CHAPTER 3

Fly Ash, Slag, Silica Fume, and Natural Pozzolans

Fig. 3-1. Supplementary cementitious materials. From left to right, fly ash (Class C), metakaolin (calcined clay), silica fume, fly ash (Class F), slag, and calcined shale. (69794)

Fly ash, ground granulated blast-furnace slag, silica fume, and natural pozzolans, such as calcined shale, calcined clay or metakaolin, are materials that, when used in conjunction with portland or blended cement, contribute to the properties of the hardened concrete through hydraulic or pozzolanic activity or both (Fig. 3-1). A pozzolan is a siliceous or aluminosiliceous material that, in finely divided form and in the presence of moisture, chemically reacts with the calcium hydroxide released by the hydration of portland cement to form calcium silicate hydrate and other cementitious compounds. Pozzolans and slags are generally catergorized as supplementary cementitious materials or mineral admixtures. Table 3-1 lists the applicable specifications these materials meet. The use of these materials in blended cements is discussed in Chapter 2 and by Detwiler, Bhatty, and Bhattacharja (1996).

The practice of using supplementary cementitious materials in concrete mixtures has been growing in North America since the 1970s. There are similarities between many of these materials in that most are byproducts of other industrial processes; their judicious use is desirable not only from the national environmental and energy conservation standpoint but also for the technical benefits they provide concrete.

Supplementary cementitious materials are added to concrete as part of the total cementitious system. They may be used in addition to or as a partial replacement of portland cement or blended cement in concrete, depending on the properties of the materials and the desired effect on concrete.

Supplementary cementitious materials are used to improve a particular concrete property, such as resistance to alkali-aggregate reactivity. The optimum amount to use should be established by testing to determine (1) whether the material is indeed improving the property, and (2) the correct dosage rate, as an overdose or underdose can be harmful or not achieve the desired effect. Supplementary cementitious materials also react differently with different cements.

Traditionally, fly ash, slag, calcined clay, calcined shale, and silica fume were used in concrete individually. Today, due to improved access to these materials, concrete producers can combine two or more of these materials to optimize concrete properties. Mixtures using three cementitious materials, called ternary mixtures, are becoming more

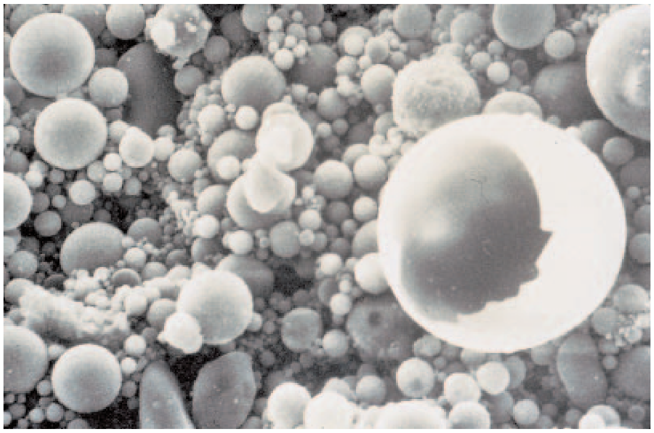


Fig. 3-2. Scanning electron microscope (SEM) micrograph of fly ash particles at 1000X. Although most fly ash spheres are solid, some particles, called cenospheres, are hollow (as shown in the micrograph). (54048)

Fig. 3-3. Fly ash, a powder resembling cement, has been used in concrete since the 1930s. (69799)

common. Supplementary cementitious materials are used in at least 60% of ready mixed concrete (PCA 2000). ASTM C 311 provides test methods for fly ash and natural pozzolans for use as supplementary cementitious material in concrete.

FLY ASH

Fly ash, the most widely used supplementary cementitious material in concrete, is a byproduct of the combustion of pulverized coal in electric power generating plants. Upon ignition in the furnace, most of the volatile matter and carbon in the coal are burned off. During combustion, the coal's mineral impurities (such as clay, feldspar, quartz, and shale) fuse in suspension and are carried away from the combustion chamber by the exhaust gases. In the process, the fused material cools and solidifies into spherical glassy particles called fly ash (Fig. 3-2). The fly ash is then collected from the exhaust gases by electrostatic precipitators or bag filters. Fly ash is a finely divided powder resembling portland cement (Fig. 3-3).

Most of the fly ash particles are solid spheres and some are hollow cenospheres. Also present are plerospheres, which are spheres containing smaller spheres. Ground materials, such as portland cement, have solid angular particles. The particle sizes in fly ash vary from less than 1 µm (micrometer) to more than 100 µm with the typical particle size measuring under 20 µm. Only 10% to 30% of the particles by mass are larger than 45 µm. The surface area is typically 300 to 500 m^2/kg, although some fly ashes can have surface areas as low as 200 m^2/kg and as high as 700 m^2/kg. For fly ash without close compaction, the bulk density (mass per unit volume including air between particles) can vary from 540 to 860 kg/m^3 (34 to 54 lb/ft^3), whereas with close packed storage or vibration, the range can be 1120 to 1500 kg/m^3 (70 to 94 lb/ft^3).

Table 3-1. Specifications and Classes of Supplementary Cementitious Materials

Ground granulated iron blast-furnace slags—ASTM C 989 (AASHTO M 302)
- Grade 80
  - Slags with a low activity index
- Grade 100
  - Slags with a moderate activity index
- Grade 120
  - Slags with a high activity index

Fly ash and natural pozzolans—ASTM C 618 (AASHTO M 295)
- Class N
  - Raw or calcined natural pozzolans including:
    Diatomaceous earths
    Opaline cherts and shales
    Tuffs and volcanic ashes or pumicites
    Calcined clays, including metakaolin, and shales
- Class F
  - Fly ash with pozzolanic properties
- Class C
  - Fly ash with pozzolanic and cementitious properties

Silica fume—ASTM C 1240

Fly ash is primarily silicate glass containing silica, alumina, iron, and calcium. Minor constituents are magnesium, sulfur, sodium, potassium, and carbon. Crystalline compounds are present in small amounts. The relative density (specific gravity) of fly ash generally ranges between 1.9 and 2.8 and the color is generally gray or tan.

ASTM C 618 (AASHTO M 295) Class F and Class C fly ashes are commonly used as pozzolanic admixtures for general purpose concrete (Fig. 3-4). Class F materials are generally low-calcium (less than 10% CaO) fly ashes with

Fig. 3-4. Fly ash, slag, and calcined clay or calcined shale are used in general purpose construction, such as (left to right) walls for residential buildings, pavements, high-rise towers, and dams. (67279, 48177, 69554, 69555)

Fig. 3-5. Ground granulated blast-furnace slag. (69800)

Fig. 3-7. Silica fume powder. (69801)

carbon contents usually less than 5%, but some may be as high as 10%. Class C materials are often high-calcium (10% to 30% CaO) fly ashes with carbon contents less than 2%. Many Class C ashes when exposed to water will hydrate and harden in less than 45 minutes. Some fly ashes meet both Class F and Class C classifications.

Fly ash is used in about 50% of ready mixed concrete (PCA 2000). Class F fly ash is often used at dosages of 15% to 25% by mass of cementitious material and Class C fly ash is used at dosages of 15% to 40% by mass of cementitious material. Dosage varies with the reactivity of the ash and the desired effects on the concrete (Helmuth 1987 and ACI 232 1996).

SLAG

Ground granulated blast-furnace slag (Fig. 3-5), also called slag cement, is made from iron blast-furnace slag; it is a nonmetallic hydraulic cement consisting essentially of silicates and aluminosilicates of calcium developed in a molten condition simultaneously with iron in a blast furnace. The molten slag at a temperature of about 1500°C (2730°F) is rapidly chilled by quenching in water to form a glassy sandlike granulated material. The granulated material, which is ground to less than 45 microns, has a surface area fineness of about 400 to 600 m^2/kg Blaine. The relative density (specific gravity) for ground granulated blast-furnace slag is in the range of 2.85 to 2.95. The bulk density varies from 1050 to 1375 kg/m^3 (66 to 86 lb/ft^3).

The rough and angular-shaped ground slag (Fig. 3-6) in the presence of water and an activator, NaOH or CaOH, both supplied by portland cement, hydrates and sets in a manner similar to portland cement. However, air-cooled slag does not have the hydraulic properties of water-cooled slag.

Granulated blast furnace slag was first developed in Germany in 1853 (Malhotra 1996). Ground slag has been used as a cementitious material in concrete since the beginning of the 1900s (Abrams 1925). Ground granulated blast-furnace slag, when used in general purpose concrete in North America, commonly constitutes between 30% and 45% of the cementing material in the mix (Fig. 3-4) (PCA 2000). Some slag concretes have a slag component of 70% or more of the cementitious material. ASTM C 989 (AASHTO M 302) classifies slag by its increasing level of reactivity as Grade 80, 100, or 120 (Table 3-1). ASTM C 1073 covers a rapid determination of hydraulic activity of

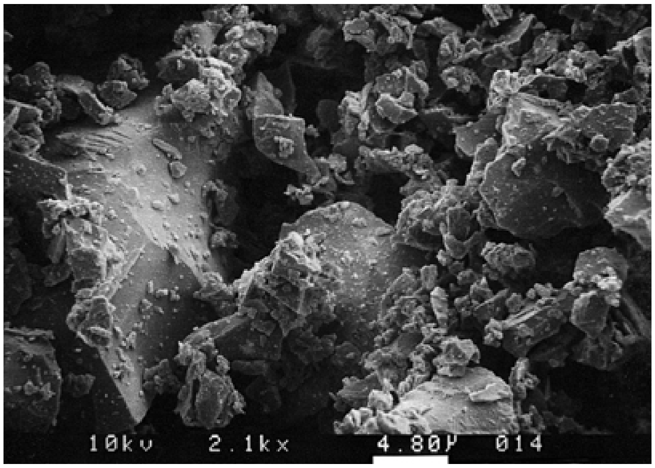


Fig. 3-6. Scanning electron microscope micrograph of slag particles at 2100X. (69541)

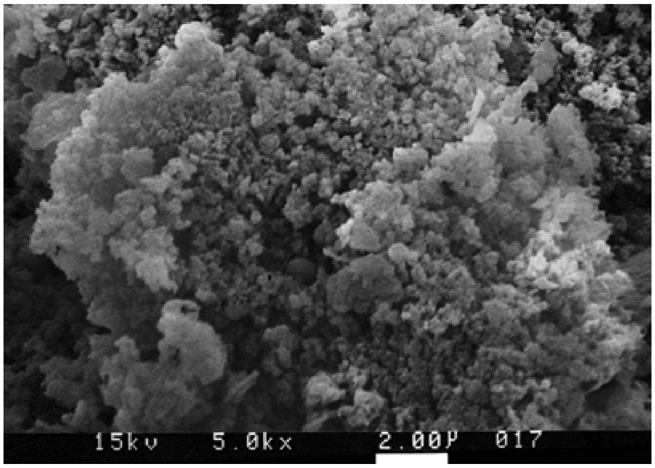


Fig. 3-8. Scanning electron microscope micrograph of silica-fume particles at 20,000X. (54095)

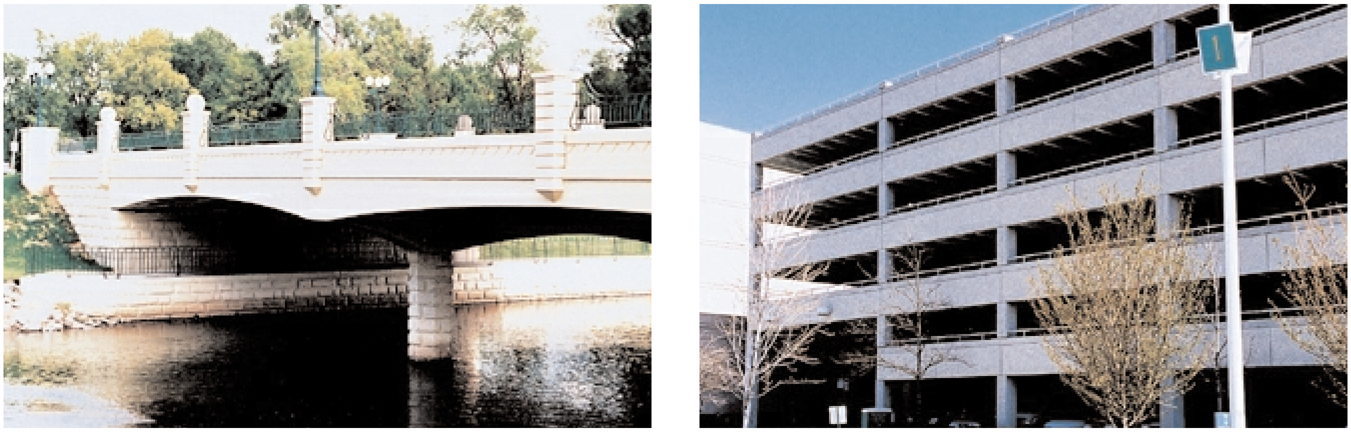


Fig. 3-9. Although they can be used in general construction, silica fume and metakaolin are often used in applications such as (left) bridges and (right) parking garages to minimize chloride penetration into concrete. (68681, 69542)

ground granulated blast furnace slag and ACI 233 (1995) provides an extensive review of slag.

SILICA FUME

Silica fume, also referred to as microsilica or condensed silica fume, is a byproduct material that is used as a pozzolan (Fig. 3-7). This byproduct is a result of the reduction of high-purity quartz with coal in an electric arc furnace in the manufacture of silicon or ferrosilicon alloy. Silica fume rises as an oxidized vapor from the 2000°C (3630°F) furnaces. When it cools it condenses and is collected in huge cloth bags. The condensed silica fume is then processed to remove impurities and to control particle size.

Condensed silica fume is essentially silicon dioxide (usually more than 85%) in noncrystalline (amorphorous) form. Since it is an airborne material like fly ash, it has a spherical shape (Fig. 3-8). It is extremely fine with particles less than 1 µm in diameter and with an average diameter of about 0.1 µm, about 100 times smaller than average cement particles.

Condensed silica fume has a surface area of about 20,000 m^2/kg (nitrogen adsorption method). For comparison, tobacco smoke's surface area is about 10,000 m^2/ kg. Type I and Type III cements have surface areas of about 300 to 400 m^2/kg and 500 to 600 m^2/kg (Blaine), respectively.

The relative density of silica fume is generally in the range of 2.20 to 2.5. Portland cement has a relative density of about 3.15. The bulk density (uncompacted unit weight) of silica fume varies from 130 to 430 kg/m^3 (8 to 27 lb/ft^3).

Silica fume is sold in powder form but is more commonly available in a liquid. Silica fume is used in amounts between 5% and 10% by mass of the total cementitious material. It is used in applications where a high degree of impermeability is needed (Fig. 3-9) and in high-strength concrete. Silica fume must meet ASTM C 1240. ACI 234 (1994) and SFA (2000) provide an extensive review of silica fume.

NATURAL POZZOLANS

Natural pozzolans have been used for centuries. The term "pozzolan" comes from a volcanic ash mined at Pozzuoli, a village near Naples, Italy, following the 79 AD eruption of Mount Vesuvius. However, the use of volcanic ash and calcined clay dates back to 2000 BC and earlier in other cultures. Many of the Roman, Greek, Indian, and Egyptian pozzolan concrete structures can still be seen today, attesting to the durability of these materials.

The North American experience with natural pozzolans dates back to early 20th century public works projects, such as dams, where they were used to control temperature rise in mass concrete and provide cementitious material. In addition to controlling heat rise, natural pozzolans were used to improve resistance to sulfate attack and were among the first materials to be found to mitigate alkali-silica reaction.

The most common natural pozzolans used today are processed materials, which are heat treated in a kiln and then ground to a fine powder (Figs. 3-10, 3-11, and 3-12); they include calcined clay, calcined shale, and metakaolin.

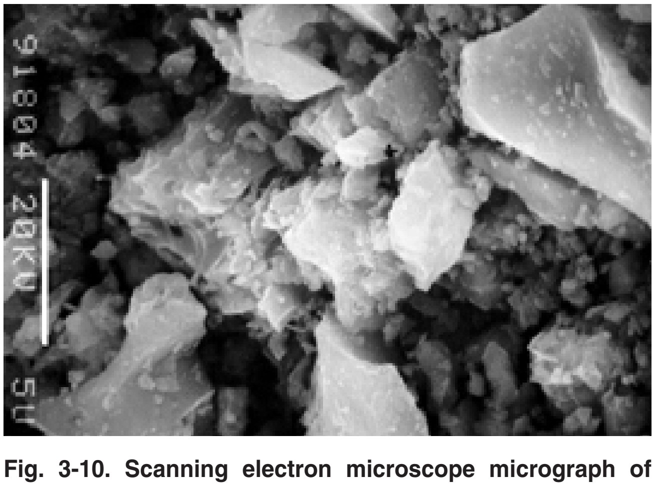


Fig. 3-10. Scanning electron microscope micrograph of calcined shale particles at 5000X. (69543)

Fig. 3-11. Metakaolin, a calcined clay. (69803)

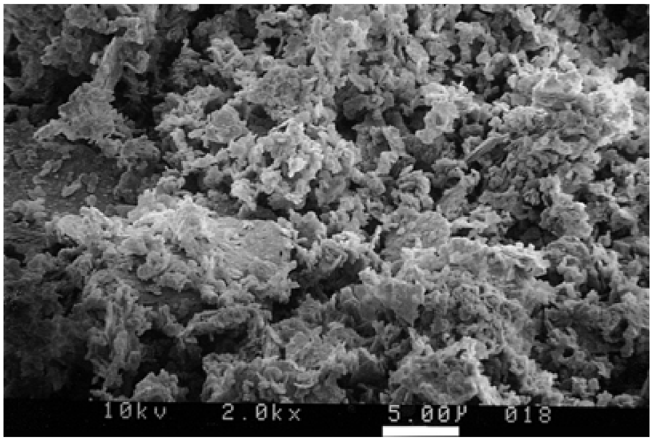


Fig. 3-12. Scanning electron microscope micrograph of calcined clay particles at 2000X. (69544)

Calcined clays are used in general purpose concrete construction much the same as other pozzolans (Fig. 3-4). They can be used as a partial replacement for the cement, typically in the range of 15% to 35%, and to enhance resistance to sulfate attack, control alkali-silica reactivity, and reduce permeability. Calcined clays have a relative density of between 2.40 and 2.61 with Blaine fineness ranging from 650 m^2/kg to 1350 m^2/kg. Calcined shale may contain on the order of 5% to 10% calcium, which results in the material having some cementing or hydraulic properties on its own. Because of the amount of residual calcite that is not fully calcined, and the bound water molecules in the clay minerals, calcined shale will have a loss on ignition (LOI) of perhaps 1% to 5%. The LOI value for calcined shale is not a measure or indication of carbon content as would be the case in fly ash.

Metakaolin, a special calcined clay, is produced by low-temperature calcination of high purity kaolin clay. The product is ground to an average particle size of about 1 to 2 micrometers. Metakaolin is used in special applications where very low permeability or very high strength is required. In these applications, metakaolin is used more as an additive to the concrete rather than a replacement of cement; typical additions are around 10% of the cement mass.

Natural pozzolans are classified by ASTM C 618 (AASHTO M 295) as Class N pozzolans (Table 3-1). ACI 232 (2000) provides a review of natural pozzolans. Table 3-2 illustrates typical chemical analysis and selected properties of pozzolans.

EFFECTS ON FRESHLY MIXED CONCRETE

This section provides a brief understanding of the freshly mixed concrete properties that supplementary cementitious materials affect and their degree of influence. First it should be noted that these materials vary considerably in their effect on concrete mixtures. The attributes of these materials when added separately to a concrete mixture can also be found in blended cements using supplementary cementitious materials.

Table 3-2. Chemical Analysis and Selected Properties of Typical Fly Ash, Slag, Silica Fume, Calcined Clay, Calcined Shale, and Metakaolin

	Class F fly ash	Class C fly ash	Ground slag	Silica fume	Calcined clay	Calcined shale	Metakaolin
SiO_2, %	52	35	35	90	58	50	53
Al_2O_3, %	23	18	12	0.4	29	20	43
Fe_2O_3, %	11	6	1	0.4	4	8	0.5
CaO, %	5	21	40	1.6	1	8	0.1
SO_3, %	0.8	4.1	9	0.4	0.5	0.4	0.1
Na_2O, %	1.0	5.8	0.3	0.5	0.2	—	0.05
K_2O, %	2.0	0.7	0.4	2.2	2	—	0.4
Total Na eq. alk, %	2.2	6.3	0.6	1.9	1.5	—	0.3
Loss on ignition, %	2.8	0.5	1.0	3.0	1.5	3.0	0.7
Blaine fineness, m^2/kg	420	420	400	20,000	990	730	19,000
Relative density	2.38	2.65	2.94	2.40	2.50	2.63	2.50

Water Requirements

Concrete mixtures containing fly ash generally require less water (about 1% to 10% less at normal dosages) for a given slump than concrete containing only portland cement. Higher dosages can result in greater water reduction (Table 3-3). However, some fly ashes can in-

Table 3-3. Effect of Fly Ash on Mixing Water Requirements for Air-Entrained Concrete

Fly ash mix identification	Class of fly ash	Fly ash content, % by mass of cementitious material	Change in mixing water requirement compared to control, %
C1A	C	25	-6
C1D	F	25	-2
C1E	F	25	-6
C1F	C	25	-8
C1G	C	25	-6
C1J	F	25	-6
C2A	C	50	-18
C2D	F	50	-6
C2E	F	50	-14
C2F	C	50	-16
C2G	C	50	-12
C2J	F	50	-10

All mixtures had cementitious materials contents of 335 kg/m^3 (564 lb/yd^3), a slump of 125 ± 25 mm (5 ± 1 in.), and an air content of 6 ± 1%. Water to cement plus fly ash ratios varied from 0.40 to 0.48 (Whiting 1989).

crease water demand up to 5% (Gebler and Klieger 1986). Fly ash reduces water demand in a manner similar to liquid chemical water reducers (Helmuth 1987). Ground slag usually decreases water demand by 1% to 10%, depending on dosage.

The water demand of concrete containing silica fume increases with increasing amounts of silica fume, unless a water reducer or plasticizer is used. Some lean mixes may not experience an increase in water demand when only a small amount (less than 5%) of silica fume is present.

Calcined clays and calcined shales generally have little effect on water demand at normal dosages; however, other natural pozzolans can significantly increase or decrease water demand.

Workability

Fly ash, slag, and calcined clay and shale generally improve the workability of concretes of equal slump. Silica fume may contribute to stickiness of a concrete mixture; adjustments, including the use of high-range water reducers, may be required to maintain workability and permit proper compaction and finishing.

Bleeding and Segregation

Concretes using fly ash generally exhibit less bleeding and segregation than plain concretes (Table 3-4). This effect makes the use of fly ash particularly valuable in concrete mixtures made with aggregates that are deficient in fines. The reduction in bleed water is primarily due to the reduced water demand in fly ash concretes. Gebler and Klieger (1986) correlate reduced bleeding of concrete to the reduced water requirement of fly ash mortar.

Concretes containing ground slags of comparable fineness to that of the cement tend to show an increased rate and amount of bleeding than plain concretes, but this appears to have no adverse effect on segregation. Slags ground finer than cement reduce bleeding.

Silica fume is very effective in reducing both bleeding and segregation; as a result, higher slumps may be used. Calcined clays, calcined shales, and metakaolin have little effect on bleeding.

Air Content

The amount of air-entraining admixture required to obtain a specified air content is normally greater when fly ash is used. Class C ash requires less air-entraining admixture than Class F ash and tends to lose less air during mixing (Table 3-5). Ground slags have variable effects on the required dosage rate of air-entraining admixtures. Silica fume has a marked influence on the air-entraining admixture requirement, which in most cases rapidly increases with an increase in the amount of silica fume used in the concrete. The inclusion of both fly ash and silica fume in non-air-entrained concrete will generally reduce the amount of entrapped air.

Table 3-4. Effect of Fly Ash on Bleeding of Concrete (ASTM C 232, AASHTO T 158)*

Fly ash mixtures		Bleeding	
Identification	Class of fly ash	Percent	mL/cm^2**
A	C	0.22	0.007
B	F	1.11	0.036
C	F	1.61	0.053
D	F	1.88	0.067
E	F	1.18	0.035
F	C	0.13	0.004
G	C	0.89	0.028
H	F	0.58	0.022
I	C	0.12	0.004
J	F	1.48	0.051
Average of:			
Class C		0.34	0.011
Class F		1.31	0.044
Control mixture		1.75	0.059

* All mixtures had cementitious materials contents of 307 kg/m^3 (517 lb/yd^3), a slump of 75 ± 25 mm (3 ± 1 in.), and an air content of 6 ± 1%. Fly ash mixtures contained 25% ash by mass of cementitious material (Gebler and Klieger 1986).

** Volume of bleed water per surface area.

Table 3-5. Effect of Fly Ash on Air-Entraining Admixture Dosage and Air Retention

Fly ash mixtures		Percent of air-entraining admixture relative to control	Air content, %			
			Minutes after initial mixing			
Identification	Class of fly ash		0	30	60	90
A	C	126	7.2	6.0	6.0	5.8
B	F	209	5.3	4.1	3.4	3.1
C	F	553	7.0	4.7	3.8	2.9
D	F	239	6.6	5.4	4.2	4.1
E	F	190	5.6	4.6	4.3	3.8
F	C	173	6.8	6.5	6.3	6.4
G	C	158	5.5	4.8	4.5	4.2
H	F	170	7.6	6.9	6.5	6.6
I	C	149	6.6	6.5	6.5	6.8
J	F	434	5.5	4.2	3.8	3.4
Control mixture		100	6.6	6.0	5.6	5.3

Concretes had a cementitious materials content of 307 kg/m^3 (517 lb/yd^3) and a slump of 75 ± 25 mm (3 ± 1 in.). Fly ash mixtures contained 25% ash by mass of cementitious material (Gebler and Klieger 1983).

The amount of air-entraining admixture required for a certain air content in the concrete is a function of the fineness, carbon content, alkali content, organic material content, loss on ignition, and presence of impurities in the fly ash. Increases in alkalies decrease air-entraining agent dosages, while increases in the other properties increase dosage requirements. The Foam Index test provides an indication of the required dosage of air-entraining admixture for various fly ashes relative to non-ash mixtures; it can also be used to anticipate the need to increase or decrease the dosage based on changes in the foam index (Gebler and Klieger 1983).

The air-entraining dosage and air retention characteristics of concretes containing ground slag or natural pozzolans are similar to mixtures made only with portland cement.

Heat of Hydration

Fly ash, natural pozzolans, and ground slag have a lower heat of hydration than portland cement; consequently their use will reduce the amount of heat built up in a concrete structure (Fig. 3-13). Calcined clay imparts a heat of hydration similar to moderate heat cement (Barger and others 1997). Some pozzolans have a heat of hydration of only 40% that of Type I portland cement. This reduction in temperature rise is especially beneficial in concrete used for massive structures. Silica fume may or may not reduce the heat of hydration. Detwiler and others (1996) provide a review of the effect of pozzolans and slags on heat generation.

Setting Time

The use of fly ash and ground granulated blast-furnace slag will generally retard the setting time of concrete (Table 3-6). The degree of set retardation depends on factors such

Table 3-6. Effect of Fly Ash on Setting Time of Concrete

Fly ash test mixtures		Setting time, hr:min		Retardation relative to control, hr:min	
Identification	Class of fly ash	Initial	Final	Initial	Final
A	C	4:30	5:35	0:15	0:05
B	F	4:40	6:15	0:25	0:45
C	F	4:25	6:15	0:10	0:45
D	F	5:05	7:15	0:50	1:45
E	F	4:25	5:50	0:10	0:20
F	C	4:25	6:00	0:10	0:30
G	C	4:55	6:30	0:40	1:00
H	F	5:10	7:10	0:55	1:40
I	C	5:00	6:50	0:45	1:20
J	F	5:10	7:40	0:55	2:10
Average of:					
Class C		4:40	6:15	0:30	0:45
Class F		4:50	6:45	0:35	1:15
Control mixture		4:15	5:30	—	—

Concretes had a cementitious materials content of 307 kg/m^3 (517 lb/yd^3). Fly ash mixtures contained 25% ash by mass of cementitious material. Water to cement plus fly ash ratio = 0.40 to 0.45. Tested at 23°C (73°F) (Gebler and Klieger 1986).

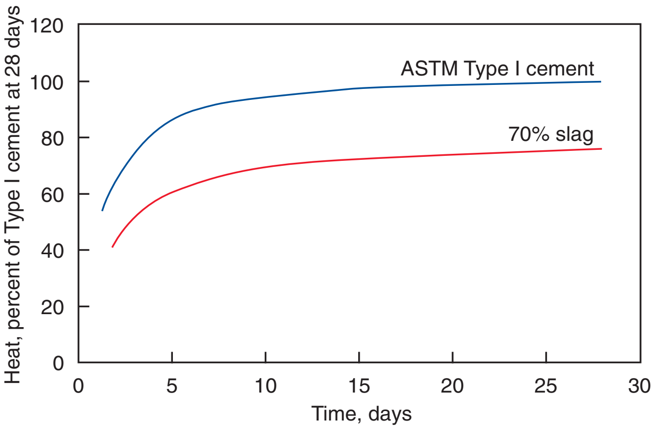


Fig. 3-13. Effect of a slag on heat of hydration at 20°C (68°F) compared to a Type I cement.

as the amount of portland cement, water requirement, the type and reactivity of the slag or pozzolan dosage, and the temperature of the concrete. Set retardation is an advantage during hot weather, allowing more time to place and finish the concrete. However, during cold weather, pronounced retardation can occur with some materials, significantly delaying finishing operations. Accelerating admixtures can be used to decrease the setting time. Calcined shale and clay have little effect on setting time.

Finishability

Concrete containing supplementary cementing materials will generally have equal or improved finishability compared to similar concrete mixes without them. Mixes that contain high dosages of cementitious materials—and especially silica fume—can be sticky and difficult to finish.

Pumpability

The use of supplementary cementing materials generally aids the pumpability of concrete. Silica fume is the most effective, especially in lean mixtures.

Plastic Shrinkage Cracking

Because of its low bleeding characteristics, concrete containing silica fume may exhibit an increase in plastic shrinkage cracking. The problem may be avoided by ensuring that such concrete is protected against drying, both during and after finishing. Other pozzolans and slag generally have little effect on plastic shrinkage cracking. Supplementary cementing materials that significantly increase set time can increase the risk of plastic shrinkage cracking.

Curing

The effects of temperature and moisture conditions on setting properties and strength development of concretes containing supplementary cementing materials are similar to the effects on concrete made with only portland cement; however, the curing time may need to be longer for certain materials with slow-early-strength gain.

High dosages of silica fume can make concrete highly cohesive with very little aggregate segregation or bleeding. With little or no bleed water available at the concrete surface for evaporation, plastic cracking can readily develop, especially on hot, windy days if special precautions are not taken.

Proper curing of all concrete, especially concrete containing supplementary cementing materials, should commence immediately after finishing. A seven-day moist cure or membrane cure should be adequate for concretes with normal dosages of most supplementary cementitious materials. As with portland cement concrete, low curing temperatures can reduce early-strength gain (Gebler and Klieger 1986).

EFFECTS ON HARDENED CONCRETE

Strength

Fly ash, ground granulated blast-furnace slag, calcined clay, metakaolin, calcined shale, and silica fume contribute to the strength gain of concrete. However, the strength of concrete containing these materials can be higher or lower than the strength of concrete using portland cement as the only cementing material. Fig. 3-14 illustrates this for various fly ashes. Tensile, flexural, torsional, and bond strength are affected in the same manner as compressive strength.

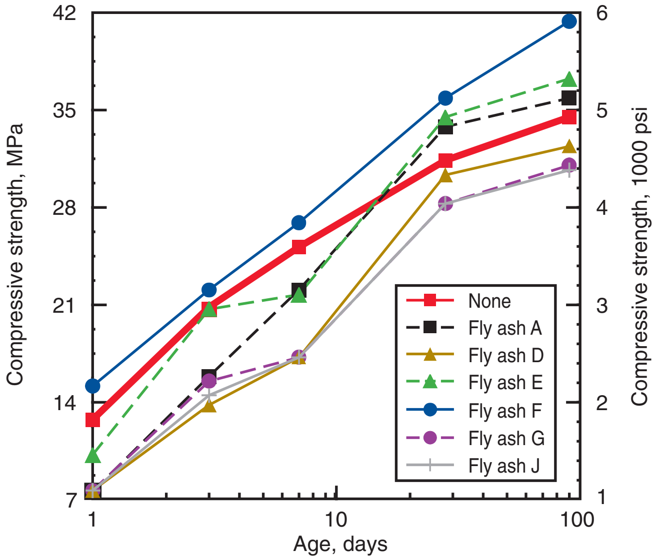


Fig. 3-14. Compressive strength development at 1, 3, 7, 28, and 90 days of concrete mixtures containing 307 kg/m³ (517 lb/yd³) of cementitious materials with a fly ash dosage of 25% of the cementitious materials (Whiting 1989).

Because of the slow pozzolanic reaction of some supplementary cementing materials, continuous wet curing and favorable curing temperatures may need to be provided for longer periods than normally required. However, concrete containing silica fume is less affected by this and generally equals or exceeds the one-day strength of a cement-only control mixture. Silica fume contributes to strength development primarily between 3 and 28 days, during which time a silica fume concrete exceeds the strength of a cement-only control concrete. Silica fume also aids the early strength gain of fly ash-cement concretes.

The strength development of concrete with fly ash, ground slag, calcined clay, or calcined shale, is similar to normal concrete when cured around 23°C (73°F). Fig. 3-15 illustrates that the rate of strength gain of concrete with fly ash, relative to its 28-day strength, is similar to concrete without fly ash. Concretes made with certain highly reactive fly ashes (especially high-calcium Class C ashes) or ground slags can equal or exceed the control strength in 1 to 28 days. Some fly ashes and natural pozzolans require 28 to 90 days to exceed a 28-day control strength, depending on the mixture proportions. Concretes containing Class C ashes generally develop higher early-age strength than concretes with Class F ashes.

Strength gain can be increased by: (1) increasing the amount of cementitious material in the concrete; (2) adding high-early strength cementitious materials; (3) decreasing the water-cementing materials ratio; (4) increasing the curing temperature; or (5) using an accelerating admixture. Fig. 3-16 illustrates the benefit of using fly ash as an addition instead of a cement replacement to improve strength development in cold weather. Mass concrete design often takes advantage of the delayed strength gain of pozzolans as these structures are often not put into full service immediately. Slow early strength gain resulting from the use of some supplementary cementitious materials is an advantage in hot weather construction as it allows more time to place and finish the concrete. With appropriate mixture adjustments, all supplementary cementitious materials can be used in all seasons.

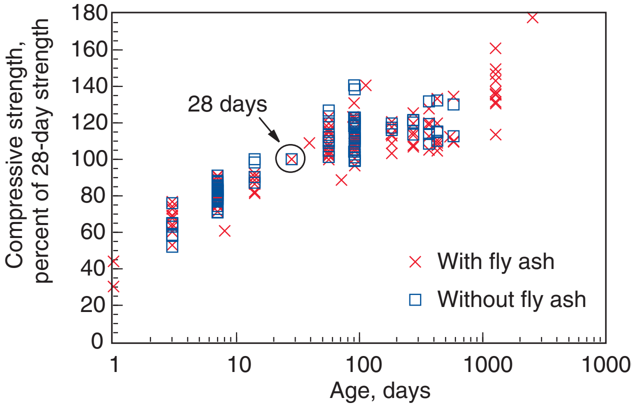


Fig. 3-15. Compressive strength gain as a percentage of 28-day strength of concretes with and without fly ash (Lange 1994).

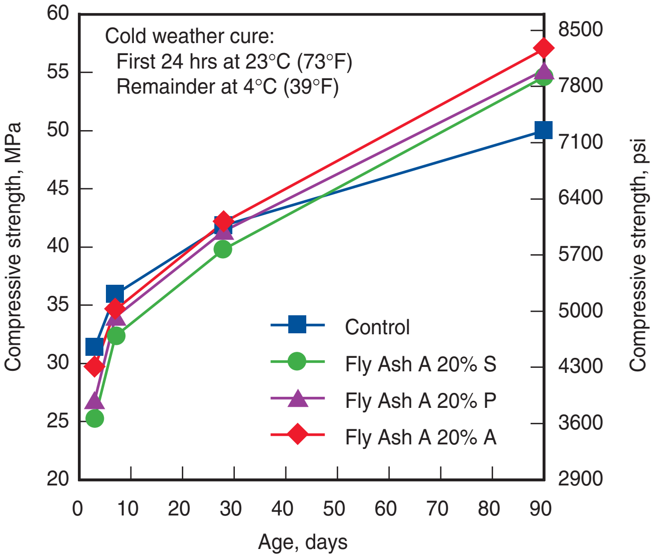


Fig. 3-16. Compressive strengths for concretes cured at 23°C (73°F) for the first 24 hours and 4°C (40°F) for the remaining time. Control had a cement content of 332 kg/m³ (560 lb/yd³) and w/c of 0.45. The fly ash curves show substitution for cement (S), partial (equal) substitution for cement and sand (P), and addition of fly ash by mass of cement (A). The use of partial cement substitution or addition of fly ash increases strength development comparable to the cement-only control, even in cold weather (Detwiler 2000).

Supplementary cementing materials are often essential to the production of high-strength concrete. Fly ash, especially, has been used in production of concrete with strengths up to 100 MPa (15,000 psi). With silica fume, ready mix producers now have the ability to make concrete with strengths up to 140 MPa (20,000 psi), when used with high-range water reducers and appropriate aggregates (Burg and Ost 1994).

Impact and Abrasion Resistance

The impact resistance and abrasion resistance of concrete are related to compressive strength and aggregate type. Supplementary cementing materials generally do not affect these properties beyond their influence on strength. Concretes containing fly ash are just as abrasion resistant as portland cement concretes without fly ash (Gebler and Klieger 1986). Fig. 3-17 illustrates that abrasion resistance of fly ash concrete is related to strength.

Freeze-Thaw Resistance

It is imperative for development of resistance to deterioration from cycles of freezing and thawing that a concrete have adequate strength and entrained air. For concrete containing supplementary cementing materials to provide the same resistance to freezing and thawing cycles as a concrete made using only portland cement as a binder, four conditions for both concretes must be met:

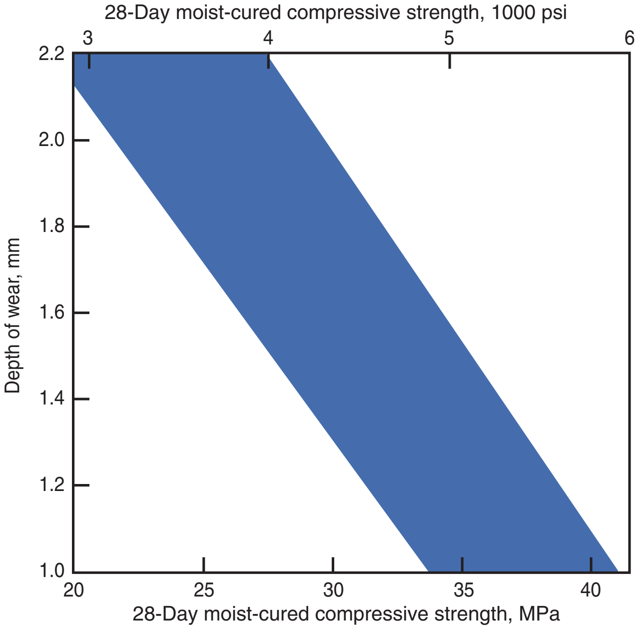


Fig. 3-17. Comparison of abrasion resistance and compressive strength of various concretes with 25% fly ash. Abrasion resistance increases with strength (Gebler and Klieger 1986).

1. They must have the same compressive strength.
2. They must have an adequate entrained air content with proper air-void characteristics.
3. They must be properly cured.
4. They must be air-dried for one month prior to exposure to saturated freezing conditions.

Table 3-7 shows equal frost resistance for concrete with and without fly ash. Fig. 3-18 illustrates the long term durability of concretes with fly ash, slag, or shale.

Deicer-Scaling Resistance

Decades of field experience have demonstrated that air-entrained concretes containing normal dosages of fly ash, slag, silica fume, calcined clay, or calcined shale are resistant to scaling caused by the application of deicing salts in a freeze-thaw environment. Laboratory tests also indicate that the deicer-scaling resistance of concrete made with supplementary cementing materials is often equal to concrete made without supplementary cementing materials.

Scaling resistance can decrease as the amount of certain supplementary cementing materials increases. However, concretes that are properly designed, placed, and cured, have demonstrated good scaling resistance even when made with high dosages of some of these materials.

Deicer-scaling resistance of all concrete is significantly improved with the use of a low water-cement ratio, a moderate portland cement content, adequate air entrainment, proper finishing and curing, and an air-drying period prior to exposure of the concrete to salts and freezing temperatures. Lean concrete with only about 240 kg/m^3 (405 lb/yd^3) or less of cementitious material can be especially vulnerable to deicer scaling. A minimum of 335 kg/m^3

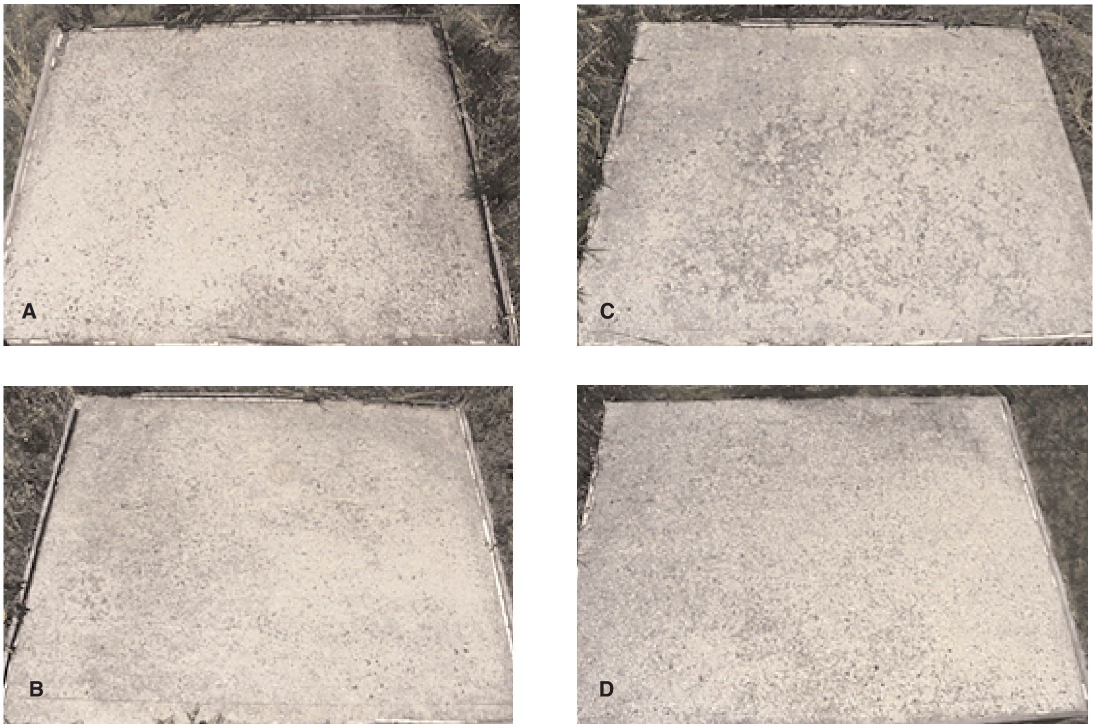


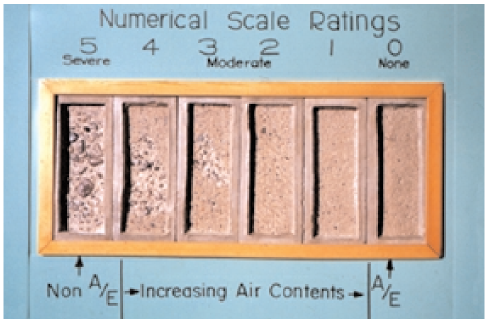
Fig. 3-18. View of concrete slabs in PCA outdoor test plot (Skokie, Illinois) containing (A) fly ash, (B) slag, (C) calcined shale, and (D) portland cement after 30 years of deicer and frost exposure. These samples demonstrate the durability of concretes containing various cementitious materials. Source: RX 157, LTS Cement No. 51, slabs with 335 kg/m^3 (564 lb/yd^3) of cementing material and air entrainment. (69714, 69716, 69715, 69717)

Table 3-7. Frost and Deicer-Scaling Resistance of Fly Ash Concrete

Fly ash mixtures*		Results at 300 cycles				
		Frost resistance in water, ASTM C 666 Method A (AASHTO T 161)			Deicer scaling resistance, ASTM C 672**	
Identification	Class of fly ash	Expansion, %	Mass loss, %	Durability factor	Water cure	Curing compound
A	C	0.010	1.8	105	3	2
B	F	0.001	1.2	107	2	2
C	F	0.005	1.0	104	3	3
D	F	0.006	1.3	98	3	3
E	F	0.003	4.8	99	3	2
F	C	0.004	1.8	99	2	2
G	C	0.008	1.0	102	2	2
H	F	0.006	1.2	104	3	2
I	C	0.004	1.7	99	3	2
J	F	0.004	1.0	100	3	2
Average of:						
Class C		0.006	1.6	101	3	2
Class F		0.004	1.8	102	3	2
Control mixture		0.002	2.5	101	2	2

* Concrete mixtures had a cementitious materials content of 307 kg/m^3 (517 lbs/yd^3), a water to cementitious materials ratio of 0.40 to 0.45, a target air content of 5% to 7%, and a slump of 75 mm to 100 mm (3 in. to 4 in.). Fly ash dosage was 25% by mass of cementitious material.
Gebler and Klieger 1986a.

** Scale rating (see at right)
0 = No scaling
1 = Slight scaling
2 = Slight to moderate scaling
3 = Moderate scaling
4 = Moderate to severe scaling
5 = Severe scaling



(2718)

(564 lb/yd^3) of cementitious material and a maximum water to cementitious materials ratio of 0.45 is recommended. A satisfactory air-void system is also critical.

The importance of using a low water-cement ratio for scale resistance is demonstrated in Fig. 3-19. The effect of high fly ash dosages and low cementing material contents is demonstrated in Fig. 3-20. The performance of scale-resistant concretes containing fly ash at a dosage of 25% of cementing material by mass is presented in Table 3-7. The table demonstrates that well designed, placed and cured concretes with and without fly ash can be equally resistant to deicer scaling.

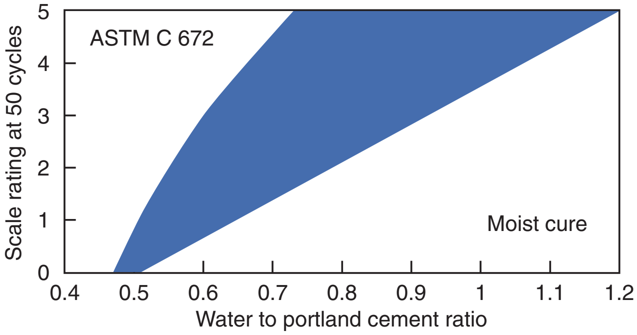


Fig. 3-19. Relationship between deicer-scaling resistance and water to portland cement ratio for several air-entrained concretes with and without fly ash. A scale rating of 0 is no scaling and 5 is severe scaling (Whiting 1989).

The ACI 318 building code states that the maximum dosage of fly ash, slag, and silica fume should be 25%, 50%, and 10% by mass of cementing materials, respectively for deicer exposures. Total supplementary cementing materials should not exceed 50% of the cementitious material. Dosages less than or higher than these limits have been shown to be durable in some cases and not in others. Different materials respond differently in different environments. The selection of materials and dosages should be based on local experience and the durability should be demonstrated by field or laboratory performance.

Drying Shrinkage and Creep

When used in low to moderate amounts, the effect of fly ash, ground granulated blast-furnace slag, calcined clay, calcined shale, and silica fume on the drying shrinkage and creep of concrete is generally small and of little practical significance. Some studies indicate that silica fume may reduce creep (Burg and Ost 1994).

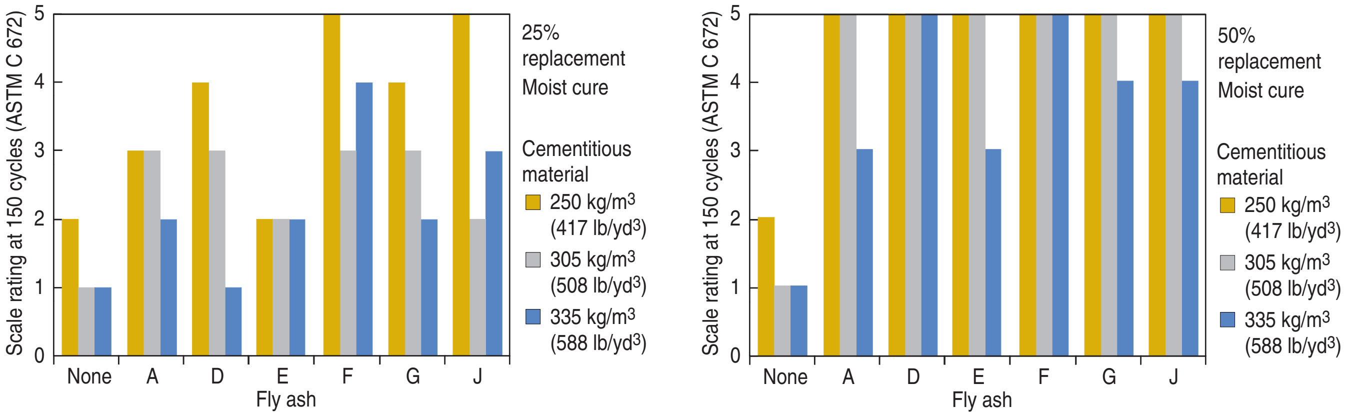


Fig. 3-20. Relationship between deicer-scaling resistance and dosage of fly ash for air-entrained concretes made with moderate to high water-cementitious materials ratios. Replacement of portland cement with fly ash: (left) 25% and (right) 50%. A scale rating of 0 is no scaling and 5 is severe scaling (Whiting 1989).

Permeability and Absorption

With adequate curing, fly ash, ground slag, and natural pozzolans generally reduce the permeability and absorption of concrete. Silica fume and metakaolin are especially effective in this regard. Silica fume and calcined clay can provide concrete with a chloride resistance of under 1000 coulombs using the ASTM C 1202 rapid chloride permeability test (Barger and others 1997). Tests show that the permeability of concrete decreases as the quantity of hydrated cementing materials increases and the water-cementitious materials ratio decreases. The absorption of fly-ash concrete is about the same as concrete without ash, although some ashes can reduce absorption by 20% or more.

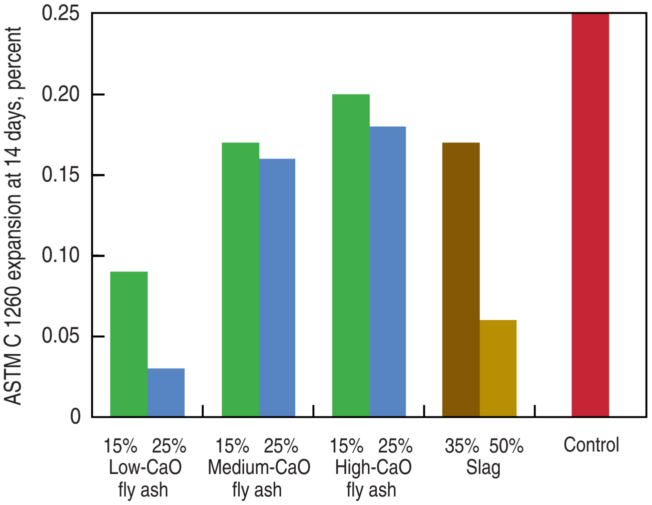


Fig. 3-21. Effect of different fly ashes and slag on alkali-silica reactivity. Note that some ashes are more effective than others in controlling the reaction and that dosage of the ash or slag is critical. A highly reactive natural aggregate was used in this test. A less reactive aggregate would require less ash or slag to control the reaction. A common limit for evaluating the effectiveness of pozzolans or slags is 0.10% expansion using this rapid mortar bar test (Detwiler 2002).

Alkali-Aggregate Reactivity

Alkali-silica reactivity can be controlled through the use of certain supplementary cementitious materials. Silica fume, fly ash, ground granulated blast-furnace slag, calcined clay, calcined shale, and other pozzolans have been reported to significantly reduce alkali-silica reactivity (Figs. 3-21 and 3-22). Low calcium Class F ashes have reduced reactivity

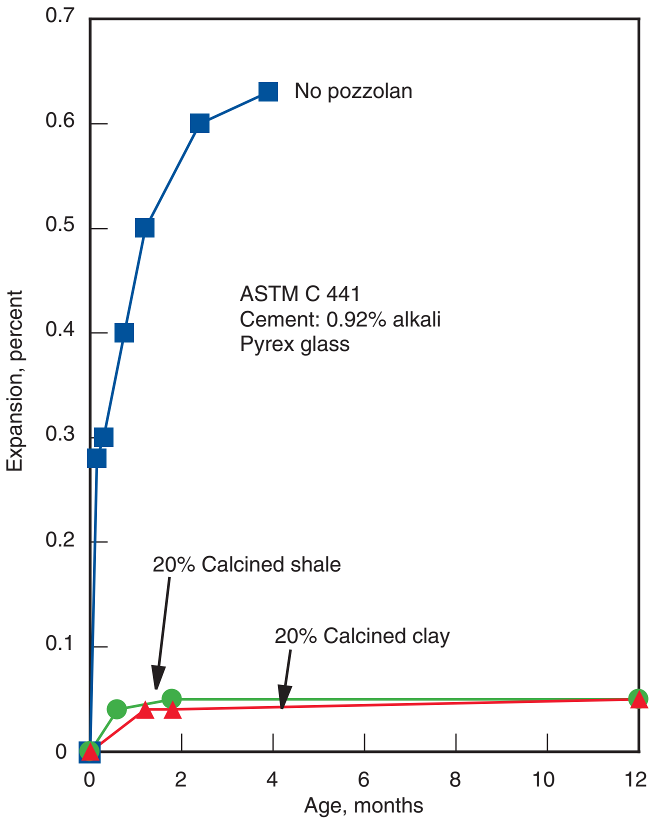


Fig. 3-22. Reduction of alkali-silica reactivity by calcined clay and calcined shale (Lerch 1950).

expansion up to 70% or more in some cases. At optimum dosage, Class C ashes can also reduce reactivity but to a lesser degree than most Class F ashes. Supplementary cementing materials provide additional calcium silicate hydrate to chemically tie up the alkalies in the concrete (Bhatty 1985, and Bhatty and Greening 1986). Determination of optimum supplementary cementing materials dosage is important to maximize the reduction in reactivity and to avoid dosages and materials that can aggravate reactivity. Dosage rates should be verified by tests, such as ASTM C 1260 (AASHTO T 303) or ASTM C 1293.

Supplementary cementing materials that reduce alkali-silica reactions will not reduce alkali-carbonate reactions, a type of reaction involving cement alkalies and certain dolomitic limestones.

Descriptions of aggregate testing and preventive measures to be taken to prevent deleterious alkali-aggregate reaction are discussed in Farny and Kosmatka (1997), PCA (1998), and AASHTO (2000).

Sulfate Resistance

With proper proportioning and material selection, silica fume, fly ash, calcined shale, and ground slag can improve the resistance of concrete to sulfate or seawater attack. This is done primarily by reducing permeability and by reducing the amount of reactive elements (such as calcium) needed for expansive sulfate reactions. For improved sulfate resistance of lean concrete, one study showed that for a particular Class F ash, an adequate amount was approximately 20% of the cement plus fly ash; this illustrates the need to determine optimum ash contents, as higher ash contents were detrimental (Stark 1989).

The sulfate resistance of high-cement-content, low water-cement ratio concrete made with a sulfate resistant cement is so great that fly ash has little opportunity to improve resistance. Concretes with Class F ashes are generally more sulfate resistant than those made with Class C ashes. Some Class C ashes have been shown to reduce sulfate resistance at normal dosage rates.

Ground slag is generally considered beneficial in sulfate environments. However, one long-term study in a very severe environment showed a slight reduction in sulfate resistance in concrete containing ground slag compared to concrete containing only portland cement as the cementing material (Stark 1986 and 1989). One reason for decreased performance with slag in this study is that the mixtures may not have been optimized for sulfate resistance.

Other studies indicate that concrete with ground slag has a sulfate resistance equal to or greater than concrete made with Type V sulfate-resistant portland cement (ACI 233 and Detwiler, Bhatty, and Bhattacharja 1996). Calcined clay has been demonstrated to provide sulfate resistance greater than high-sulfate resistant Type V cement (Barger and others 1997).

Corrosion of Embedded Steel

Some supplementary cementing materials reduce steel corrosion by reducing the permeability of properly cured concrete to water, air, and chloride ions. Fly ash can significantly reduce chloride-ion ingress. Silica fume greatly decreases permeability and chloride-ion ingress and also significantly increases electrical resistivity, thereby reducing the electrochemical reaction of corrosion. Concrete containing silica fume or metakaolin is often used in overlays and full-depth slab placements on bridges and parking garages; these structures are particularly vulnerable to corrosion due to chloride-ion ingress.

Carbonation

Carbonation of concrete is a process by which carbon dioxide from the air penetrates the concrete and reacts with the hydroxides, such as calcium hydroxide, to form carbonates. In the reaction with calcium hydroxide, calcium carbonate is formed. Carbonation lowers the alkalinity of concrete. High alkalinity is needed to protect embedded steel from corrosion; consequently, concrete should be resistant to carbonation to help prevent steel corrosion.

The amount of carbonation is significantly increased in concretes with a high water-cementing materials ratio, low cement content, short curing period, low strength, and a highly permeable or porous paste. The depth of carbonation of good quality concrete is generally of little practical significance. At normal dosages, fly ash is reported to slightly increase carbonation, but usually not to a significant amount in concrete with short (normal) moist-curing periods (Campbell, Sturm, and Kosmatka 1991).

Chemical Resistance

Supplementary cementing materials often reduce chemical attack by reducing the permeability of concrete. Although many of these materials may improve chemical resistance, they do not make concrete totally immune to attack. Concrete in severe chemical exposure should be protected using barrier systems. Kerkhoff (2001) provides a discussion of methods and materials to protect concrete from aggressive chemicals and exposures.

Soundness

Normal dosages of fly ash, slag, silica fume and natural pozzolans do not affect the soundness of concrete. Concrete soundness is protected by soundness requirements, such as autoclave expansion limits, on the materials. Dosages in concrete should not exceed dosages deemed safe in the autoclave test.

Concrete Color

Supplementary cementitious materials may slightly alter the color of hardened concrete. Color effects are related to the color and amount of the material used in concrete. Many supplementary cementing materials resemble the color of portland cement and therefore have little effect on color of the hardened concrete. Some silica fumes may give concrete a slightly bluish or dark gray tint and tan fly ash may impart a tan color to concrete when used in large quantities. Ground slag and metakaolin can make concrete whiter. Ground slag can initially impart a bluish or greenish undertone.

CONCRETE MIX PROPORTIONS

The optimum amounts of supplementary cementing materials used with portland cement or blended cement are determined by testing, by the relative cost and availability of the materials, and by the specified properties of the concrete.

Several test mixtures are required to determine the optimum amount of pozzolan or slag. These mixtures should cover a range of blends to establish the relationship between strength and water to cementing materials ratio. These mixtures should be established according to ACI Standard 211.1 or 211.2, taking into account the relative densities of the supplementary cementing materials. These are usually different from the relative density of portland cement. The results of these tests will be a family of strength curves for each age at which the concrete is required to meet certain specified requirements. The dosage of a cementitious material is usually stated as a mass percentage of all the cementitious materials in a concrete mixture.

Typical practice in the United States uses fly ash, slag, silica fume, calcined clay, or calcined shale as an addition to portland cement or as a partial replacement for some of the portland cement. Blended cements, which already contain pozzolans or slag, are designed to be used with or without additional supplementary cementitious materials.

Concrete mixtures with more than one supplementary cementitious material are also used. For example, a concrete mixture may contain portland cement, fly ash, and silica fume. Such mixes are called ternary concretes. When fly ash, slag, silica fume, or natural pozzolans are used in combination with portland or blended cement, the proportioned concrete mixture should be tested to demonstrate that it meets the required concrete properties for the project.

AVAILABILITY

All supplementary cementitious materials may not be available in all areas. Consult local material suppliers on available materials. Class F fly ashes are usually available in the Eastern United States, while Class C ashes are available in the Midwest and West. Silica fume is available in most locations because only small dosages are used. Calcined clays and shales are available in select areas. Ground granulated slags are available in most regions.

STORAGE

In most cases, moisture will not affect the physical performance of supplementary cementing materials. These materials should, however, be kept dry to avoid difficulties in handling and discharge. Class C fly ash and calcined shale must be kept dry as they will set and harden when exposed to moisture. Equipment for handling and storing these materials is similar to that required for cement. Additional modifications may be required where using silica fume, which does not have the same flowing characteristics as other supplementary cementing materials (and may be supplied as a liquid).

These materials are usually kept in bulk storage facilities or silos, although some products are available in bags. Because the materials may resemble portland cement in color and fineness, the storage facilities should be clearly marked to avoid the possibility of misuse and contamination with other materials at the batch plant. All valves and piping should also be clearly marked and properly sealed to avoid leakage and contamination. Fly ash, slag, and natural pozzolans should be weighed after the portland or blended cement in the batching sequence to avoid overdosing in case valves stick.

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