressure twin roller press, six stage preheater, precalciner and vertical roller mill. The latest process includes stacker and reclaimer, on-line X-ray analyser, Fuzzy Logic kiln control system and other modern process control. In one of the recently built cement plant at Reddypalayam near Trichy, by Grasim Indistries, employed Robot for automatic collection of hourly samples from 5 different places on the process line and help analyse the ame, throughout 24 hours, untouched by men, to avoid human errors in quality control. With all the above sophisticated equipments and controls, consistent quality of clinker is produced.

The methods are commonly employed for direct control of quality of clinker. The first method involves reflected light optical microscopy of polished and etched section of clinker,

RAW MILL

The proportioned raw materials are transported by belt conveyor to Raw Mill for grinding into powder form before burning.

RAW MEAL SILO

After grinding, the powdered raw mix, is stored in a raw meal-silo where blending takes place. Blending is done by injecting compressed air. Generally blending ratio is 1:10. This powder material (Raw meal) is fed to the kiln for burning.

ROBO LAB

Consists of automatic sampling and sending station located at different locations in the plant. Samples are being sent through pneumatic tubes to Robo lab. This avoids human error in sampling and ensures accurate quality in semi finished and finished products. 1st of its kind in India has been used at Grasim Cement plant at Reddypalayam.


Robot receiving samples.

Close circuit grinding technology is most modern grinding system for raw mix as well as for clinker grinding. The systems are in compound mode and are equipped with high efficiency Roller press and separators. The above mentioned system enables to maintain low power consumption for grinding as well as narrow particle size distribution. With this circuit, it is possible to manufacture higher surface area of product as per customers, requirement.

Electronic packers: it has continuous weighing system and it ensures that the bags separating from the nozzles have accurate weight of cement. The weight of filled bag is also displayed on the packer.

Multi-compartment silo.
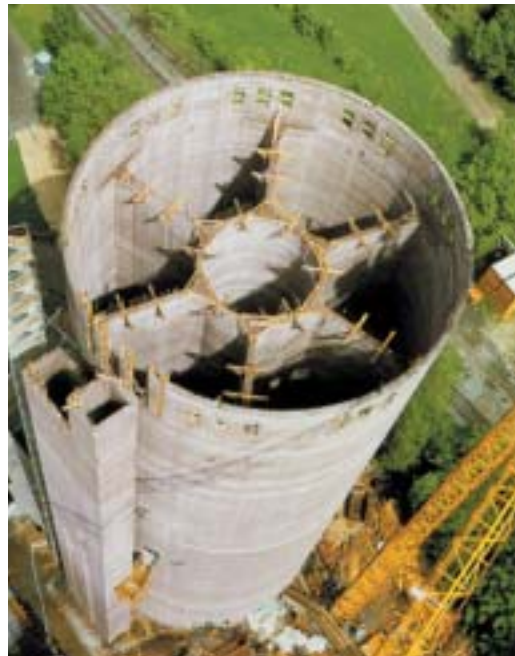
Cross section of multi-compartment silo.

Jumbo bag transportation.

followed by point count of areas occupied by various compounds. The second method, which is also applicable to powdered cement, involves X-ray diffraction of powder specimen. Calibration curves based on known mixtures of pure compounds, help to estimate the compound composition. As a rough and ready method, litre weight (bulk density) of clinker is made use of to ascertain the quality. A litre weight of about 1200 gms. is found to be satisfactory.

Jumbo bag packing.

It is important to note that the strength properties of cement are considerably influenced by the cooling rate of clinker. This fact has of late attracted the attention of both the cement manufacturers and machinery producers. The experimental results reported by Enkegaard are shown in table 1.3.

Table 1.3. Influence of Rate of Cooling on Compressive Strength[1.3]

Type of cement	Cooling conditions	Compressive Strength MPa		
		3 days	7 days	28 days
Normal Cement	Quick	9.9	15.3	26
	Moderate	9.7	21.0	27
	Slow	9.7	19.3	24
	Very slow	8.7	18.7	23
High early strength cement	Quick	10.2	18.8	29
	Moderate	14.2	26.7	33
	Slow	10.2	21.0	29
	Very Slow	9.1	18.1	28

It can be seen from the table that a moderate rate of cooling of clinker in the rotary cooler will result in higher strength. By moderate cooling it is implied that from about 1200°C, the clinker is brought to about 500°C in about 15 minutes and from the 500°C the temperature is brought down to normal atmospheric temperature in about 10 minutes.

The rate of cooling influences the degree of crystallisation, the size of the crystal and the amount of amorphous materials present in the clinker. The properties of this amorphous material for similar chemical composition will be different from the one which is crystallined.

Chemical Composition

The raw materials used for the manufacture of cement consist mainly of lime, silica, alumina and iron oxide. These oxides interact with one another in the kiln at high temperature to form more complex compounds. The relative proportions of these oxide compositions are responsible for influencing the various properties of cement; in addition to rate of cooling and fineness of grinding. Table 1.4 shows the approximate oxide composition limits of ordinary Portland cement.

Table 1.4. Approximate Oxide Composition Limits of Ordinary Portland Cement

Oxide	Per cent content
CaO	60–67
SiO_2	17–25
Al_2O_3	3.0–8.0
Fe_2O_3	0.5–6.0
MgO	0.1–4.0
Alkalies (K_2O, Na_2O)	0.4–1.3
SO_3	1.3–3.0

Indian standard specification for 33 grade cement, IS 269-1989, specifies the following chemical requirements:

(a) Ratio of percentage of lime to percentage of silica, alumina and iron oxide; known as Lime Saturation Factor, when calculated by the formula

$$\frac{CaO - 0.7\,SO_3}{2.8\,SiO_2 + 1.2\,Al_2O_3 + 0.65\,Fe_2O_3}$$ Not greater than 1.02 and not less than 0.66

(b) Ratio of percentage of alumina to that of iron oxide   Not less tan 0.66

(c) Weight of insoluble residue   Not more than 4 per cent

(d) Weight of magnesia   Not more than 6 per cent

(e) Total sulphur content, calculated as sulphuric when   Not more than 2.5%

anhydride (SO_3) C_3A is 5% or less. Not more than 3%, when C_3A is more than 5%

(f) Total loss on ignition   Not more than 5 per cent

As mentioned earlier the oxides persent in the raw materials when subjected to high clinkering temperature combine with each other to form complex compounds. The identification of the major compounds is largely based on R.H. Bogue's work and hence it is called "Bogue's Compounds". The four compounds usually regarded as major compounds are listed in table 1.5.

Table 1.5. Bogue's Compounds

Name of Compound	Formula	Abbreviated Formula
Tricalcium silicate	3 $CaO.SiO_2$	C_3S
Dicalcium silicate	2 $CaO.Sio_2$	C_2S
Tricalcium aluminate	3 $Cao.Al_2O_3$	C_3A
Tetracalcium aluminoferrite	4 $CaO.Al_2O_3.Fe_2O_3$	C_4AF

It is to be noted that for simplicity's sake abbreviated notations are used. C stands for CaO, S stands for SiO_2, A for Al_2O_3, F for Fe_2O_3 and H for H_2O.

The equations suggested by Bogue for calculating the percentages of major compounds are given below.

$$C_3S = 4.07 \, (CaO) - 7.60 \, (SiO_2) - 6.72 \, (Al_2O_3) - 1.43 \, (Fe_2O_3) - 2.85 \, (SO_3)$$
$$C_2S = 2.87 \, (SiO_2) - 0.754 \, (3CaO.SiO_2)$$
$$C_3A = 2.65 \, (Al_2O_3) - 1.69 \, (Fe_2O_3)$$
$$C_4AF = 3.04 \, (Fe_2O_3)$$

The oxide shown within the brackets represents the percentage of the same in the raw materials.

Table 1.6. The Oxide Composition of a Typical Portland Cement and the Corrosponding Calculated Compound Composition.

Oxide composition Per cent		Calculated compound composition using Bogue's equation per cent	
CaO	63	C_3S	54.1
SiO_2	20	C_2S	16.6
Al_2O_3	6	C_3A	10.8
Fe_2O_3	3	C_4AF	9.1
MgO	1.5		
SO_2	2		
K_2O	1.0		
Na_2O			

In addition to the four major compounds, there are many minor compounds formed in the kiln. The influence of these minor compounds on the properties of cement or hydrated compounds is not significant. Two of the minor oxides namely K_2O and Na_2O referred to as alkalis in cement are of some importance. This aspect will be dealt with later when discussing alkali-aggregate reaction. The oxide composition of typical Portland cement and the corresponding calculated compound composition is shown in table 1.6.
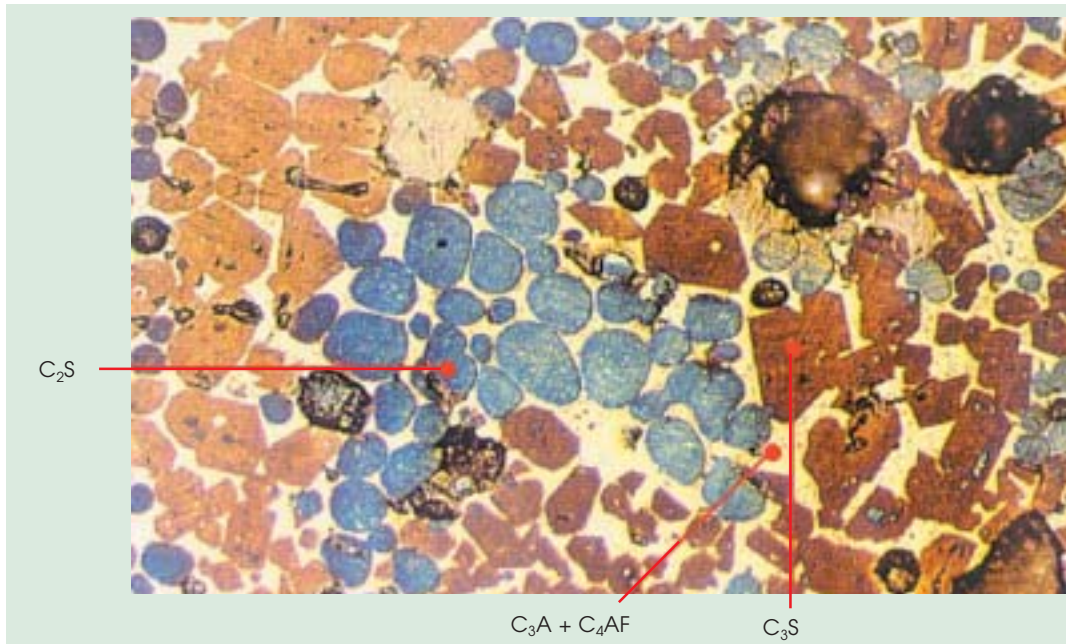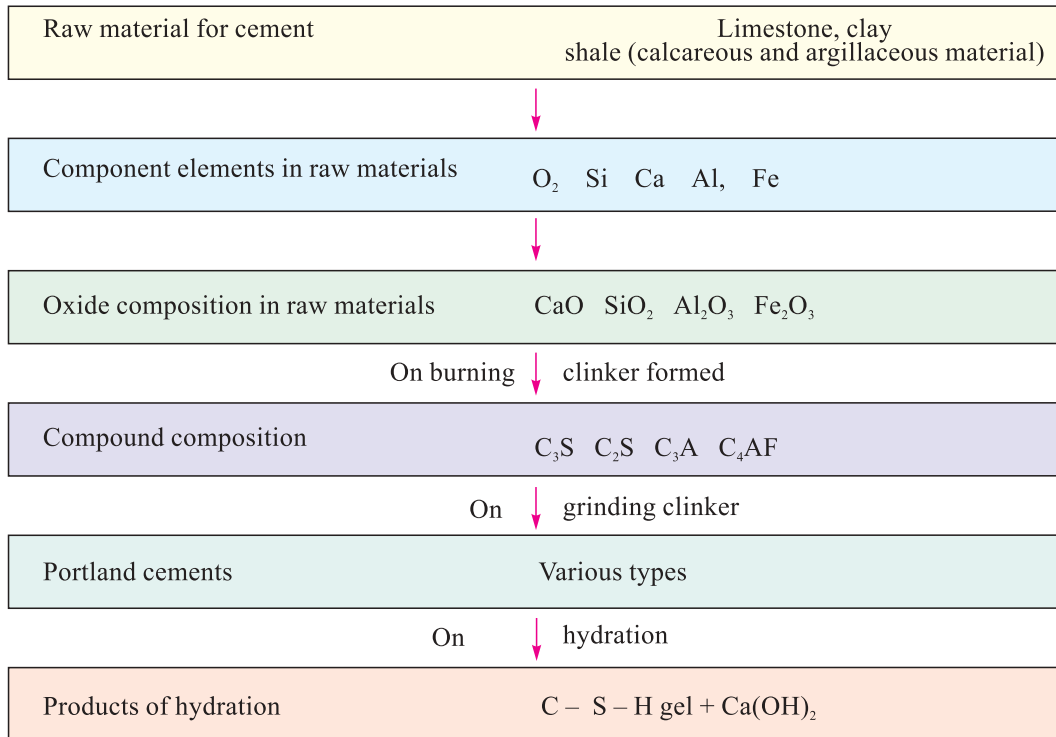
Schematic presentation of various compounds in clinker
Courtesy : All the photographs on manufacture of cement are by Grasim Industries Cement Division

Tricalcium silicate and dicalcium silicate are the most important compounds responsible for strength. Together they constitute 70 to 80 per cent of cement. The average C_3S content in modern cement is about 45 per cent and that of C_2S is about 25 per cent. The sum of the contents of C_3A and C_4AF has decreased slightly in modern cements. The calculated quantity of the compounds in cement varies greatly even for a relatively small change in the oxide composition of the raw materials. To manufacture a cement of stipulated compound composition, it becomes absolutely necessary to closely control the oxide composition of the raw materials. An increase in lime content beyond a certain value makes it difficult to combine with other compounds and free lime will exist in the clinker which causes unsoundness in cement. An increase in silica content at the expense of the content of alumina and ferric oxide will make the cement difficult to fuse and form clinker. Cements with a high total alumina and high ferric oxide content is favourable to the production of high early strengths in cement. This is perhaps due to the influence of these oxides for the complete combining of the entire quantity of lime present to form tricalcium silicate.

The advancement made in the various spheres of science and technology has helped us to recognise and understand the micro structure of the cement compounds before hydration and after hydration. The X-ray powder diffraction method, X-ray fluorescence method and use of powerful electron microscope capable of magnifying 50,000 times or even more has helped to reveal the crystalline or amorphous structure of the unhydrated or hydrated cement.

Both Le Chatelier and Tornebohm observed four different kinds of crystals in thin sections of cement clinkers. Tornebohm called these four kinds of crystals as Alite, Belite, Celite and Felite. Tornebohm's description of the minerals in cement was found to be similar to Bogue's description of the compounds. Therefore, Bogue's compounds C_3S, C_2S, C_3A and C_4AF are sometimes called in literature as Alite, Belite, Celite and Felite respectively.

Cement and hydration of Portland cement can be schematically represented as below:

Raw material for cement	Limestone, clay shale (calcareous and argillaceous material)

↓

Component elements in raw materials	O_2 Si Ca Al, Fe

↓

Oxide composition in raw materials	CaO SiO_2 Al_2O_3 Fe_2O_3

On burning ↓ clinker formed

Compound composition	C_3S C_2S C_3A C_4AF

On ↓ grinding clinker

Portland cements	Various types

On ↓ hydration

Products of hydration	C – S – H gel + $Ca(OH)_2$

Hydration of Cement

Anhydrous cement does not bind fine and coarse aggregate. It acquires adhesive property only when mixed with water. The chemical reactions that take place between cement and water is referred as hydration of cement.

The chemistry of concrete is essentially the chemistry of the reaction between cement and water. On account of hydration certain products are formed. These products are important because they have cementing or adhesive value. The quality, quantity, continuity, stability and the rate of formation of the hydration products are important.

Anhydrous cement compounds when mixed with water, react with each other to form hydrated compounds of very low solubility. The hydration of cement can be visualised in two ways. The first is "through solution" mechanism. In this the cement compounds dissolve to produce a supersaturated solution from which different hydrated products get precipitated. The second possibility is
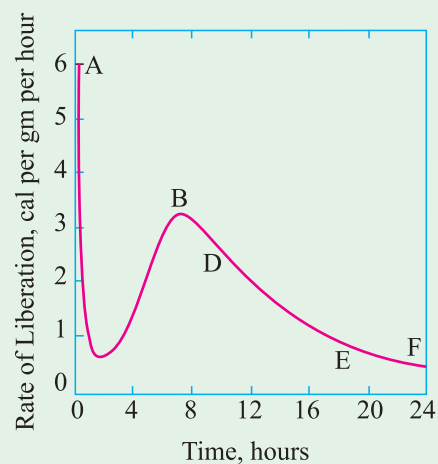

Fig. 1.2. Heat Liberation from a Setting Cement.[1.4]

that water attacks cement compounds in the solid state converting the compounds into hydrated products starting from the surface and proceeding to the interior of the compounds with time. It is probable that both "through solution" and "solid state" types of mechanism may occur during the course of reactions between cement and water. The former mechanism may predominate in the early stages of hydration in view of large quantities of water being available, and the latter mechanism may operate during the later stages of hydration.

Heat of Hydration

The reaction of cement with water is exothermic. The reaction liberates a considerable quantity of heat. This liberation of heat is called heat of hydration. This is clearly seen if freshly mixed cement is put in a vaccum flask and the temperature of the mass is read at intervals. The study and control of the heat of hydration becomes important in the construction of concrete dams and other mass concrete constructions. It has been observed that the temperature in the interior of large mass concrete is 50°C above the original temperature of the concrete mass at the time of placing and this high temperature is found to persist for a prolonged period. Fig 1.2 shows the pattern of liberation of heat from setting cement[1.4] and during early hardening period.

On mixing cement with water, a rapid heat evolution, lasting a few minutes, occurs. This heat evolution is probably due to the reaction of solution of aluminates and sulphates (ascending peak A). This initial heat evolution ceases quickly when the solubility of aluminate is depressed by gypsum. (decending peak A). Next heat evolution is on account of formation of ettringite and also may be due to the reaction of C_3S (ascending peak B). Refer Fig. 1.2.

Different compounds hydrate at different rates and liberate different quantities of heat. Fig. 1.3 shows the rate of hydration of pure compounds. Since retarders are added to control the flash setting properties of C_3A, actually the early heat of hydration is mainly contributed from the hydration of C_3S. Fineness of cement also influences the rate of development of heat but not the total heat. The total quantity of heat generated in the complete hydration will depend upon the relative quantities of the major compounds present in a cement.

Analysis of heat of hydration data of large number of cements, Verbec and Foster[1.5] computed heat evolution of four major compounds of cement. Table 1.7. shows the heats of hydration of four compounds.
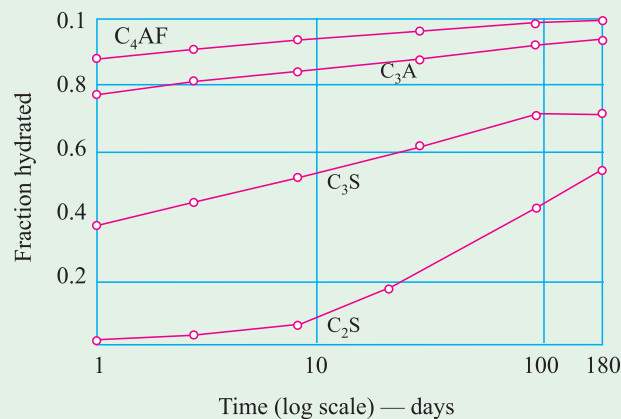

Fig. 1.3. Rate of Hydration of Pure Compounds.

Table 1.7. Heat of Hydration[1.5]

Compound	Heat of hydration at the given age (cal/g)		
	3 days	90 days	13 years
C_3S	58	104	122
C_2S	12	42	59
C_3A	212	311	324
C_4AF	69	98	102

Since the heat of hydration of cement is an additive property, it can be predicted from an expression of the type $\qquad H = aA + bB + cC + dD$

Where *H* represents the heat of hydration, *A*, *B*, *C*, and *D* are the percentage contents of C_3S, C_2S, C_3A and C_4AF. and *a*, *b*, *c* and *d* are coefficients representing the contribution of 1 per cent of the corresponding compound to the heat of hydration.

Normal cement generally produces 89-90 cal/g in 7 days and 90 to 100 cal/g in 28 days.

The hydration process is not an instantaneous one. The reaction is faster in the early period and continues idenfinitely at a decreasing rate. Complete hydration cannot be obtained under a period of one year or more unless the cement is very finely ground and reground with excess of water to expose fresh surfaces at intervals. Otherwise, the product obtained shows unattacked cores of tricalcium silicate surrounded by a layer of hydrated silicate, which being relatively impervious to water, renders further attack slow. It has been observed that after 28 days of curing, cement grains have been found to have hydrated to a depth of only 4μ. It has also been observed that complete hydration under normal condition is possible only for cement particles smaller than 50μ.

A grain of cement may contain many crystals of C_3S or others. The largest crystals of C_3S or C_2S are about 40μ. An average size would be 15-20μ. It is probable that the C_2S crystals present in the surface of a cement grain may get hydrated and a more reactive compound like C_3S lying in the interior of a cement grain may not get hydrated.

The hydrated product of the cement compound in a grain of cement adheres firmly to the unhydrated core in the grains of cement. That is to say unhydrated cement left in a grain of cement will not reduce the strength of cement mortar or concrete, as long as the products of hydration are well compacted. Abrams obtained strength of the order of 280 MPa using mixes with a water/cement ratio as low as 0.08. Essentially he has applied tremendous pressure to obtain proper compaction of such a mixture. Owing to such a low water/cement ratio, hydration must have been possible only at the surface of cement grains, and a considerable portion of cement grains must have remained in an unhydrated condition.
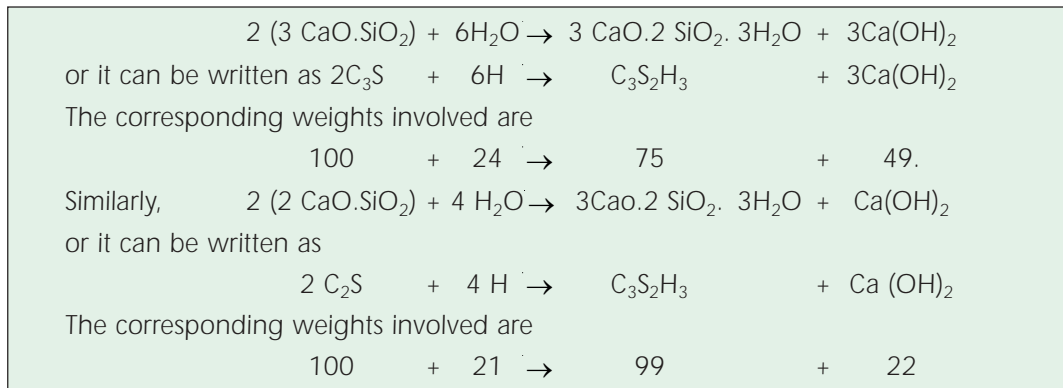
The present day High Performance concrete is made with water cement ratio in the region of 0.25 in which case it is possible that a considerable portion of cement grain remains unhydrated in the core. Only surface hydration takes place. The unhydrated core of cement grain can be deemed to work as very fine aggregates in the whole system.

Calcium Silicate Hydrates

During the course of reaction of C_3S and C_2S with water, calcium silicate hydrate, abbreviated C-S-H and calcium hydroxide, $Ca(OH)_2$ are formed. Calcium silicate hydrates are the most important products. It is the essence that determines the good properties of concrete.

It makes up 50-60 per cent of the volume of solids in a completely hydrated cement paste. The fact that term C-S-H is hyphenated signifies that C-S-H is not a well defined compound. The morphology of C-S-H shows a poorly crystalline fibrous mass.

It was considered doubtful that the product of hydration of both C_3S and C_2S results in the formation of the same hydrated compound. But later on it was seen that ultimately the hydrates of C_3S and C_2S will turn out to be the same. The following are the approximate equations showing the reactions of C_3S and C_2S with water.

$$2 (3\ CaO.SiO_2) + 6H_2O \rightarrow 3\ CaO.2\ SiO_2.\ 3H_2O + 3Ca(OH)_2$$

or it can be written as $2C_3S + 6H \rightarrow C_3S_2H_3 + 3Ca(OH)_2$

The corresponding weights involved are

$$100 + 24 \rightarrow 75 + 49.$$

Similarly, $\quad 2 (2\ CaO.SiO_2) + 4\ H_2O \rightarrow 3Cao.2\ SiO_2.\ 3H_2O + Ca(OH)_2$

or it can be written as

$$2\ C_2S + 4\ H \rightarrow C_3S_2H_3 + Ca\ (OH)_2$$

The corresponding weights involved are

$$100 + 21 \rightarrow 99 + 22$$

However, the simple equations given above do not bring out the complexities of the actual reactions.

It can be seen that C_3S produces a comparatively lesser quantity of calcium silicate hydrates and more quantity of $Ca(OH)_2$ than that formed in the hydration of C_2S. $Ca(OH)_2$ is not a desirable product in the concrete mass, it is soluble in water and gets leached out making the concrete porous, particularly in hydraulic structures. Under such conditions it is useful to use cement with higher percentage of C_2S content.

C_3S readily reacts with water and produces more heat of hydration. It is responsible for early strength of concrete. A cement with more C_3S content is better for cold weather concreting. The quality and density of calcium silicate hydrate formed out of C_3S is slightly inferior to that formed by C_2S. The early strength of concrete is due to C_3S.

C_2S hydrates rather slowly. It is responsible for the later strength of concrete. It produces less heat of hydration. The calcium silicate hydrate formed is rather dense and its specific surface is higher. In general, the quality of the proudct of hydration of C_2S is better than that produced in the hydration of C_3S. Fig 1.4 shows the development of strength of pure compounds.

Calcium Hydroxide

The other products of hydration of C_3S and C_2S is calcium hydroxide. In contrast to the C-S-H, the calcium hydroxide is a compound with a distinctive hexagonal prism morphology. It constitutes 20 to 25 per cent of the volume of solids in the hydrated paste. The lack of durability of concrete, is on account of the presence of calcium hydroxide. The calcium hydroxide also reacts with sulphates present in soils or water to form calcium sulphate which further reacts with C_3A and cause deterioration of concrete. This is known as sulphate attack. To reduce the quantity of $Ca(OH)_2$ in concrete and to overcome its bad effects by converting it into cementitious product is an advancement in concrete technology. The use of blending

materials such as fly ash, silica fume and such other pozzolanic materials are the steps to overcome bad effect of $Ca(OH)_2$ in concrete. This aspect will be dealt in greater detail later.

The only advantage is that $Ca(OH)_2$, being alkaline in nature maintain pH value around 13 in the concrete which resists the corrosion of reinforcements.

Calcium Aluminate Hydrates

The hydration of aluminates has been the subject of numerous investigations, but there is still some uncertainty about some of the reported products. Due to the hydration of C_3A , a calcium aluminate system $CaO – Al_2O_3 – H_2O$ is formed. The cubic compound C_3AH_6 is probably the only stable compound formed which remains stable upto about 225°C.

The reaction of pure C_3A with water is very fast and this may lead to flash set. To prevent this flash set, gypsum is added at the time of grinding the cement clinker. The quantity of gypsum added has a bearing on the quantity of C_3A present.

The hydrated aluminates do not contribute anything to the strength of concrete. On the other hand, their presence is harmful to the durability of concrete particularly where the concrete is likely to be attacked by sulphates. As it hydrates very fast it may contribute a little to the early strength.

Fig. 1.4. Development of Strength of Pure Compounds

On hydration, C_4AF is believed to form a system of the form $CaO – Fe_2O_3 – H_2O$. A hydrated calcium ferrite of the form C_3FH_6 is comparatively more stable. This hydrated product also does not contribute anything to the strength. The hydrates of C_4AF show a comparatively higher resistance to the attack of sulphates than the hydrates of calcium aluminate.

From the standpoint of hydration, it is convenient to discuss C_3A and C_4AF together, because the products formed in the presence of gypsum are similar. Gypsum and alkalies go into solution quickly and the solubility of C_3A is depressed. Depending upon the concentration of aluminate and sulphate ions in solution, the pricipitating crystalline product is either the calcium aluminate trisulphate hydrate ($C_6A\overline{S}_3H_{32}$) or calcium aluminate monosulhphate hydrate ($C_4A\overline{S}H_{18}$). The calcium aluminate trisulphate hydrate is known as ettringite.

Ettringite is usually the first to hydrate and crystallise as short prismatic needle on account of the high sulphate/aluminate ratio in solution phase during the first hour of hydration. When sulphate in solution gets depleted, the aluminate concentration goes up due to renewed hydration of C_3A and C_4AF. At this stage ettringite becomes unstable and is gradually converted into mono-sulphate, which is the final product of hydration of portland cements containing more than 5 percent C_3A.

The amount of gypsum added has significant bearing on the quantity of aluminate in the cement. The maintenance of aluminate-to-sulphate ratio balance the normal setting
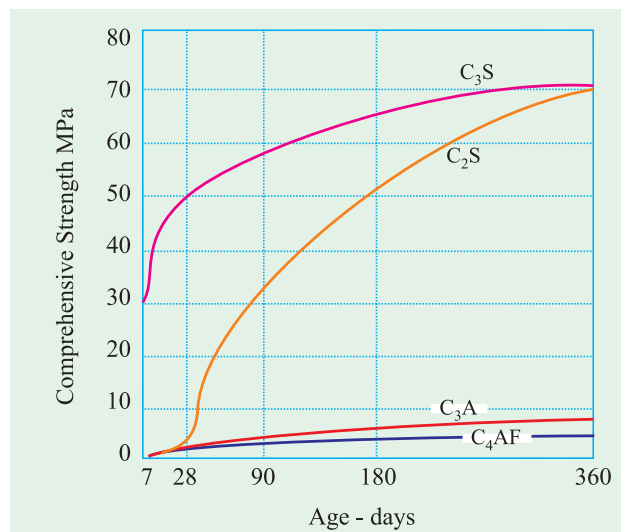
behaviour of cement paste. The various setting phenomena affected by an imbalance in the $A/\overline{S}$ ratio is of practical significance in concrete technology.

Many theories have been put forward to explain what actually is formed in the hydration of cement compounds with water. It has been said earliar that product consisting of ($CaO.SiO_2.H_2O$) and $Ca(OH)_2$ are formed in the hydration of calcium silicates. $Ca(OH)_2$ is an unimportant product, and the really significant product is ($CaO.SiO_2.H_2O$). For simplicity's sake this product of hydration is sometime called tobermorite gel because of its structural similarity to a naturally occurring mineral tobermorite. But very commonly the product of hydration is referred to as C – S – H gel.

It may not be exactly correct to call the product of hydrations as gel. Le chatelier identified the products as crystalline in nature and put forward his crystalline theory. He explained that the precipitates resemble crystals interlocked with each other. Later on Michaelis put forward his colloidal theory wherein he considered the precipitates as colloidal mass, gelatinous in nature. It is agreed that an element of truth exists in both these theories. It is accepted now that the product of hydration is more like gel, consisting of poorly formed, thin, fibrous crystals that are infinitely small. A variety of transitional forms are also believed to exist and the whole is seen as bundle of fibres, a fluffy mass with a refractive index of 1.5 to 1.55, increasing with age.

Since the gel consists of crystals, it is porous in nature. It is estimated that the porosity of gel is to the extent of 28%. The gel pores are filled with water. The pores are so small that the specific surface of cement gel is of the order of 2 million sq. cm. per gm. of cement. The porosity of gel can be found out by the capillary condensation method or by the mercury porosimetry method.

Structure of Hydrated Cement

To understand the behaviour of concrete, it is necessary to acquaint ourselves with the structure of hydrated hardened cement paste. If the concrete is considered as two phase material, namely, the paste phase and the aggregate phase, the understanding of the paste phase becomes more important as it influences the behaviour of concrete to a much greater extent. It will be discussed later that the strength, the permeability, the durability, the drying shrinkage, the elastic properties, the creep and volume change properties of concrete is greatly influenced by the paste structure. The aggregate phase though important, has lesser influence on the properties of concrete than the paste phase. Therefore, in our study to understand concrete, it is important that we have a deep understanding of the structure of the hydrated hardened cement paste at a phenomenological level.

Transition Zone

Concrete is generally considered as two phase material *i.e.*, paste phase and aggregates phase. At macro level it is seen that aggregate particles are dispersed in a matrix of cement paste. At the microscopic level, the complexities of the concrete begin to show up, particularly in the vicinity of large aggregate particles. This area can be considered as a third phase, the transition zone, which represents the interfacial region between the particles of coarse aggregate and hardened cement paste. Transition zone is generally a plane of weakness and, therefore, has far greater influence on the mechanical behaviour of concrete.

Although transition zone is composed of same bulk cement paste, the quality of paste in the transition zone is of poorer quality. Firstly due to internal bleeding, water accumulate below elongated, flaky and large pieces of aggregates. This reduces the bond between paste

and aggregate in general. If we go into little greater detail, the size and concentration of crystalline compounds such as calcium hydroxide and ettringite are also larger in the transition zone. Such a situation account for the lower strength of transition zone than bulk cement paste in concrete.

Due to drying shrinkage or temperature variation, the transition zone develops microcracks even before a structures is loaded. When structure is loaded and at high stress levels, these microcracks propagate and bigger chracks are formed resulting in failure of bond. Therefore, transition zone, generally the weakest link of the chain, is considered strength limiting phase in concrete. It is because of the presence of transition zone that concrete fails at considerably lower stress level than the strength of bulk paste or aggregate.

Sometimes it may be necessary for us to look into the structure of hardening concrete also. The rate and extent of hydration of cement have been investigated in the past using a variety of techniques. The techniques used to study the structure of cement paste include measurements of setting time, compressive strength, the quantity of heat of hydration evolved, the optical and electron microscope studies coupled with chemical analysis and thermal analysis of hydration products. Continuous monitoring of reactions by X-ray diffractions and conduction calorimetry has also been used for the study.

Measurements of heat evolved during the exothermic reactions also gives valuable insight into the nature of hydration reactions. Since approximately 50% of a total heat
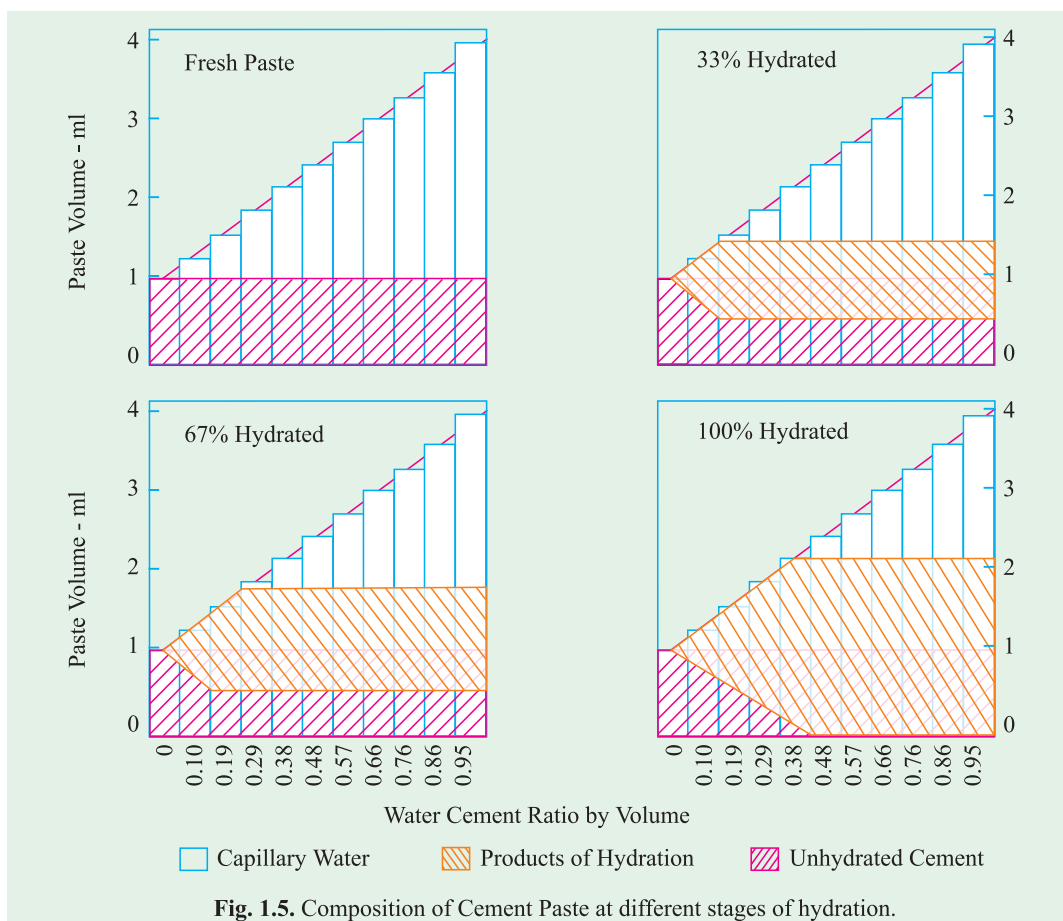

Fig. 1.5. Composition of Cement Paste at different stages of hydration.

evolution occurs during the first 3 days of hydration, a continuous record of the rate of heat liberation during this time is extremely useful in understanding the degree of hydration and the resultant structure of the hardening cement paste. Fig. 1.5 shows the composition of cement pastes at different stages of hydration.
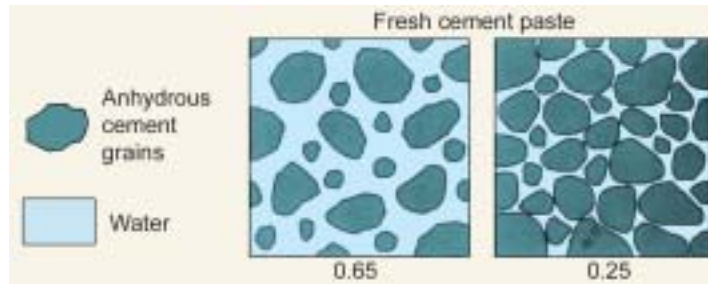
Schematic representation of two fresh cement pastes having a water/cement ratio of 0.65 and 0.25.

The mechanical properties of the hardened concrete depend more on the physical structure of the products of hydration than on the chemical composition of the cement. Mortar and concrete, shrinks and cracks, offers varying chemical resistance to different situations, creeps in different magnitude, and in short, exhibits complex behaviour under different conditions. Eventhough it is difficult to explain the behaviour of concrete fully and exactly, it is possible to explain the behaviour of concrete on better understanding of the structure of the hardened cement paste. Just as it is necessary for doctors to understand in great detail the anatomy of the human body to be able to diagnose disease and treat the patient with medicine or surgery, it is necessary for concrete technologists to fully understand the structure of hardened cement paste in great detail to be able to appreciate and rectify the ills and defects of the concrete.
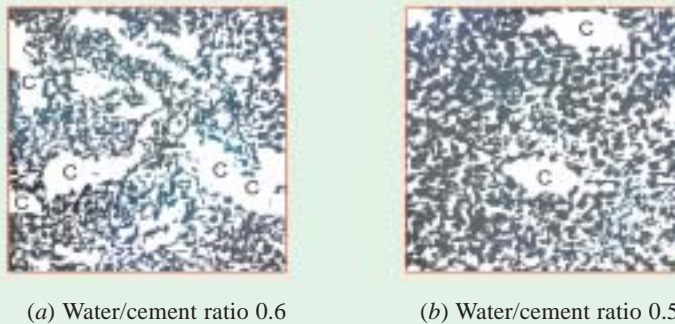

(*a*) Water/cement ratio 0.6   (*b*) Water/cement ratio 0.5

Fig. 1.6. Diagram representing paste structures. c represents capillary cavities.[1.6]
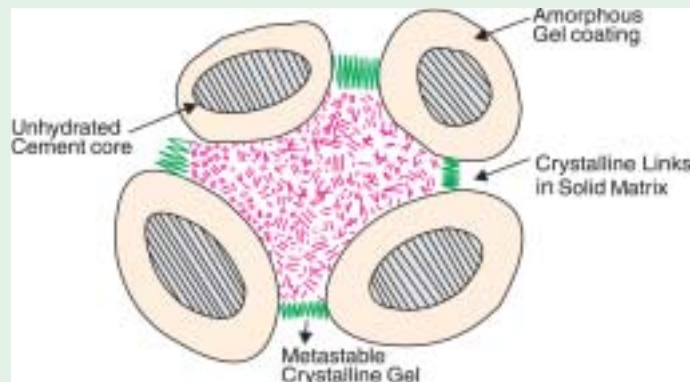

Fig. 1.7. Microscopic schematic model representing the structure of hardened cement paste.

For simplicitys sake we will consider only the structure of the paste phase. Fresh cement paste is a plastic mass consisting of water and cement. With the lapse of time, say one hour, the hardening paste consists of hydrates of various compounds, unhydrated cement particles and water. With further lapse of time the quantity of unhydrated cement left in the paste decreases and the hydrates of the various compounds increase. Some of the mixing water is used up for chemical reaction, and some water occupies the gel-pores and the remaining water remains in the paste. After a sufficiently long time (say a month) the hydrated paste can be considered to be consisting of about 85 to 90% of hydrates of the various compounds and 10 to 15 per cent of unhydrated cement. The mixing water is partly used up in the chemical reactions. Part of it occupies the gel-pores and the remaining water unwanted for hydration or for filling in the gel-pores causes capillary cavities. These capillary cavities may have been fully filled with water or partly with water or may be fully empty depending upon the age and the ambient temperature and humidity conditions. Figure 1.6 (*a*) and (*b*) schematically depict the structure of hydrated cement paste. The dark portion represents gel. The small gap within the dark portion represents gel-pores and big space such as marked "*c*" represents capillary cavities.[1.6] Fig. 1.7 represents the microscopic schematic model of structure of hardened cement paste.

Water Requirements for Hydration

It has been brought out earlier that C_3S requires 24% of water by weight of cement and C_2S requires 21%. It has also been estimated that on an average 23% of water by weight of cement is required for chemical reaction with Portland cement compounds. This 23% of water chemically combines with cement and, therefore, it is called bound water. A certain quantity of water is imbibed within the gel-pores. This water is known as gel-water. It can be said that bound water and gel-water are complimentary to each other. If the quantity of water is inadequate to fill up the gel-pores, the formations of gel itself will stop and if the formation of gel stops there is no question of gel-pores being present. It has been further estimated that about 15 per cent by weight of cement is required to fill up the gel-pores. Therefore, a total 38 per cent of water by weight of cement is required for the complete chemical reactions and to occupy the space within gel-pores. If water equal to 38 per cent by weight of cement is
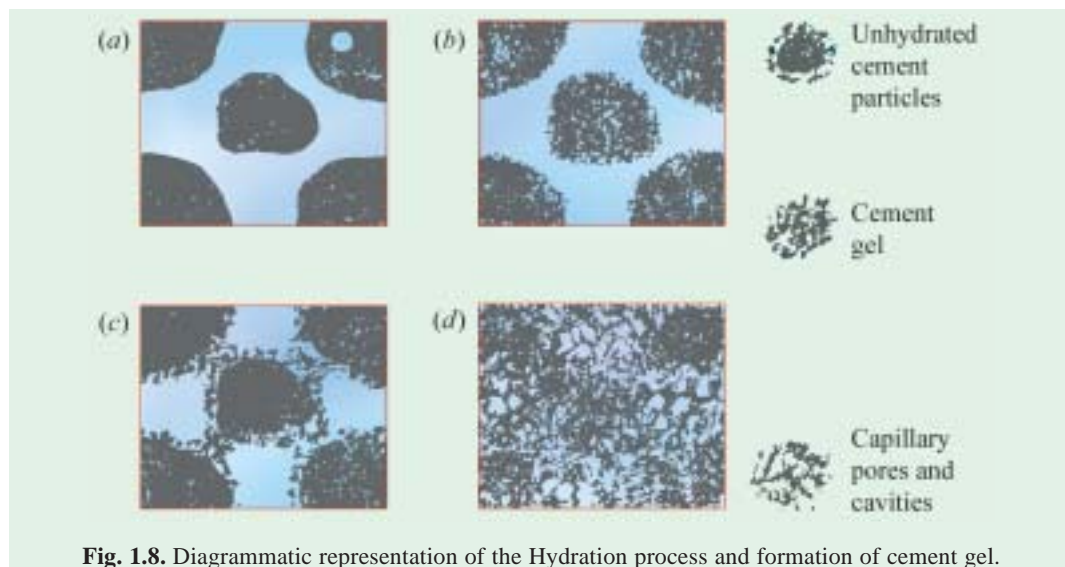

Fig. 1.8. Diagrammatic representation of the Hydration process and formation of cement gel.

only used it can be noticed that the resultant paste will undergo full hydration and no extra water will be available for the formation of undesirable capillary cavities. On the other hand, if more than 38 per cent of water is used, then the excess water will cause undesirable capillary cavities. Therefore greater the water above the minimum required is used (38 per cent), the more will be the undesirable capillary cavities. In all this it is assumed that hydration is taking place in a sealed container, where moisture to and from the paste does not take place.

It can be seen that the capillary cavities become larger with increased water/cement ratio. With lower w/c ratio the cement particles are closer together. With the progress of hydration, when the volume of anhydrous cement increases, the product of hydration also increases. The increase in the volume of gel due to complete hydration could fill up the space earlier occupied by water upto a w/c ratio of 0.6 or so. If the w/c ratio is more than 0.7, the increase in volume of the hydrated product would never be sufficient to fill up the voids created by water. Such concrete would ever remain as porous mass. This is to say that gel occupies more and more space, that once occupied by mixing water. It has been estimated that the volume of gel would be about twice the volume of unhydrated cement.

The diagrammatic representation of progress of hydration is sown in Fig. 1.8. Fig. 1.8 (*a*) represents the state of cement particles immediately when dispersed in an aqueous solution. During the first few minutes, the reaction rate is rapid and the calcium silicate hydrate forms a coating around the cement grains See Fig. 1.8 (*b*). As hydration proceeds, hydration products, including calcium hydroxide are precipitated from the saturated solution and bridge the gap between the cement grains, and the paste stiffens into its final shape, see Fig. 1.8 (*c*). Further hyudration involving some complex form of diffusion process results in further deposition of the cement gel at the expense of the unhydrated cement and capillary pore-water Fig. 1.8 (*d*).

What has been described briefly is the approximate structure of hardened cement paste on account of the hydration of some of the major compounds. Very little cognisance is taken of the product of hydration of the other major and minor compounds in cement. The morphology of product of hydration and the study of structure of hardened cement paste in its entirety is a subject of continued research.

The development of high voltage electron microscopy, combined with developments of skill in making very thin sections is making possible high resolution photography and diffractometry while at the same time reducing damage to the specimen while under observation. The scanning electron provides stereographic images and a detailed picture of structure of cement paste. These facilitate further to understand aggregate cement bond, micro fracture and porosity of cement gel.

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