Chapter 2
Fly Ash

Introduction

Fly ash is a by-product of the combustion of pulverized coal in thermal power plants. The dust-collection system removes the fly ash, as a fine particulate residue, from the combustion gases before they are discharged into the atmosphere.

Fly ash particles are typically spherical, ranging in diameter from <1 μm up to 150 μm. The type of dust collection equipment used largely determines the range of particle sizes in any given fly ash. The fly ash from boilers at some older plants using mechanical collectors alone is coarser than from plants using electrostatic precipitators.

The types and relative amounts of incombustible matter in the coal used determine the chemical composition of fly ash. More than 85 % of most fly ashes comprise chemical compounds and glasses formed from the elements silicon, aluminum, iron, calcium, and magnesium. Generally, fly ash from the combustion of subbituminous coals contains more calcium and less iron than fly ash from bituminous coal. Unburned coal collects with the fly ash carbon particles, the amount of which is determined by such factors as the rate of combustion, the air/fuel, and the degree of pulverization of the coal. In general, fly ash from subbituminous coals contains very little unburned carbon. Plants that operate only intermittently (peak-load stations), burning bituminous coals, produce the largest percentage of unburned carbon.

The term fly ash was first used in the electrical power industry ca. 1930, the first comprehensive data on its use in concrete in North America were reported in 1937 by Davis et al. [1]. The first major practical application was reported in 1948 with the publication by the United States Bureau of Reclamation if data on the use of fly ash in the construction of the Hungry Horse Dam. Worldwide acceptance of fly ash slowly followed these early efforts, but interest has been particularly noticeable in the wake of the rapid increase in energy costs (and hence cement costs) that occurred during the 1970s.

In 1980 [2], Manz reported the 1977 estimated world production of coal ash was 278.443 Mt, of which ~14 % was used. In a recent report dealing with the

A. A. Ramezanianpour, *Cement Replacement Materials*,
Springer Geochemistry/Mineralogy, DOI: 10.1007/978-3-642-36721-2_2,

worldwide production and use of coal ash, Manz [3] indicated that ~562 Mt of coal ash was produced in 1989, of which ~90 Mt or 16.1 %, was used. The total amount used in concrete was about 27.9 Mt consisting of 2.8 % as cement raw material, 7.6 Mt in blend cement, and 17.5 Mt for cement replacement. Compared with 1977 [2], an approximately threefold increase has occurred in the amount used as cement replacement.

In recent years, it has become evident that fly ashes differ in significant and definable ways, reflecting their combustion and, to some extent, their origin. The Canadian Standards Association (CSA) [4] and ASTM [5] recognize two general classes of fly ash:

- Class C, normally produced from lignite of subbituminous coals; and
- Class F, normally produced from bituminous coals.

Physical, Chemical, and Mineralogical Properties of Fly Ash

Physical Properties

Fly ash is a fine-grained material consisting mostly of spherical particles. Some ashes also contain irregular of angular particles. The size of particles varies depending on the sources. Some ashes may be finer or coarser than Portland cement particles. Figures 2.1 and 2.2 show the scanning electron microscope (SEM) micrographs of polished sections of subbituminous and lignite fly ashes [6]. Figure 2.3 shows a secondary electron SEM image of bituminous fly ash particles. Some of these particles appear to be solid, whereas some larger particles appear to be portions of thin, hollow spheres containing many smaller particles.

Fineness

Dry- and wet-sieving methods are commonly used in the measurement of fineness of fly ashes. ASTM designation C311-77 recommends determining the amount of the sample retained when wet sieved on a 45 µm sieve, in accordance with ASTM method C 430, except that a representative sample of the fly ash of natural pozzolan is substituted for hydraulic cement in the determination. Dry sieving on a 45 µm sieve can be performed according to a method established at CANMET [7]. Several countries specify standards for maximum residue (in percentage) retained on a 45 µm sieve as follows [7].

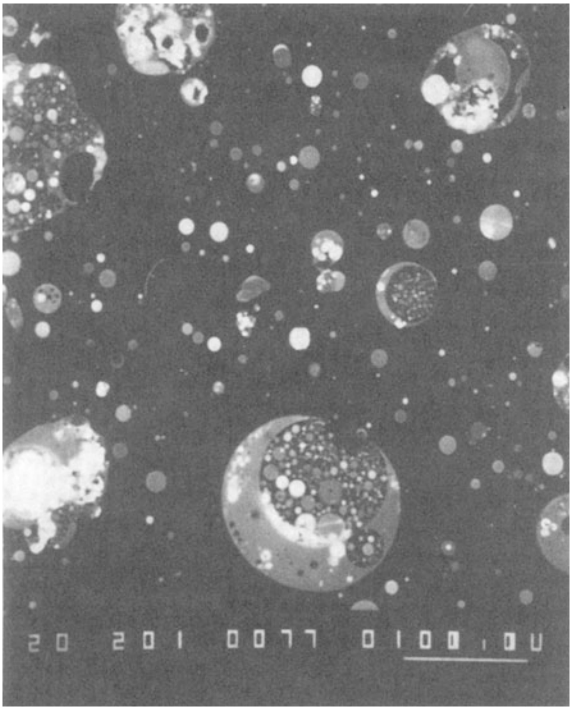


Fig. 2.1 SEM micrograph of a subbituminous ash [6] (Backscattered electron image of a polished section of the dispersed sample)

Germany	50
Australia	50
United States	34
Canada	34
Japan	25
Spain	14
United Kingdom	12.5

Results of SEM and particle-size analysis have shown that spherical and rounded fly ashes vary in size from 1.0 to 150 μm fly ashes of irregular and angular shape are usually larger.

Particle- size distribution of fly ash can be determined by various means, such as X-ray micrograph, laser particle-size analyzer, and coulter counter. In some cases, the agglomeration of a number of small particles may form a large particle. In most cases, fly ashes contain particles of >1 μm diameter. Mehta [9], using an X-ray sedimentation technique, reported particle-size distribution data for several U.S. fly ashes. Mehta found that high-calcium fly ashes were finer than the low-calcium fly ashes, and he related this difference to the presence of larger amounts of alkali sulphates in high-calcium fly ashes.

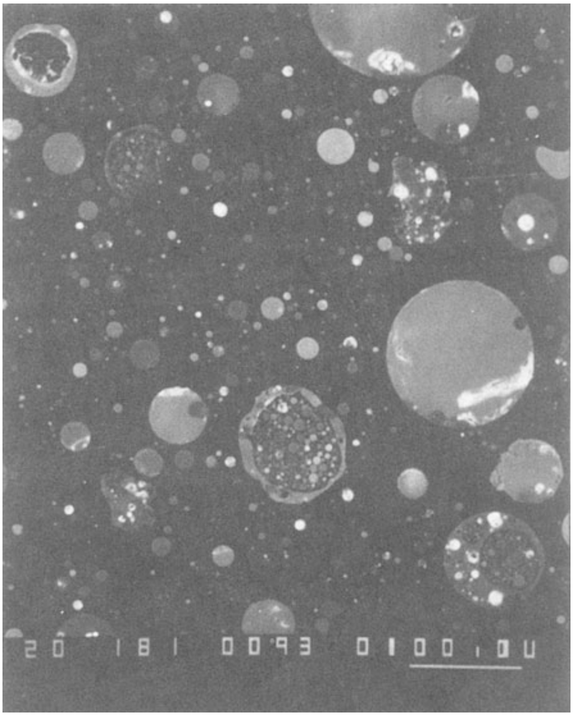


Fig. 2.2 SEM micrograph of a lignite fly ash [6] (Backscattered electron image of a polished section of the dispersed sample)

Specific Surface Area

The specific surface area of fly ash, which is the area of a unit of mass, is measurable by different technique, which measures the resistance of compacted particles to an air flow. ASTM C 204 describes this method for the measurement of the surface area of Portland cement.

Particle-size analysis can also be used for the determination of the specific surface area of fly ash; a laser particle-size analyzer is usually used for the measurement. The Brunauer–Emmett–Teller (BET) nitrogen absorption technique has also been used for determining the specific surface of the particles, but the results obtained by this method are usually higher than the results obtained by the Blaine specific surface-area technique or particle-size analysis.

Cabrera et al. [10] using the Blain technique, particle-size analysis, and the BEST technique, measured and calculated the specific surface area of various fly ashes. The results of their investigation are shown in Table 2.1.

The specific surface values measured by the BEST technique (Table 2.1) are higher than the values obtained with the Blaine technique and particle-size

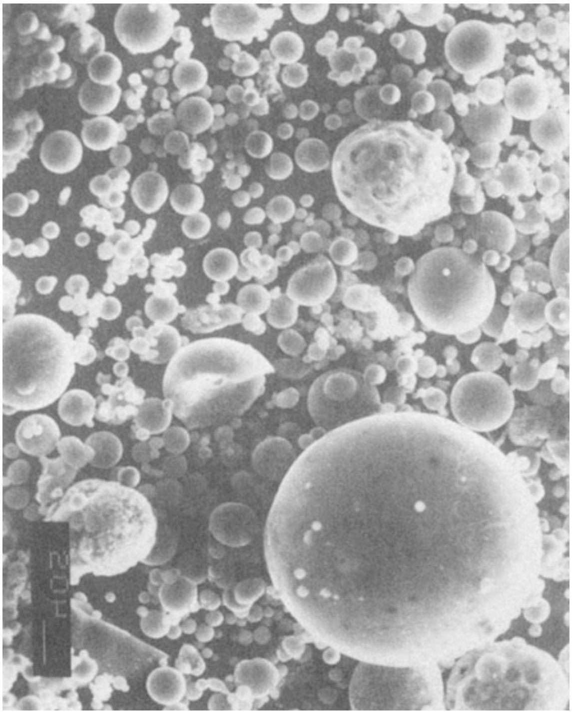


Fig. 2.3 SEM micrograph of a bituminous ash [6] (Secondary electron image of the sample)

analysis. This large difference is due to the face that BET technique measures the totality of voids in the surface of particles.

In experiments conducted at CANMET [6] the specific surface area measured by the Blaine technique was found to vary from a low value of 130 m^2/kg for a bituminous ash to high value of 581 m^2/kg for a lignite ash (see Table 2.2). Fly ashes collected in electrostatic precipitators have shown surface areas of 400–700 m^2/kg [8]. The specific surface area of cyclone-collected (mechanically collected) ashes varies between 150 and 200 m^2/kg. Some modern electrostatic precipitators have collected fly ashes with a surface area of $\leq$1200 m^2/kg.

Specific Gravity

The specific gravity of hydraulic cement is determined according to ASTM C 188. This test method can also be used to determine the specific gravity of fly ashes. If fly ashes contain water-soluble compounds, the use of a non-aqueous solvent, instead of water, is recommended.

The specific gravity of different fly ashes varies over a wide range, like the other physical properties. In the CANMET investigation of 11 fly ashes [6], the specific gravity ranged from a low value of 1.90 for a subbituminous ash to a high

Table 2.1 Specific surface area of nine fly ashes, measured by three different methods Enrollment in local colleges [10]

Fly ash	Blaine (m^2/kg)	Particle-size analysis (m^2/kg)	BET (m^2/kg)
A	305	81	4070
B	413	97	3820
C	335	115	1020
D	209	92	480
E	193	NA	4700
F	671	102	8900
G	311	81	6500
H	288	NA	1240
I	254	80	970

Table 2.2 Physical properties of fly ashes [6]

Fly ash source	Type of coal[a]	Physical properties			
		Specific gravity (Le Chatelier method)	Fineness (% retained on 45 μm sieve)		Blaine specific surface area (m^2/kg)
			Wet sieving[b]	Dry sieving (Alpine jet)	
1	B	2.35	17.3 (14.9)	12.3	289
2	B	2.58	14.7 (12.7)	10.2	312
3	B	2.88	25.2 (21.7)	18.0	127
4	B	2.96	19.2 (16.6)	14.0	198
5	B	2.38	21.2 (18.3)	16.1	448
6	B	2.22	40.7 (35.1)	30.3	303
7	SB	1.90	33.2 (28.7)	26.4	215
8	SB	2.05	19.4 (16.7)	14.3	326
9	SB	2.11	46.0 (39.7)	33.0	240
10	L	2.38	24.9 (21.5)	18.8	286
11	L	2.53	2.7 (2.4)	2.5	581

[a] *B*, Bituminous; *SB*, Subbituminous; *L*, Lignite
[b] Values in parentheses do not include sieve correction factor

value of 2.96 for an iron-rich bituminous ash. Three subbituminous ashes had a comparatively low specific gravity of ~2.0, and this suggested that hollow particles, such as cenospheres or plerosferes (Fig. 2.1), were present in significant proportions in the three ashes (see Table 2.2).

Chemical Composition

The chemical composition of fly ashes depends on the characteristics and composition of the coal burned in power stations. The chemical analysis of fly ashes by means of X-ray fluorescence (XRF) and spectrometry techniques shows that SiO_2,

Al_2O_3, Fe_2O_3, and CaO are the major constituents of most fly ashes. Other elements are MgO, Na_2O, K_2O, SO_3, MnO, TiO_2, and C.

The chemical analysis of various fly ashes has indicated a wide range of compositions, reflecting wide variations in the coal used in power plants over the world. A CANMET [11] review of the chemical, physical, and pozzolanic properties of fly ash emphasized the wide variations in fly ash compositions.

In the United States, a typical chemical analysis for low-calcium fly ashes (<10 % CaO), usually formed by the combustion of bituminous coal, shows 45–65 wt% SiO_2, 20–30 wt% Al_2O_3, 4–20 wt% Fe_2O_3, 1–2 wt% MgO, $\leq$3 wt% alkalis, and $\leq$5 wt% loss on ignition (LOI) [9, 12, 13]. The high-calcium fly ashes ($\geq$10 % CaO) formed by the combustion of subbitummious and lignite coal typically contain 20–50 wt% SiO_2, 15–20 wt% Al_2O_3, 15–30 wt% CaO, 5–10 wt% Fe_2O_3, 3–5 wt% MgO, $\leq$8 wt% alkalis, and <1 wt% LOI.

ASTM C 311 describes the standard method for sampling fly ash for use as a mineral admixture in Portland cement concrete. According to this standard, silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), iron oxide (Fe_2O_3), calcium oxide (CaO), free CaO, Magnesium oxide (MgO), sulphur trioxide (SO_3), available alkalis, Na_2O and K_2O LOI at 1000 °C, and moisture content at 105 °C must be determined.

Loss on ignition, the weight loss of fly ashes burned at temperatures $\leq$1000 °C, is related to the presence of carbonates, combined water in residual clay minerals, and combustion of free carbon. Carbon is the most important component of LOI. The water required for workability of mortars and concretes depends on the carbon content of fly ashes: the higher the carbon content of a fly ash, the more water is needed to produce a paste of normal consistency.

A comparison of low-calcium and high-calcium fly ashes shows that high-calcium fly ashes usually contain a smaller amount of unburned carbon (<1 %). In the case of low-calcium fly ashes, complete removal of carbon is rare. Indeed, the carbon may be encapsulated in glass, but a major portion appears to occur as cellular particles that have a very large specific surface and are, therefore, able to adsorb significant quantities not only of water, but of chemical admixtures in concrete, such as air-entraining admixtures (AEA), water-reducing admixtures, and retarders.

Several authors have reported the chemical composition of various fly ashes produced in North America. Diamond [14] discussed the range of chemical and mineralogical constituents. This study included both ASTM Type C (high-calcium) and ASTM Type F (low-calcium) ashes. Carette and Malhotra [6], in their study of 11 Canadian fly ashes, indicated a wide range of chemical composition. Table 2.3 gives the chemical composition of each fly ash as determined by inductively coupled argon plasma (ICAP) spectrometry. Manz et al. [15], examined 19 North American lignite fly ashes and characterized these for bulk and intergrain chemical composition. Table 2.4 shows the bulk chemical composition of each ash. The results of CANMET investigations [6] and the data reported by Manz et al. [15], on bituminous, subbituminous, and lignite ashes obtained from various coal-fired power plants in North America show significant differences among the chemical compositions of the fly ashes.

Table 2.3 Chemical composition of fly ashes [6]

Fly ash source	Type of coal[b]	Chemical composition (wt%)[a]												
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	BaO	SO_3	LOI[c]
1	B	47.1	23.0	20.4	1.21	1.17	0.54	3.16	0.85	0.16	0.78	0.07	0.67	2.88
2	B	44.1	21.4	26.8	1.95	0.99	0.56	2.32	0.80	0.25	0.12	0.07	0.96	0.70
3	B	35.5	12.5	44.7	1.89	0.63	0.10	1.75	0.56	0.59	0.12	0.04	0.75	0.75
4	B	38.3	12.8	39.7	4.49	0.43	0.14	1.54	0.59	1.54	0.20	0.04	1.34	0.88
5	B	45.1	22.2	15.7	3.77	0.91	0.58	1.52	0.98	0.32	0.32	0.12	1.40	9.72
6	B	48.0	21.5	10.6	6.72	0.96	0.56	0.86	0.91	0.26	0.36	0.21	0.52	6.89
7	SB	55.7	20.4	4.61	10.7	1.53	4.65	1.00	0.43	0.41	0.50	0.75	0.38	0.44
8	SB	55.6	23.1	3.48	12.3	1.21	1.67	0.50	0.64	0.13	0.56	0.47	0.30	0.29
9	SB	62.1	21.4	2.99	11.0	1.76	0.30	0.72	0.65	0.10	0.69	0.33	0.16	0.70
10	L	46.3	22.1	3.10	13.3	3.11	7.30	0.78	0.78	0.44	0.13	1.18	0.80	0.65
11	L	44.5	21.1	3.38	12.9	3.10	6.25	0.80	0.94	0.66	0.17	1.22	7.81	0.82

[a] By inductively coupled argon (ICAP) technique, except for Na_2O, K_2O, SO_3, and LOI

[b] *B*, Bituminous; *SB*, Subbituminous; *L*, Lignite

[c] 105–750 °C

Table 2.4 Chemical analyses for North American lignite fly ashes

Fly ash no.	Bulk chemical analysis (wt%)										
	SiO_2	Al_2O_3	Fe_2O_3	Sum	CaO	MgO	SO_3	Na_2O	K_2O	Avail. alkalis	LOI
North Dakota and Montana lignite											
81-271	25.7	15.0	9.2	49.9	26.8	7.2	8.8			1.2	0.3
81-560	30.2	12.5	4.6	47.3	23.6	7.9	9.6	7.3	0.6	5.2	1.8
82-179	42.1	12.0	8.1	62.2	18.5	5.0	4.1	8.0	1.2	3.8	0.4
83-275	45.6	15.5	7.3	68.4	20.3	5.0	1.9	1.0	1.7	0.8	0.1
85-352	39.6	14.0	10.7	64.3	15.9	5.7	2.6	4.4	1.4	2.2	0.1
87-139	27.9	10.7	9.9	48.5	21.6	5.5	12.3	5.4	1.5	3.7	1.4
86-305	35.2	20.3	6.3	61.8	25.0	6.8	1.1	0.2	0.5	0.2	0.3
Saskatchewan lignite											
85-147	50.4	21.4	3.5	75.3	11.6	3.0	0.5	0.9	3.1	3.1	0.5
86-805	46.4	24.5	4.9	75.8	13.7	4.0	0.6	1.6	0.7	0.7	0.1
87-144	47.9	21.9	4.9	74.7	13.3	2.9	1.1	1.0	2.9	2.9	0.1
Texas and Louisiana lignite											
87-146	50.3	20.2	5.5	76.0	14.4	4.0	0.7	0.9	1.2		0.2
87-147	57.9	26.3	3.9	88.1	9.6	2.1	0.4	0.0	0.4	0.3	0.3
87-154	62.3	20.9	2.2	85.3	6.1	0.7	0.5	4.1	2.1	5.5	0.2
87-155	52.2	18.0	10.5	80.7	11.9	2.5	1.3	0.2	1.4	0.5	0.1
87-156	55.5	18.6	4.3	78.4	7.0	0.8	0.3	0.6	1.9	0.3	0.1
87-159	57.5	20.6	7.0	85.1	9.1	2.6	0.2	0.4	1.4	0.3	0.1
87-219	62.0	20.1	2.0	84.1	6.9	1.2	0.6	0.9	0.9	1.5	0.4
87-239	48.9	18.5	21.8	89.1	7.3	2.6	0.5	0.4	0.9	0.8	0.1
87-157	52.8	23.6	8.9	85.3	9.5	2.7	0.4	1.1	0.8	1.6	0.0

Note ASTM C 618 specification limits: Class F fly ash: $SiO_2 + Al_2O + Fe_2O_3 = 70$ %; $SO_3 = 5$ % max; Class C fly ash: $SiO_2 + Al_2O_3 + Fe_2O_3 = 50$ %; $SO_3 = 5$ % max; LOI = 5 % max

Mineralogical Composition

In general, both the type and source of fly ash influence its mineralogical composition. Owing to the rapid cooling of burned coal in the power plant, fly ashes consist of non-crystalline particle (≤90 %), or glass, and a small amount of crystalline material. Depending on the system of burning, some unburned coal may be collected with ash particles.

The X-ray diffraction (XRD) and infrared spectroscopy techniques are usually used for the determination of crystalline phases in fly ashes. The glass phases are determined by the low-angle XRD technique.

In addition to substantial amount of glassy material, each fly ash may contain one or more of the four major crystalline phase: quartz, mullite, magnetite, and hematite. In subbituminous fly ashes, the crystalline phases may include C_3A, $C_4A\overline{S}$, calcium sulphate, and alkali sulphates [16].

As was observed with chemical composition, the mineralogical composition of fly ashes by Carrette and Malhotra [6] varied over a wide range. Figure 2.4 shows an X-ray diffractogram for one of the bituminous fly ashes. A quantitative determination of the major crystalline phase contained in the fly ashes was also made by a quantitative XRD technique. The results are given in Table 2.5.

Watt and Thorne [17] examined 14 fly ashes by microscopic and XRD techniques and found that most of them, after extraction with water, contained only four crystalline phases in significant amounts: quartz, mullite, magnetite, and hematite.

The reactivity of fly ashes is related to the non-crystalline phase glass. The reasons for the high reactivity of high-calcium fly ashes may partially lie in the chemical composition of the glass, which is different from that of the glass in low-calcium fly ashes. Diamond and Lopez-Flores [18] and Mehta [13] pointed out that

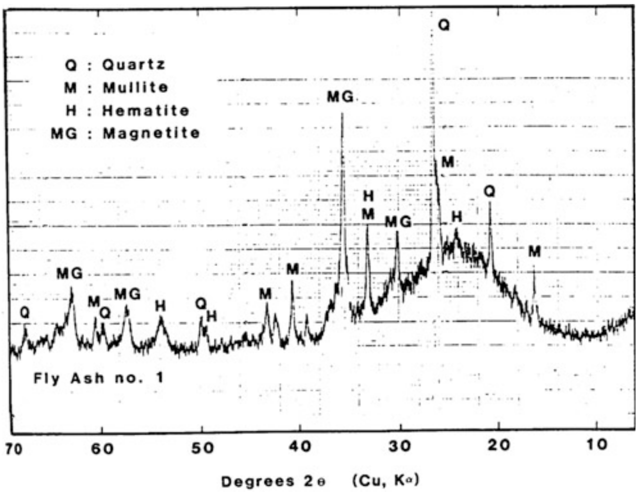


Fig. 2.4 X-ray diffractogram for a bituminous fly ash [6]

Table 2.5 Mineralogical composition of some selected fly ashes [6]

Fly ash source	Type of coal[a]	Phase composition (%)					
		Glass	Quartz	Mullite	Magnetite	Hematite	LOI (%)
1	B	72.1	4.0	12.6	6.2	1.6	3.5
4	B	70.1	3.2	3.3	17.2	4.7	1.5
5	B	55.6	6.2	19.8	5.6	3.1	9.7
6	B	54.2	8.3	23.5	4.4	2.1	7.5
7	SB	90.2	2.9	6.1	–	–	0.8
8	SB	83.9	4.1	10.2	–	1.4	0.4
9	SB	79.8	8.7	11.5	–	–	0.8
10	L	94.5	4.6	–	–	–	0.9

[a] *B*, Bituminous; *SB*, Subbituminous; *L*, Lignite

the composition of glass in low-calcium fly ashes show diffused halo maxima at 21–25° 2θ (CuK_α radiation); high-calcium fly ashes, at 30–34° 2θ.

The Fly Ash Hydration Reactions

High-calcium fly ash, which is mainly composed of glass phase and some crystalline phases (including C_2S, C_3A, $CaSO_4$, MgO, free CaO, and $C_4A_3\overline{S}$) has self-hardening properties. Ettringite, mono sulphoaluminate hydrate, and C–S–H cause hardening of the fly ash when mixed with water. Ghosh and Pratt [20] reported that the hydration behavior of C_3A and C_2S in fly ash is the same as that in cement, but the rate of formation of C–S–H from the glass phase is comparatively slow.

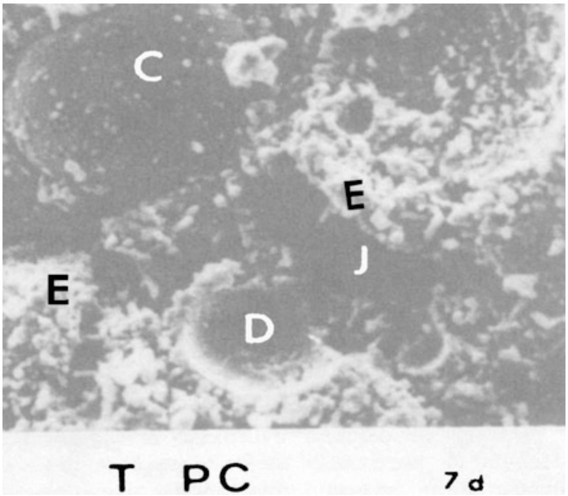
Low-calcium fly ash, which has very little of no self-cementing properties, hydrates when alkalis and $Ca(OH)_2$ are added. The hydration products such as C–S–H, C_2ASH_8 and C_4AH_{13} are formed, and hydrogarnet is produced at a later stage [21]. As more $Ca(OH)_2$ is supplied, more of it is fixed by silica and alumina in fly ash. The degree of hydration of fly ash increased in the presence of gypsum because the surface is activated by the destruction of the structure of the glass and crystalline phases caused by the dissociation of Al_2O_3 reacting with SO_4^{2-}.

The Effect of Fly Ash on the Hydration of Cement Compounds

Figure 2.5 shows the SEM micrograph of the fracture surface of hardened pozzolanic Cement Paste.

The hydration and reaction mechanisms of fly ash and cement compounds, such as C_3S and C_3A are more complicated than fly ash reactions with lime. Takemoto and Uchikawa [19] proposed schematic explanations of the C_3S-pozzolan reaction

Fig. 2.5 SEM micrograph of the fracture surface of hardened pozzolanic cement paste [21]. *A*, ettringite; *B*, type I C–S–H; *C*, fly ash grain; *D*, cast-off shell of fly ash; *E*, type III C–S–H; *F*, calcium hydroxide; *G*, mono sulphoaluminate; *H*, pozzolan grain; *I*, pozzolan grain; and *J*, capillary space



and C_3A-pozzolan reaction, which are shown in Figs. 2.6 and 2.7, respectively. According to the authors, in C_3S-pozzolan system, calcium ions dissolved from C_3S run about freely in liquid and are adsorbed on the surfaces of pozzolan particles. C–S–H formed by the hydration of C_3S precipitate as the hydrates of high Ca/Si ratio on the surface of C_3S grains and as the porous hydrates of low Ca/Si ratio on the surfaces of pozzolan particles. Attack of the pozzolan surface in water brings about gradual dissolution of Na^+ and K^+, resulting in Si and Al rich amorphous layer on the surfaces. Dissolved Na^+ and K^+ increase the OH^- concentration and accelerate the dissolution of SiO_4^{4-} and layer. Due to the osmotic pressure, the layer swells gradually and the void between layer and pozzolan particle is formed. When the pressure in the void ruptures the film, $SiO_4^{4-}$and AlO_2^- diffuse into the Ca^{2+}- rich solution. Additional C–S–H and Ca–Al hydrate precipitate on the surface of outer hydrates of C_3S particles and to a slight extent on the ruptured film. Vacant space remains inside the film as the hydrates do not precipitate there because of high concentration of alkalies. For pozzolans with low alkalies, destruction of amorphous Si, Al rich film enables Ca^{2+} to move into the inside of the film and precipitate calcium silicate and calcium aluminate hydrates on the surface of pozzolan grain. Therefore no space is observed between pozzolan grains and hydrates.

Figure 2.8 shows the SEM micrograph of the fracture surface of C_3S-pozzolan paste.

The hydration of the C_3A-pozzolan system was first observed by Uchikawa and Uchida [22]. Figure 2.7 illustrates the schematic development of the C_3A-pozzolan system in the presence of calcium hydroxide and gypsum. According to Uchikawa and Uchida, the presence of the pozzoaln accelerates the hydration of C_3A by adsorbing Ca^{2+} from the liquid phase and by providing precipitation sites for ettringite and other hydrates. The C_3A-pozzolan reaction system is similar to

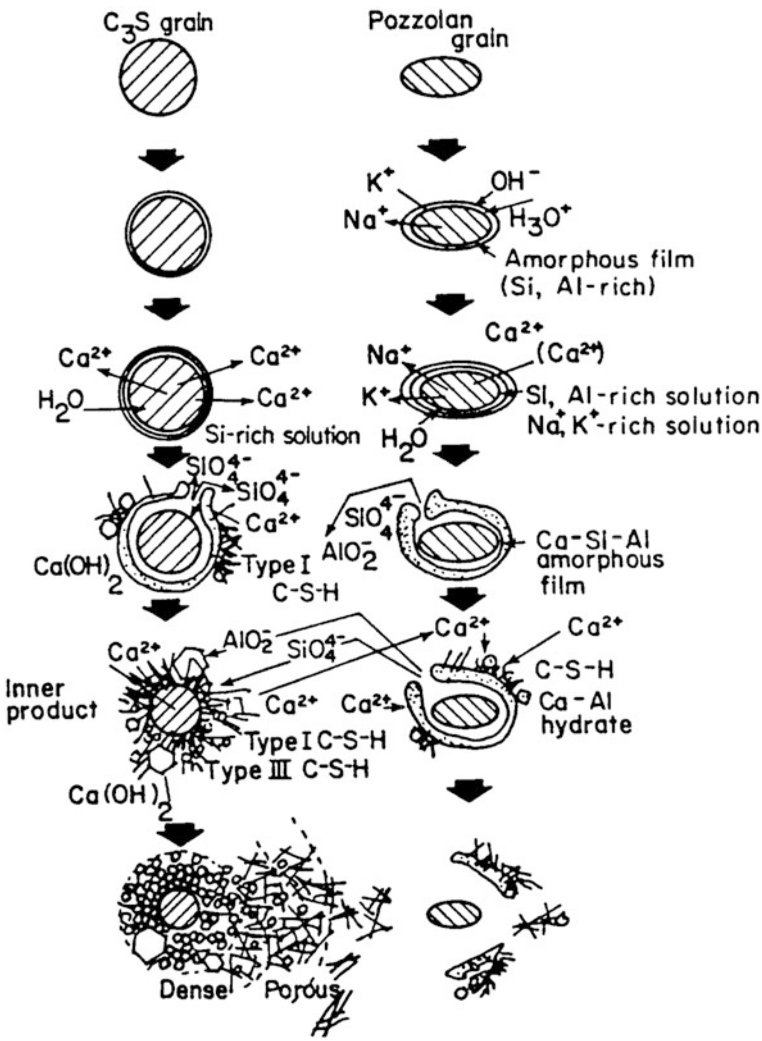


Fig. 2.6 Schematic representation of the mechanism of hydration in the C_3S-pozzolan system [19]

aluminate hydrate, and calcium silicate hydrate are formed on the surface film outside the pozzolan particles of on the surface hydrate layer of the C_3A particles, depending on the concentration of Ca^{2+} and SO_4^{2-} in solution.

As in the case of slag and some natural pozzolans, fly ash retards the hydration of C_3S at stages I and II (Fig. 2.6) and accelerates that at stage III and later (Fig. 2.6). In an investigation [23], C_3S with and without 30 % fly ash, composed of small quantities of quartz and mullite as well as the glass phase, was hydrated at 298 K with a water/cement of 0.5. The degree of hydration of C_3S was determined

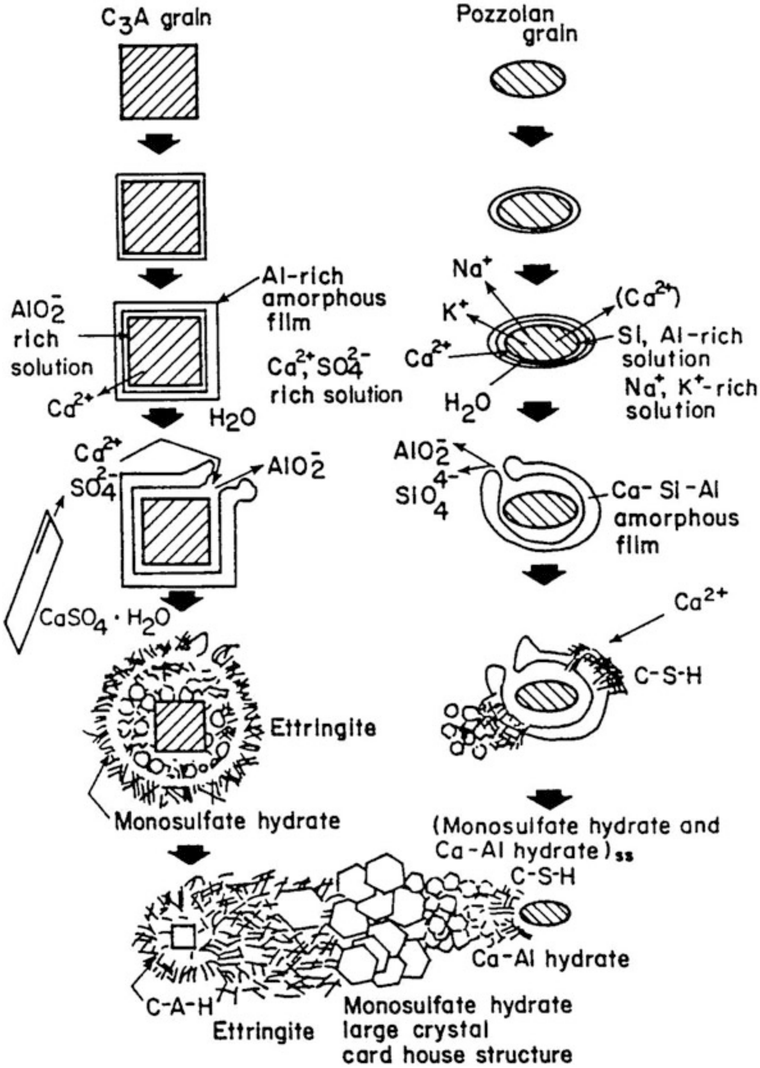


Fig. 2.7 Schematic explanation of the mechanism of hydration in the C_3A-pozzolan system in the presence of $Ca(OH)_2$ and $CaSO_4$ $2H_2O$ [19]

by XRD. The degree of hydration of C_3S alone after 1 day was 35 %, while that of the mixture with fly ash was 45 %. This result obviously shows that the hydration of C_3S at stage III (Fig. 2.6) is accelerated by adding fly ash.

Many researchers [24, 25] have reported that fly ash retards the hydration of C_3A. The degree of this retardation mainly depends on the sulphate content of fly ash, the amount of dissolved alkalis, and the calcium adsorption capacity. Ca^{2+} and SO_4^{2-} are dissolved from some high-calcium fly ashes. Dissolved Ca^{2+} is adsorbed

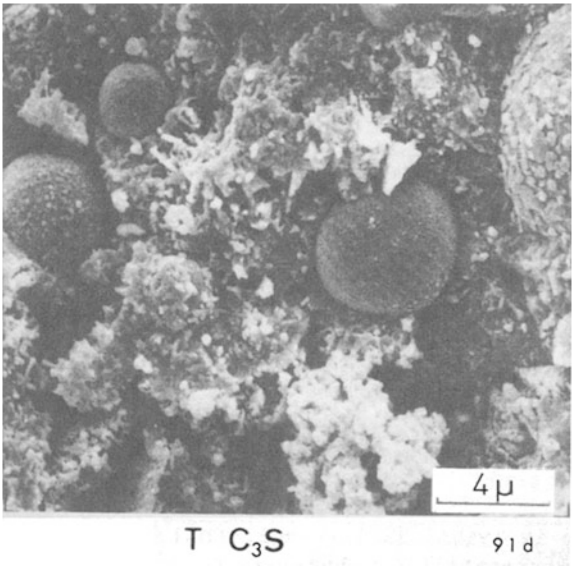


Fig. 2.8 SEM micrograph of the fracture surface of the C_3S-pozzolan paste, showing the clearance between the hydrates [19]

onto the Al-rich surface (produced by non-stoichiometric dissolution), lowering the hydration activity. Furthermore, the adsorption of SO_4^{2-} also retards the hydration of C_3A sulphate in fly ash retards the hydration more than the equivalent amount of added gypsum. This may be due to ions other than sulphate dissolved from the fly ash.

Diamond et al. [26] described the morphological aspect of the early reactions of a fly ash–cement system. Their research showed the occurrence of so-called duplex films, which rapidly develop in hydrating cement systems around exposed surfaces, such as sand grains and coarse aggregates. Such films consist of thin (0.50 μm), uniform, continuous layer of calcium hydroxide deposited quickly on the exposed surface and a thin, single layer of parallel, more or less widely spaced C–S–H gel particles. The gel is usually of type I, with the elongated particles oriented roughly perpendicular to the calcium hydroxide layer and the underlying surface. The total thickness of two layers usually >1 μm. As hydration proceeds, these duplex films may become bonded by other hydration products to other particles. The duplex film was formed on both fly ash and cement particles in a fly ash–cement system after 1 day at room temperature.

Factors Affecting Pozzolanic Reactivity of Fly Ashes

The reactivity of fly ash and other pozzolans with lime or cement is affected by inherent characteristics of the fly ash of pozzolan: chemical and mineralogical composition, morphology, fineness, and the amount of glass phase. External factors, such as thermal treatments and the addition of admixtures, also affect pozzolanic reactivity.

The sum of the silica + alumina + iron of fly ash has been stipulated by ASTM and some other standards associations as a major requirement. The silica + alumina content of fly ashes shows a good correction with long-term pozzolanic activity [27], although silica and alumina in an amorphous form only contribute to the pozzolanic activity, whereas mullite and quartz, which form by partial crystallization of the glassy phases in the fly ash, are nonreactive. Also, in most fly ashes, most of the iron oxide (Fe_2O_3) is present as nonreactive hematite and magnetite. A small amount of iron, which is present in glass, is reported to have a deleterious effect on the pozzolanic activity of fly ashes. Therefore, it has to be separated from silica and alumina when chemical requirements and pozzolanic activity of fly ashes are considered. For the above- mentioned reasons, other researchers [28, 29] have reported poor correlations between the compressive-strengths ratio (according to the pozzolanic activity index) and the sum of silicon + aluminum + iron oxides. These investigators reported that the carbon content did not significantly influence pozzolanic activity index in terms of compressive-strengths ratio.

Fineness of fly ashes is one of the most important physical properties affecting pozzolanic reactivity. The different techniques used for the measurement of the fineness of fly ash have shown different results. It is, therefore, difficult to explain the effect of fineness on pozzolanic activity.

Watt and Thorne [27, 30, 31] examined 14 well-characterized fly ashes to identify which physical and chemical characteristics determine the pozzolanic properties of fly ashes, based on the strength test. These authors developed a theoretical model that shows the relationship between the rate or degree of reaction of fly ash with lime and the fineness of the fly ash. They then compared the calculated values of the reacted material with those obtained experimentally. Their experimental results, however, suggested that the fly ashes with larger median particle size were more reactive than expected from the model. They related this to the spongy form of larger particles; microscopic observation confirmed that the larger particles became perforated during the reaction with lime.

Watt and Thorne [30] also reported that under normal and accelerated curing conditions, there were poor correlations between compressive strength and carbon content, glass content, silica + alumina content, density, and the specific surface area of the fly ash as single variables. However, the best correlation was with the specific surface area as determined by particle-size analysis. In accelerated tests performed on glasses of composition and fineness similar to those of fly ashes, the same conclusion was reached by other researchers [32].

Effects of Fly Ash on the Properties of Fresh Concrete

Fresh concrete is a concentrated suspension of particulate materials of widely differing densities, particle sizes, and chemical compositions in a solution of lime and other components. The system is not static. As soon as the cement and water mix, reactions commence that ultimately produce the binder that consolidates the concrete mass. New particles are formed, and the Original particles dissolve or are coated with cementitious products. The forces of dispersion, flocculation, and gravity compete to determine the spatial distribution of the materials in the changing mass. Heat is released during the chemical reactions, and the temperature rises. In all of these events, fly ash plays some role. Low-calcium fly ash will act largely as a fine aggregate of spherical form; high-calcium fly ash, on the other band, may participate in the early cementing reactions, in addition 10 being part of the particulate suspension.

Because concrete must be mixed and placed, frequently in a heavily reinforced formwork, it is necessary that in most cases a level of fluidity, generally termed workability, be maintained. This is determined by the rheological properties of the system, which are, in turn, influenced by all the components. Control of workability is one of the objectives of mixture proportioning.

Therefore, it is essential to understand the role of fly ash in the rheology of fresh concrete to fully exploit the potential of fly ash for improving concrete.

In practical terms, the fluidity of concrete is expressed by such properties as workability, pumpability, water needed 10 mix, and bleeding. As the use of fly ash has increased, a gradual understanding has started to form of its role in determining these properties. This chapter is largely concerned with these issues and with the other important properties of fresh concrete: temperature rise and air entrainment. Work carried out at CANMET [6], illustrates some of the effects of fly ash on the general properties of fresh concrete. The study dealt with the examination of II fly ashes from widely different sources in Canada. Table 2.3 gives the chemical properties of these ashes. A number of air-entrained concretes were prepared using the simple replacement method, and me mixtures were proportioned to obtain equal water/(cement + fly ash) at a fixed total cementitious-materials content.

In general, it is clear that at a fixed water/(cement + fly ash), slump does not always increase with the incorporation of fly ash. Another important factor revealed by the CANMET work is that the amount of air-entraining admixture (AEA) required to provide 6 % air varied greatly from one ash to another and was not always greater than that required by the control. Both of these issues are discussed in detail in this chapter.

Table 2.6 Results for time-of-set tests

Mixture no.	Nominal 28 days compressive strength (MPa)	Nominal percentage of fly ash	Time of setting (h:min)	
			Initial	Final
1	21	35	6:55	8:30
2	21	45	7:45	9:55
3	21	55	8:45	11:20
4	28	35	7:35	9:25
5	28	45	7:30	9:50
6	28	55	7:55	10:25
7	34	35	6:30	8:15
8	34	45	7:15	9:25
9	34	55	7:00	9:15

Influence of Fly Ash on the Setting Time of Portland Cement Concrete

The rate at which concrete sets during the first few hours after mixing is expressed as initial and final setting time and is determined by some form of penetrometer test. Fly ash may be expected to influence the rate of hardening of cement for a number of reasons:

- The ash itself may be cementitious (high calcium).
- Fly ash may contain sulphates that react with cement in the same way as the gypsum added to Portland cement does.
- The fly ash–cement mortar may contain less water as a consequence of the presence of fly ash, and this will influence the rate of stiffening.
- The ash may absorb surface-active agents added to modify the rheology (water reducers) of concrete, and again this influences the stiffness of me mortar.
- Fly ash particles may act as nuclei for crystallization of cement hydration products [34, 35].

There seems to be general agreement in the literature that low-calcium fly ashes retard the setting of cement. In experiments conducted at CANMET [6], the data obtained (see Table 2.6) show that all except 2 of the II ashes significantly increased both the initial and final setting times. Fly ashes with CaO content of 1.2–13.3 wt % were included in this study.

Effect of Fly Ash on Workability, Water Requirement, and Bleeding of Fresh Concrete

The small size and the essentially spherical of low-calcium fly ash particles influence the rheological properties of cement pastes, causing a reduction in the water required or an increase in workability compared with that of an equivalent

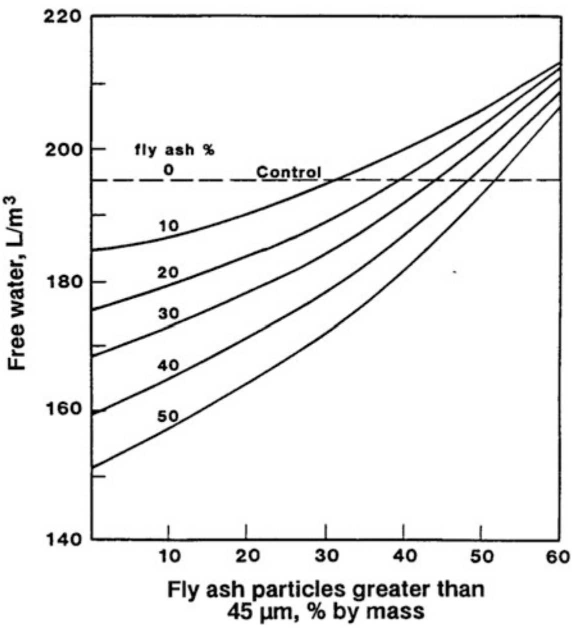


Fig. 2.9 Influence of coarse-particulate content of fly ash on the water required for equal workability in concrete [38]

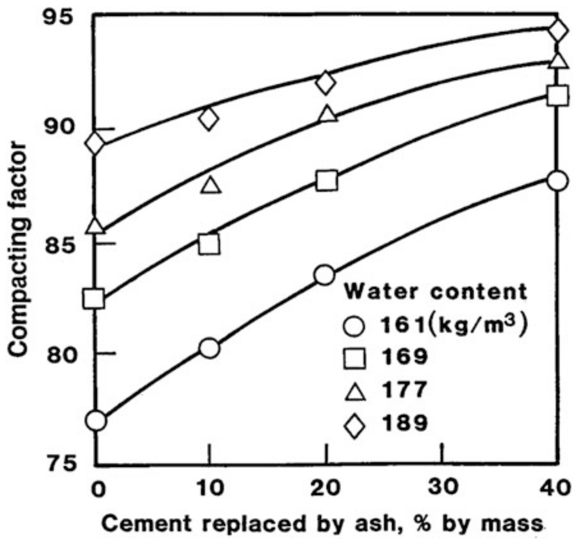
paste without fly ash. As Davis et al. [1] noted, fly ash differs from other pozzolans, which usually increase the water requirement of concrete mixtures. The improved workability allows a reduction in the amount of water used in concrete. According to Owens [38], the major factor influencing the effects of ash on the workability of concrete is the proportion of coarse material (>45 µm) in the ash. Owens has shown that, for example, substitution of 50 % of the material >45 µm has no effect on the water requirement. The general effect of coarse fly ash particles on the water requirement is illustrated in Fig. 2.9.

In a comprehensive analysis of the data from several major experimental studies Minnick et al. [39] showed statistically significant correlations between the water requirement of mortars and certain characteristics of the fly ashes. The most consistent correlations with the water requirement were obtained for LOI and of fly ashes on the water requirement of mortars is related to the absorption of water by porous carbon particles; the correlation with No. 325 (45 µm) sieve residue should be expected because of particle interference effects.

Stuart et al. [40] studied the effect of high-range water-reducing admixtures and fly ashes on the water requirements of various mortars. The results showed that the fly ashes themselves were effective in reducing water content but differed considerably in their effectiveness as water-reducing admixtures.

Following up on Stuart's results, Helmuth [41] suggested that the water reduction caused by the fly ash was the result of an absorption and dispersion process an much like that of organic water-reducing admixtures. Helmuth suggested an alternative hypothesis-that the water reduction in mixtures without the

Fig. 2.10 Influence of replacement of cement by fly ash on the workability of concrete [42]



organic admixtures was a result of the adherence of a thin layer of very fine fly ash particles on portions of the surfaces of the cement particles.

Brown [42] examined the workability of four concretes with water/cement in which ash was substituted for cement. Slump, V–B time, and compacting factor were measured for each mixture. It was found that both slump and V–B workability improved with increased ash substitution. The changes were found to depend on the level of ash substitution (with small additions sometimes ineffectual) and on the water content. The data relating compacting factor and ash replacement are shown in Fig. 2.10. An empirical estimate indicates that for each 10 % of ash substituted for cement, the compacting factor changed to the same degree (as it would by increasing the water content of the mixture by 3–4 %).

In another series of experiments, Brown [42] determined the effects of ash substitution for equal volumes of aggregate of send in one concrete, keeping all other mixture proportions (and the aggregate grading) constant. The test concrete was modified by replacing either 10, 20, or 40 % of the volume of sand by ash of 10, 20, or 40 % of the volume of the total aggregate by ash. The replacement of 40 % of the total aggregate gave a mixture that was unworkable. The changes in slump and compacting factor are shown in Fig. 2.11.

Brown [42] concluded that when ash was substituted for sand or total aggregate, (workability increased to a maximum value of ~8 % ash by volume of aggregate). Further substitution caused rapid decreases in workability.

To the present, data obtained by two-point test for fly ash concrete are limited. Ellis [43] reported measurements of g and h for ash concretes proportioned for mass and volume replacement of cement. The different densities of ash and cement result in an increased volume of total cementitious material when replacement is based on mass. Figure 2.12 shows the effect of replacement on medium-

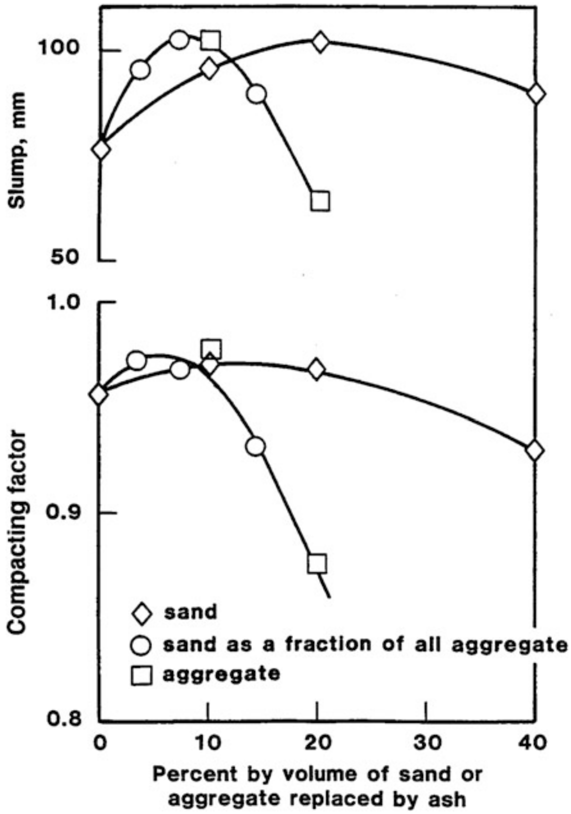


Fig. 2.11 Influence of replacement of aggregate by fly ash on the workability of concrete [42]

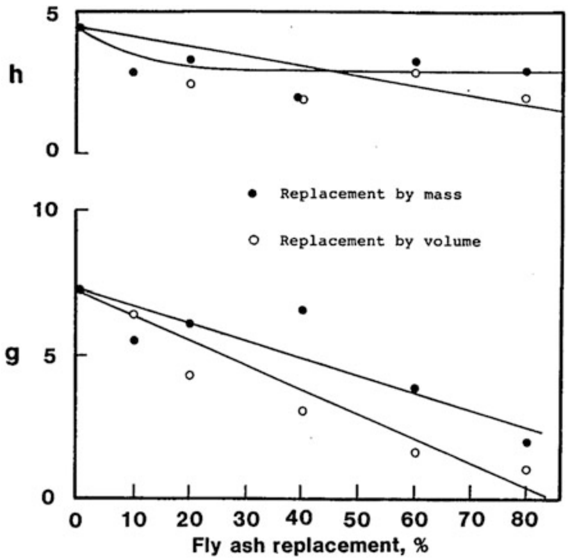


Fig. 2.12 Influence of partial replacement of cement by fly ash on the yield stress and plastic viscosity of various concrete mixtures [43]

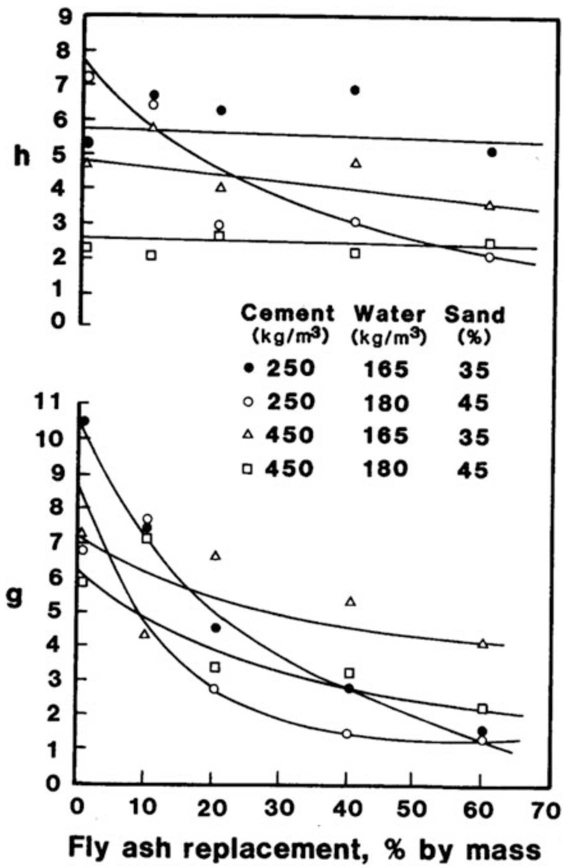


Fig. 2.13 Influence of partial replacement of cement by fly ash on the yield stress and plastic viscosity of concrete [43]

workability concretes. Figure 2.13 shows the effect of replacement by mass on mixtures of similar workability but with different cement contents and aggregate gradings. Both sets of data indicate that fly ash improves workability of concrete and, hence, reduces the water required for constant workability.

Copeland [44] reported that in the field the use of fly ash reduces bleeding in concretes made from aggregates that produce harsh mixes normally prone to bleeding. Johnson [45] reported that most concrete made in the Cape Town (South Africa) area suffers from excessive bleeding resulting from a lack of fines in the locally available dune sands. Johnson added that the problem can be overcome by using fly ash in the concrete to increase the overall paste volume.

In the CANMET study [34], it was found that 6 of the 11 ashes increased bleeding.

In line with the improved rheological properties and as a result of the fine-particular content, some fly ashes give a markedly improved finish when used as a replacement for either sand or cement, effects such as these make fly ash particularly valuable in lean mixtures and in concretes made with aggregates deficient of fines.

Effect of Fly Ash on Temperature Rise of Fresh Concrete

The hydration or setting of Portland cement paste is accompanied by an evolution of heat that causes a temperature rise in fresh concrete. Replacement of cement by fly ash results in a reduction in the temperature rise in fresh concrete. This is of particular importance in mass concrete, where cooling following a large temperature rise can lead to cracking. The first major use of fly ash in concrete was in the construction of a gravity dam, where it was employed principally to control temperature rise [46].

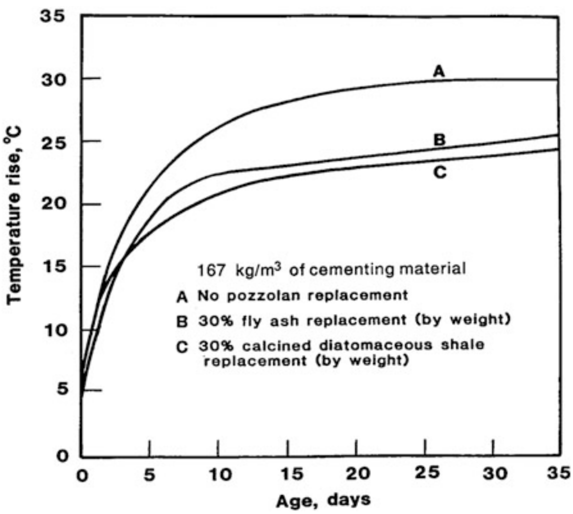
Data reported by Elfert [47] show the effects of fly ash and a calcined diatomaceous shale on the temperature rise of mass concrete (Fig. 2.14).

It has been estimated that the contribution of fly ash to early-age heat generation is 15–30 % of that of the equivalent of Portland cement [33].

Temperature rise, of course, depends on more than the rate of heat generation. It also depends on the rate of heat loss and the thermal properties of the concrete and its surroundings. Williams and Owens [48] presented an estimation (Fig. 2.15) of the effect of element size on the temperature rise in fly ash concretes.

Crown and Dunstan [50] reported the adiabatic temperature-rise data on concrete mixtures shown in Fig. 2.16. Whereas concrete containing 25 % low-calcium fly ash showed a reduced rate of heat generation, concrete with 25 % high-calcium fly ash produced as much heat (at a similar rate) as a Portland cement control.

Fig. 2.14 Influence of pozzolans on the temperature rise of concrete [47]



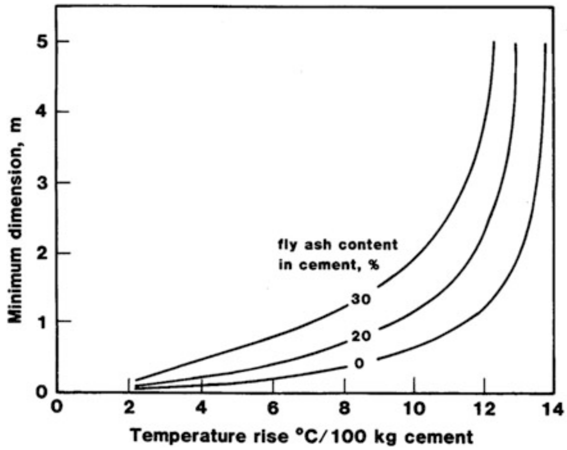


Fig. 2.15 Effect of unit minimum size on the temperature rise in fly ash and plain concrete [48]

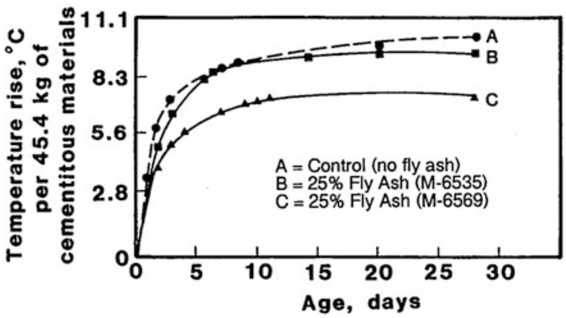


Fig. 2.16 Adiabatic temperature rise in concretes made with high-calcium and low-calcium fly ashes [49]

Effect on the Mechanical Properties of Hardened Concrete

Fly ash affects most of the properties of hardened concrete in one way or another. This chapter is concerned with the ways that the use of fly ash influences the following properties:

- Strength development
- Elasticity
- Creep, shrinkage, and thermal expansion.

The previous CANMET study [34] showed that concretes made under similar conditions, from the same cement and aggregates but incorporating different fly ashes, may develop strength at markedly different rates. Table 2.7 shows the strength development of the concrete mixtures. The different reactivities of the fly ashes are clearly seen from these date.

Table 2.7 Properties of hardened concrete [6]

Mixture no.	Compressive strength of 150 mm × 300 mm cylinders (MPa)				Flexural strength of 75 mm × 100 mm × 400 mm prisms (MPa)		
	7 days	28 days	91 days	365 days	14 days	28 days	91 days
Control	23.4	30.6	34.9	39.2	4.9	5.4	5.9
F1	18.4	35.7	31.4	38.3	4.4	4.4	5.4
F2	16.9	35.2	34.8	37.0	3.9	4.8	5.5
F3	14.4	21.0	27.6	34.4	4.0	5.0	5.3
F4	17.8	23.3	32.3	36.9	4.1	4.4	5.2
F5	20.1	28.0	33.9	44.3	3.5	4.4	5.3
F6	18.4	24.8	31.8	39.2	3.5	4.6	5.6
F7	16.7	24.1	29.1	35.7	3.9	4.5	5.4
F8	17.9	27.7	29.0	40.4	4.6	5.0	6.1
F9	16.7	24.9	31.1	35.6	4.3	4.2	5.7
F10	19.2	28.5	33.7	39.7	4.1	5.1	5.8
F11	21.1	29.4	35.3	40.1	4.8	5.3	6.6

Strength Development in Fly Ash Concrete

As discussed before, the main factors determining strength in concrete are the amount of cement used and water/cement. In practice, these are established as a compromise between the needs of workability in the freshly mixed state, strength and durability in the hardened state, and cost. The degree and manner in which fly ash affects workability are major factors in its influence on strength development. As was shown before, a fly ash that permits a reduction in the total water requirement in concrete will generally present no problems in the selection of mixture proportion any desired rate of strength development.

This chapter is concerned with the factors, other than mixture proportioning and workability that determine the rate of strength development in fly ash concrete. These are the characteristics of fly ash that mixture proportioning seeks to accommodate.

Many variables influence the strength development of fly ash concrete, the most important being the following:

- The properties of the fly ash
- Chemical composition
- Particle size
- Reactivity
- Temperature and other curing conditions.

Effect of Fly Ash Type on Concrete Strength

The first difference among fly ashes that should be recognized is that some are cementitious even in the absence of Portland cement. Frequently, these are the so-called ASTM Class C, or high-calcium, fly ashes usually produced at power plants burning subbituminous or lignitic coals.

In general, the rate of strength development in concretes tends to be only marginally affected by high-calcium fly ashes. A number of authors have noted that concrete incorporating high-calcium fly ashes can be made on an equal-weight or equal-volume replacement basis without any significant effect on strength at early ages [51–53].

Yuan and Cook [52] examined the strength development of concrete with and without high-calcium fly ash (CaO = 30.3 wt%). The data from their research are shown in Fig. 2.17. Using a simple replacement method of mixture proportioning (Table 2.8), they found the rate of strength development of fly ash concrete comparable to that of the control concrete, with or without air entrainment.

Raba and Smith [53] examined the concrete-making properties of a subbituminous fly ash (CaO = 20.0 wt%). Data on compressive strength gain attributed to the presence of high-calcium fly ash shown in Table 2.9. It should be noted that the mixture-proportioning approach replaced fine aggregate by volume. The mass of cement and coarse aggregate was kept constant for each series of determinations.

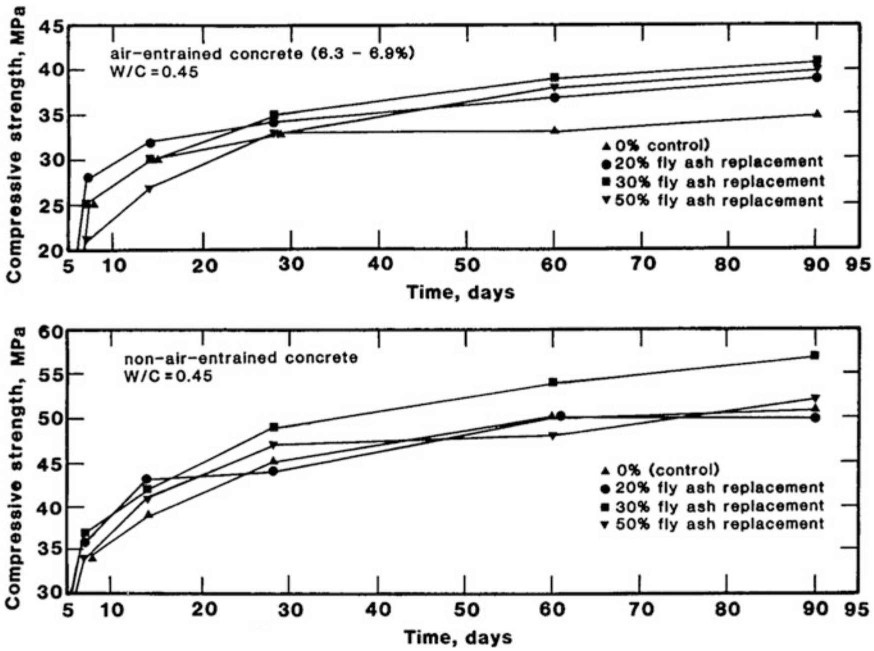


Fig. 2.17 Compressive-strength development of concrete containing high-calcium fly ash [52]

Table 2.8 Mixture designations, proportions, and properties of concretes incorporating high-calcium fly ash [52]

	Mixture designation			
	C1	C2	C3	C4
Proportion (kg/m³)				
Cement	387	309	272	196
Fly ash	0	77	117	196
Cement + fly ash	387	386	389	392
Water	145	145	146	147
Coarse aggregate	1146	1144	1153	1160
Fine aggregate	701	690	678	654
Properties				
Slump	3	9	12	21
Air content	2.1	1.9	1.9	1.4
Unit weight	2377	2364	2364	2352
Fly ash as percentage of cement	0	20	30	50

Table 2.9 Compressive-strength gains attributed to the presence of high-calcium fly ash [53]

Cement (kg/m³)	Fly ash (kg/m³)	Compressive strength[a]		
		Percentage of control values		Gained (%)
		28 days	56 days	28–56 days
91	50	–	354	15.2
	59	–	393	16.0
	68	–	435	13.6
	77	–	494	10.5
136	50	210	228	10.2
	59	231	256	11.8
	68	245	269	11.1
	77	253	274	10.3
182	50	149	155	8.2
	59	153	167	12.4
	68	163	177	12.0
	77	187	190	6.2

[a] In these mixes, fly ash was used to replace fine aggregate

Low-calcium fly ashes, the so-called ASTM Class F ashes, usually a by-product of the burning of bituminous coals, were the first to be examined for use in concrete. Most of what has been written on the behavior of fly ash concrete examines using Class F ashes. In addition, the ashes used in much of the early work came from older power plants and were coarse in particle size, contained unburned fuel, and were often relatively inactive as Pozzolans. Used in concrete, proportioned by simple replacement, these ashes showed exceptionally slow rates of strength development. This has led to the general view that "fly ash reduces strength at all ages" [54]. Conversely, it has also resulted in considerable efforts to understand the factors affecting strength in fly ash concrete and ways to obtain desired rates of strength gain.

Gebler and Klieger [55] evaluated the effect of ASTM Class F and Class C fly ashes from 10 different sources on the compressive-strength development of concretes under different curing conditions, including the effects of low temperature and moisture availability. Their tests indicated that concrete containing fly ash had the potential to produce satisfactory compressive-strength development. The influence of the class of fly ash on the long-term compressive strength of concrete was not significant. In general, compressive-strength development of concretes containing Class F fly ash was more susceptible to low curing temperature than concretes with Class C fly ash or control concretes.

Gebler and Klieger concluded Class F fly ash concretes required more initial moist curing for long-term, air-cured compressive-strength development than did concretes containing Class C fly ashes or control concretes. At early ages, compressive strength of concretes containing fly ash, regardless of class, was essentially unaffected by moisture availability during curing, compared with concretes without fly ash. This showed the importance of proper curing for strength development of concrete with or without fly ash. Generally, at later ages, concretes without fly ash were less sensitive to unavailability of moisture than concretes containing fly ash.

Tikalsky et al. [56] examined concretes containing both Class C and Class F fly ashes ranging from 0 to 35 % by weight of Portland cement. They proportioned their mixtures to have similar slump and constant cementitious materials content by weight. As reported in other studies, they also found that compressive and flexural strengths of fly ash concretes were slightly lower at early ages than those of control concretes but exceeded those of concrete without fly ash at later ages. The creep of fly ash concretes was reduced for similar applied stress/strength, and shrinkage was similar or reduced under similar curing conditions when compared with control concrete.

Particle Size and Strength of Fly Ash Concretes

Particle size can influence strength development in two ways. First, as discussed before, particles >45 μm appear to influence water requirement in an adverse way. They counteract the proportioning methods used to compensate for the slow rate of reaction of fly ash at early ages. Secondly, cementing activity occurs on the surface of solid phases and through heterogeneous processes of diffusion and dissolution of materials in concentrated pastes. Surface area of particles must play a considerable role in determining the kinetics of such processes.

Results of studies of the influence of particle size on strength development are contradictory. On the one hand, in a study of 36 concrete mixtures, most containing fly ashes with a wide variety of properties, Crow and Dunstan [50] concluded that

> fineness of ash compared loosely with the pozzolanic activity, thus finer ashes reacted more readily with Portland cement. Fineness appeared more critical to the reaction of the low-calcium ashes than to those higher in calcium content.

This suggests that there was a relationship between the fineness of fly ash and strength development in concrete. On the other Cabrera et al. [57], in their study of the properties of 18 fly ashes produced from bituminous coals by power stations in the United Kingdom, showed there was no relationship between the 45 μm sieve retention values and the 28 days cube strengths of fly ash concretes. From their results they concluded that differences in the chemical and mineralogical compositions and physical of fly ashes did not influence the strength properties of fly ash concrete. They believed that a much wider range of ashes could be used in concrete than those allowed by British Standard BS3892.

Wesche and vom berg [58], from more than 340 tests on fly ashes from 14 sources, also found no correlation between fineness and compressive strength of mortars at 7 or 28 days, but they did find a minor correlation at 90 days.

In some respects, these results are predictable when samples from a large number of sources are examined in experiments designed to determine only one factor. Many fly-ash-related variables may influence strength development; poor correlation with particle size only indicates that particle size is not the dominant variable in fly ash reactivity. To establish a relationship with particle size, it is necessary either to limit all other variables to a minimum number or to perform a multi-variable experiment. To date, only the former, minimum-number approach has been taken.

Both Joshi [59] and Ravina [60] exploited the phenomenon of particle-size segregation that occurs in electrostatic precipitators. They used this to obtain fly ash fractions of different fineness from a single source.

When fly ash is collected in a multistage, electrostatic precipitator, segregation by particle size occurs: particles in the finer size categories are collected in the chambers farthest from the furnace. By taking ash from each chamber, one may obtain particles of different size distributions from the same source at the same time.

Unfortunately, size is not the only property that differs among fly ashes from different chambers. The chemical properties, density, and morphology of the particles also differ. Carbon is segregated with the larger particles, and alkali sulphates and chlorides collect on the surface of the finer particles in the cooler regions of the precipitator. Low-density particles are differentially distributed in the precipitator; cenospheres and irregularly shaped particles tend to precipitate from the gases in the first chamber and, thus, affect average density measurements. Examination of ashes from one source, segregated by size, would seem to be the simplest way of determining the influence of particle size on strength, and even then other, uncontrolled factors may influence the results.

Joshi [59] examined ash from different chambers of the precipitator of a modern power plant (Sundance, Alberta) burning subbituminous coal. The ashes had the following percentages of particles > 45 μm:

Ash	% retained on 45 μm sieve
1	5
2	16
3	32
4	38

Concretes were made with 10 and 20 % replacement of cement for each of the four ashes. Resulting compressive-strength data are shown in Fig. 2.18.

These experiments show that at both 10 and 20 % replacement, the finer fly ashes imparted greater strength. The coarse fraction appears not to have contributed significantly to the strength.

Ravina [60] reported similar results from an examination of the pozzolanic activity index of low-calcium ash from each of four hoppers (chambers) in one precipitator.

An alternative way to obtain specific sizes of ash from one source is by grinding. Monk [61] examined ashes in blended cements and cements interground with Portland cement. The ashes were from four base-load power plants the principal conclusions from this research were as follows:

- Portland fly ash cements prepared by intergrinding clinker, gypsum, and fly ash have a water requirement equal to, or lower than, that of equivalent cements produced by blending ordinary Portland cement and fly ash.
- Intergrinding did not reduce the workability of fly ash concrete. Breakdown of spherical particles was not observed, but the agglomerates of spheres in coarse ashes were separated.
- Compressive strengths at all ages for the interground cements were equal to, or higher than, those for the blended cements.

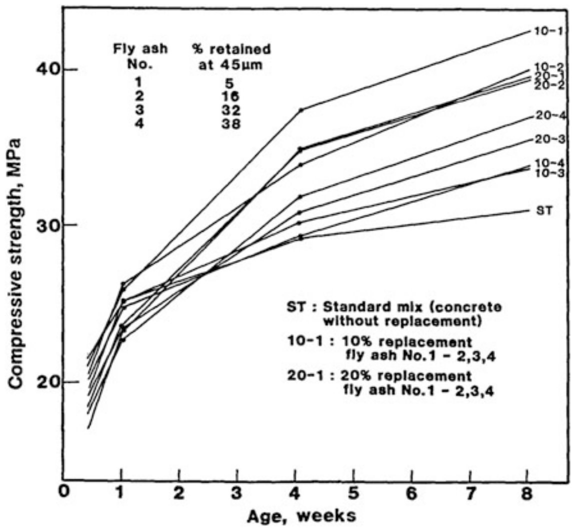


Fig. 2.18 Effect of coarse fractions of fly ash on compressive-strength development of concretes [59]

- Intergrinding improved the water-reducing properties and pozzolanic activity of coarse ashes, as indicated by compressive-strength improvement at later ages.

Matsufuji et al. [62] examined the properties of concrete containing ultra-fine particles produced from fly ash with ultra-high-temperature treatment. This treatment results in an increase of the specific surface area, from 20 to 130 m^2/g.

The specific surface area of the ultra-fine particles affects the mechanical properties of concretes made with these particles. In their experiment, Matsufuji et al. achieved a compressive strength of $\sim$118 MPa (W/C = 0.25) with ash particles with a surface area of 71 m^2/g. The early-age compressive strength of concretes containing ultra-fine ash particles was lower than that of the plain concrete but higher at $\geq$28 days.

When experimental efforts are made to eliminate the effects of multi-variable interference, there is a well-defined correlation between strength development and particle size (or surface area). This suggests that for ash from one source, particle size is an important indication of reactivity. This viewpoint is reflected in almost all the quality control procedures recommended for selecting ash for use in concrete and has been incorporated in most standards.

Effects of Temperature and Curing Regime on the Strength Development in Fly Ash Concretes

When concrete made with Portland cement is cured at temperatures of >30 °C, there is an increase in strength at early ages but a marked decrease in strength in the mature concrete [63].

Concretes containing fly ash and control concretes behave significantly differently. Figure 2.19 shows the general way in which the temperature, maintained during early ages of curing, influences the 28 days strength of concrete.

Whereas ordinary Portland cement loses strength as a consequence of heating, fly ash concretes show strength gains. This is of great value in the construction of mass concrete or in concrete construction at elevated temperatures.

Kobayashi [64] reported that fly ash was used at a 25 % cement-replacement level in the concrete for an intake tunnel of the Kurobegwa No. 3 Power Station in Japan [65]. Because this tunnel is located in rock at temperatures of 100–160 °C, fly ash was used to combat the loss of strength that would have resulted had Portland cement concrete been used alone.

Bamforth [49] reported on the in situ and laboratory-observed effects of temperature on the strength development of mass concrete containing either fly ash or slag substituents.

Figure 2.20a shows the strength development of standard cubes made from the three concretes studied by Bamforth under standard laboratory curing conditions. Strength approximately equal to that of the control was reached at 28 days; in fact,

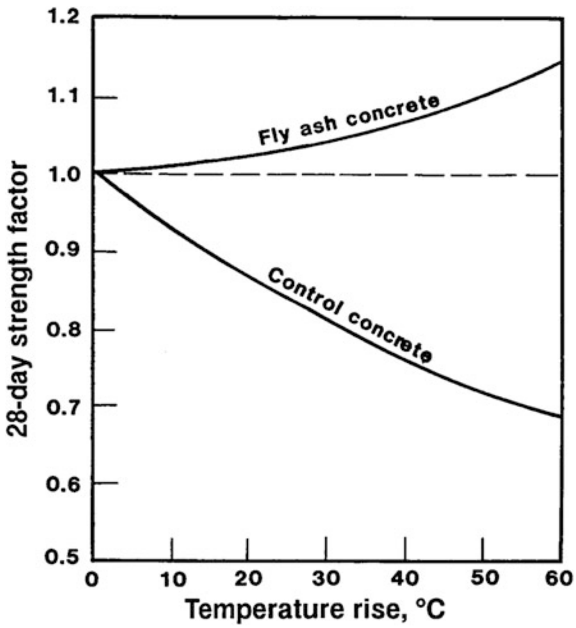


Fig. 2.19 Effect of temperature rise during on the compressive-strength development of concretes [48]

the strength of the fly ash concrete was close to that of the control concrete at earlier ages.

Figure 2.20b shows the effects of curing under temperature-matched conditions that simulated the effects of the early-age temperature cycle at the centre of the concrete mass. In all cases, early strength development was accelerated.

However, at 28 days, the strength of the fly ash concrete was enhanced by temperature, whereas the control concrete bad significantly less strength (30 % below that of the standard water-cured concrete).

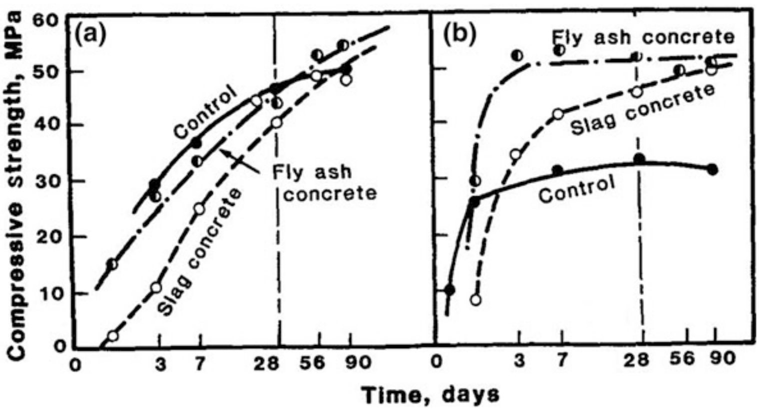


Fig. 2.20 Compressive-strength development of concretes **a** cured under normal conditions and **b** cured by temperature matching [49]

Ravina [66] discussed bow the effects of fly ash in concrete cured at moderately elevated temperatures may be advantageous in precast operations. Ravina's paper is of considerable interest for its examination of the way in which fly ash reacted in concrete cured under a controlled regime that included some exposure to beat.

Ravina examined concrete made with fly ashes of two size fractions from the same source:

- Coarse ash from the first precipitator field (with 30–35 % retained on a 45 μm sieve); and
- Fine ash from the third precipitator field (with 14–17 % retained on a 45 μm sieve).

Control mixtures contained no fly ash but had two cement contents. Ravina kept control specimens for 22 days at 23 °C prior to demolding and then placed them for 7 days in the fog room at 23 °C. He then stored the samples at 23 °C and 65 % RH before testing them.

Ravina kept thermally cured specimens at 23 °C for 2 days and then transferred them to a steam chamber, where be raised the temperature from 23 to 75 °C over a 2 days period and kept it at 75 °C for 4 days. He then discontinued beating and allowed the specimens to cool in the chamber. After 22 h, be demolded the samples and then stored them under the same conditions as those for the control specimens.

Ravina made two series of non-air-entrained mixtures (Table 2.10). In the first series, coarse ash alone replaced either all or 50 % (by volume) of the pit sand. In the second series, fine fly ash replaced 20 % of the cement (by weight) and coarse ash replaced 50 % (by volume) of the sand.

The compressive-strength data from Ravina's study are shown in Fig. 2.21. Ravina drew the following conclusions:

- Large quantities of fly ash in concrete cured at elevated temperatures significantly improve its compressive strength, but fly ash contributes less to the strength of concrete cured normally at ages ≤28 days.

Table 2.10 mixture designations and proportions of concretes cured at elevated temperatures [66]

	Mixture designation					
	1-A	1-B	1-C	2-A	2-B	3
Proportions (kg/m³)						
Corse and medium aggregate	1165	1165	1125	1165	1165	1160
Quarry sand	535	535	520	535	535	535
Pit sand	380	190	–	370	180	430
Cement	300	300	300	240	240	240
Water	205	210	230	190	200	205
Coarse fly ash	–	155	305	–	150	–
Fine fly ash	–	–	–	60	60	–

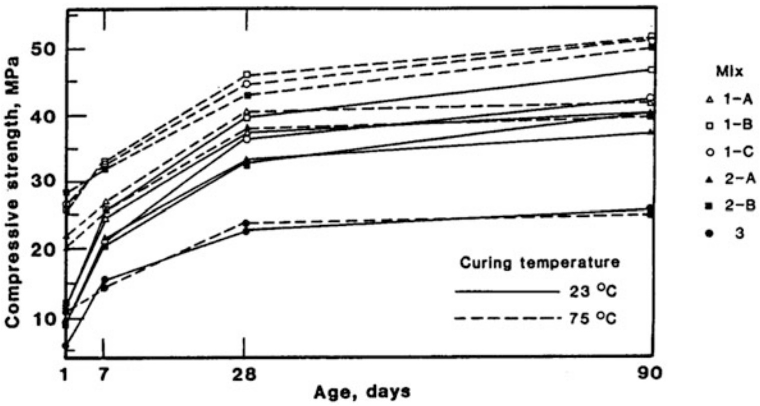


Fig. 2.21 Effect of curing temperature on the compressive-strength development of concretes incorporating fine and coarse fractions of fly ash [66]. *Note* For mix details, see Table 2.10

- Curing coarse and fine fly ash concrete at elevated temperatures bas a significant beneficial effect on the strength of the concrete at early and later ages.

Ravina's work and the observations of other authors [48] raise some significant issues regarding the nature of pozzolanic reactivity. The following would seem to warrant further investigation:

- The rate of reaction of fly ash–cement systems is clearly increased by temperature, as is the case for Portland cement. Yet, the products of hydration do not exhibit the poor mechanical properties associated with curing Portland cement at elevated temperatures. This suggests that the products of fly ash-cement hydration, their relative proportions, and their morphology are significantly different from those formed from thermally accelerated hydration of Portland cement alone.
- The rate of reaction of fly ash in cement systems is so significantly increased by temperature that the effects of particle size on pozzolanic behavior are largely overcome. This suggests that some pozzolanic activity tests that use thermal acceleration may give seriously misleading results.
- The pozzolanic reaction, once initiated by heat, appears to continue when the source of external heat is removed, even with coarse fly ash. This indicates the possibility of an activation effect similar to that observed for slags, which has not previously been associated with pozzolanic activity.

The sensitivity of fly ash to elevated temperature implies that it will also be sensitive to reduced temperature, with a consequent reduction in the rate of strength development. This has been observed in practice, and it is generally noted that fly ash concretes require more attention to curing in cold weather.

Curing regime is more important to the compressive-strength development of fly ash concrete, compared with plain concrete. Gopalan and Haque [67] reported the strength of normal and fly ash concretes cured in a fog room and in an uncontrolled environment. The strength of 91 days air-cured specimens was less than that of 7 days fog-cured specimens. On air curing, the percentage loss of strength increased both with an increase in fly ash content and the curing period. Haque et al. [68] also studied the effects of various curing regimes on the strength development of both plain concretes and two subbituminous fly ash concretes.

In situ strengths of low-grade 20 MPa fly ash concretes were 60–90 % of the fog-cured strengths. In situ strengths of high-grade 40 MPa fly ash concretes were consistently 90 % of the fog-cured strengths. The strength ratio obtained at 6 months appeared to be independent of the ash content.

Effect of Fly Ash on Elastic Properties of Concrete

Published data indicate that fly ash has little influence on the elastic properties of concrete.

Abdun-Nur [69] made the following observations on the early literature:

The modulus of elasticity of fly ash concrete is lower at early ages, and higher at later ages [1, 70]. In general, fly ash increases the modulus of elasticity of concrete when concretes of the same strength with and without fly ash are compared [71–73].

Lane and Best [36] stated the following:

Fly ash properties controlling the compressive strength of concrete also influence the modulus of elasticity, but to a lower extent. The modulus of elasticity, like compressive strength, is lower at early strength and higher at ultimate strength when compared with concrete without fly ash.

Figure 2.22 shows typical stress–strain relationships for concrete with and without fly ash.

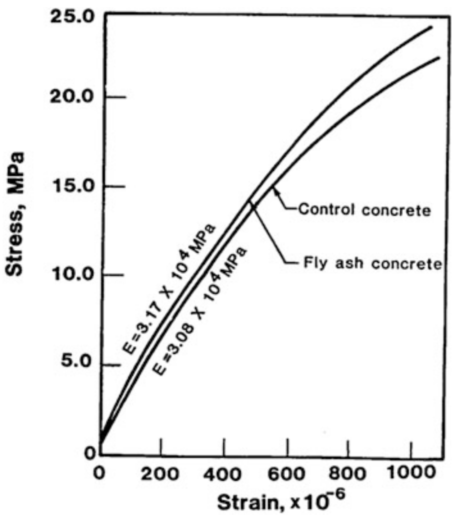


Fig. 2.22 Stress–strain relationship for concretes with and without fly ash [36]

Crow and Dunstan [50] who reported on an examination of the properties of 36 concretes, most containing fly ash at different levels and from different sources, drew the following conclusions about elastic properties:

> The elastic properties of concretes containing both Portland cement and fly ash are similar to those expected with Portland cement (alone). The modulus of elasticity and Poisson's ratio both increased with age, paralleling the compressive-strength development. The modulus of elasticity ranged from a low of 18.8 GPa at 28 days to a high of 39.6 GPa at 365 days. Most of the ashes (in concrete) had a 28-day Poisson's ratio in the range of 0.14–0.25.

Ghosh and Timusk [74] studied fly ash concretes, proportioned for equivalent 28 days strength, over a range of nominal strength values. They showed the relationship between strength and modulus of elasticity, reproduced in Fig. 2.23, and concluded that for all strength levels the modulus of elasticity of fly ash concrete is generally equivalent to that of the reference concrete. In all instances, the modulus was found to exceed that given by the ACI formula.

Nasser and Marzo [75] examined the effects of temperature on modulus of elasticity of concrete made from fly ash (from a Saskatchewan lignite source) and a sulphate-resistant, ASTM type V cement. They reported that over the temperature range of 21–232 °C, the modulus of elasticity was reduced by 910 % for specimens that were both sealed and unsealed to prevent moisture loss.

In a CANMET study [6], the 28 days Young's modulus of elasticity values for the fly ash concretes were 29–35.8 GPa, compared with the value of 33.5 GPa for the control concrete. The data obtained in this investigation showed no significant effect of fly ash or type of fly ash on the modulus of elasticity.

Nasser and Ojha [76], in a study of Saskatchewan lignite fly ash, reached a similar conclusion—the modulus of elasticity of concretes containing ≤20 % fly ash was similar to that of the control concrete. At higher percentages, fly ash reduces both the compressive strength of concrete and the modulus of elasticity.

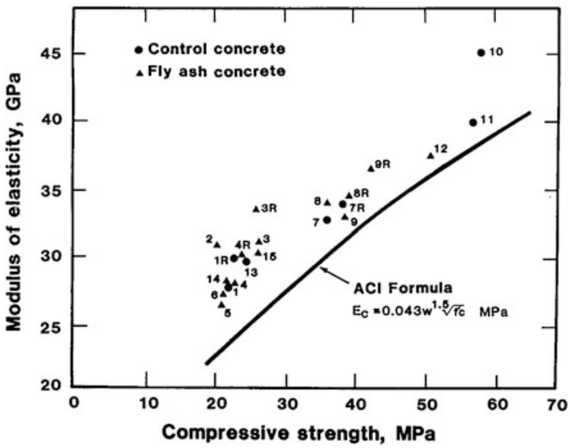


Fig. 2.23 Moduli of elasticity of fly ash concretes [74]

Effect of Fly Ash on Creep Properties of Concrete

Data on creep of fly ash concrete are limited. Lohtia et al. [77] reported the results of studies on creep and creep recovery of plain and fly ash concretes under stress/strength of 20 and 35 %. The concretes were made by replacing cement with equal weights of fly ash in the range of 0–25 %. From this work, they drew the following conclusions:

- Replacement of 15 % of cement by fly ash was found the optimum for strength, elasticity, shrinkage, and creep for the fly ash concretes studied.
- Creep versus time curves for plain and fly ash concretes were similar, with creep linearly related to the logarithm of time.
- Increase in creep with ~15 % fly ash content was negligible. However, slightly higher creep took place at fly ash contents of >15 %.
- The creep coefficients were similar for concrete with fly ash contents in the range of 0–25 %.
- Creep recovery was 22–43 % of the corresponding 150 days creep. For cement replacement >15 %, the creep recovery was smaller. No definite trend of creep recovery as a function of stress/strength was observed.

In another study, Ghosh and Timusk [74] examined bituminous fly ashes of different carbon contents and fineness values in concretes at nominal strength levels of 20, 35, and 55 MPa (water/cement of 1.0, 0.4, and 0.2, respectively). Each concrete was proportioned for equivalent strength at 28 days. Fly ash concretes showed less creep in the majority of specimens than the reference concretes showed. This was attributed to a relatively higher rate of strength gain after the time of loading for the fly ash concretes than for the reference concretes.

Yuan and Cook [52] reported the data in Fig. 2.24 from studies of high-strength concrete containing a high-calcium fly ash. The figure shows that concrete containing 30 and 50 % fly ash exhibited more creep than either the control concrete or a concrete with 20 % fly ash.

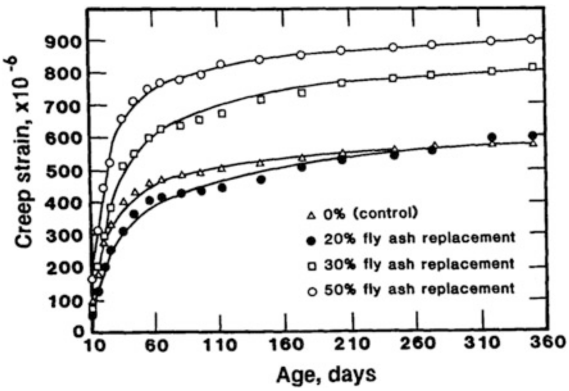


Fig. 2.24 Creep of fly ash concretes [45]

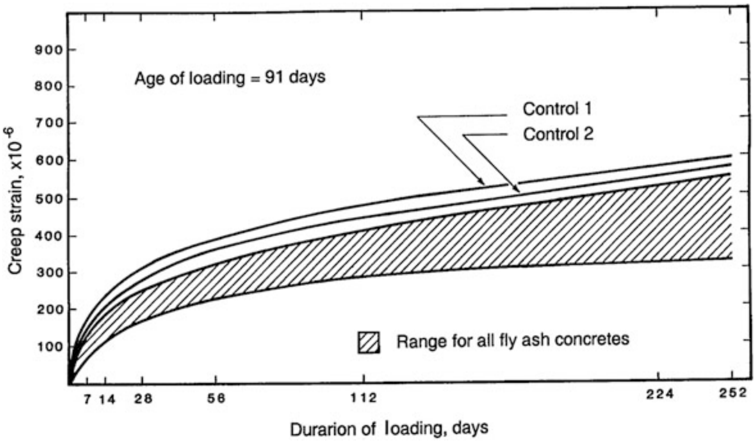


Fig. 2.25 Creep strains after initial moist curing of 91 days [6]

Gifford and Ward [78] examined lean mass concrete and concluded that fly ash reduces creep, as a result of a number of factors including the following:

- Fly ash increases the elastic modulus.
- Fly ash contributes to the total aggregate and reduces the volume of paste available to creep.

Investigation by Bamforth [49] on mass concrete showed that a reduction in creep of ~50 % can be obtained when cement is replaced by ~30 % fly ash. However, the results of Nasser and Al-Manaseer's work [79] showed that there was an increase in creep of—15 % in concretes containing 20 % fly ash and other admixtures. In another study, the same authors [80] examined the creep of sealed and unsealed concrete made with ASTM type I cement containing 50 % Saskatchewan fly ash. They tested the concrete specimens at different stress/strength and measured their creep for a maximum period of 112 days. The experimental results showed that the creep of concrete made with 50 % lignite fly ash was a linear function of stress/strength. The creep of this concrete was lower than that of plain concrete by—13 % for the unsealed and 39 % for the sealed specimens. In addition, they found that the ratio of creep values of sealed and unsealed concrete was about 2.44 for plain concrete and 3.67 for concrete with 50 % fly ash.

In a CANMET investigation, the creep-strain data for control and fly ash concretes were compared [6]. Figure 2.25 shows the creep strains after 91 days of initial moist curing. All fly ash concretes are shown to produce consistently lower creep strains than the control concrete. The strain reduction, which in most cases varies between 20 and 45 %, does not appear to be related to the type of ash.

Effect of Fly Ash on Volume Changes of Concrete

It has been generally reported that the use of fly ash in normal proportions does not significantly influence the drying shrinkage of concrete. Typical of the conclusions of most researchers in this area are those made by Davis et al. [1], who commented as follows:

For masses of ordinary thickness, such as are normally found in highway slabs and in the walls and frames of buildings, the drying shrinkage at the exposed surfaces of concrete up to the age of one year for fly ash cements is about the same as, or somewhat less than, that for corresponding Portland cements. At a short distance from the exposed surface the drying shrinkage up to the age of one year is substantially less for concretes containing corresponding Portland cements.

For very thin sections and for cements of normal fineness the drying shrinkage of concretes containing finely ground high-early-strength cements may be somewhat reduced by the use of fly ash.

Figure 2.26 shows data presented by Elfert [47] comparing the drying shrinkage and autogenous length change of fly ash concrete, plain concrete, and concrete made with other pozzolans. Typically, fly ash concrete performed better in these respects than the other concretes studied.

In their study, Ghosh and Timusk [74] showed that for the same maximum size of aggregate and for all strength levels, the shrinkage of concrete containing fly ash is lower than that for concrete not containing fly ash.

In their studies of concrete using high-calcium fly ash, Yuan and Cook [52, 81] concluded that the replacement of cement by fly ash has little influence on drying shrinkage. Their data are shown in Fig. 2.27. Similar conclusions may also be

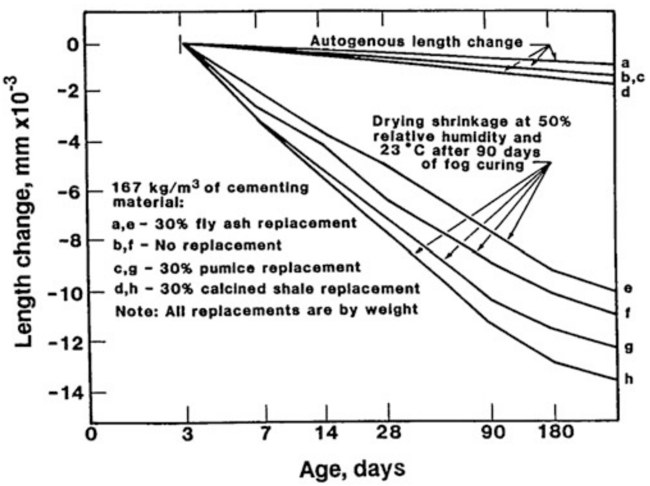


Fig. 2.26 Drying shrinkage and autogenous length change for concretes containing various pozzolans [47]

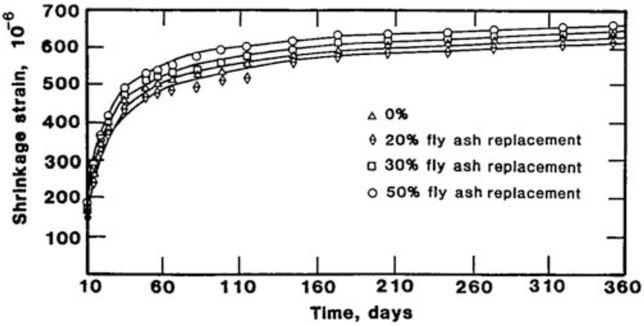


Fig. 2.27 Drying shrinkage of concretes incorporating high-calcium fly ash [52]

Table 2.11 Drying shrinkage of fly ash concretes [34]

Mixture no.	Shrinkage measurements			
	Initially cured for 7 days in water		Initially cured for 91 days in water	
	Moisture loss (%)	Drying shrinkage (10^{-6})	Moisture loss (%)	Drying shrinkage (10^{-6})
Control 2	55.0	442	53.7	453
F1	57.5	447	47.9	365
F2	57.3	364	45.4	280
F3	56.9	411	56.2	405
F4	54.7	379	49.2	387
F5	58.8	404	51.1	403
F6	60.6	475	56.4	454
F7	64.3	397	54.1	433
F8	56.3	400	–	327
F9	58.2	390	49.3	361
F10	58.4	642	55.2	500
F11	49.5	454	48.9	362

Notes Duration of drying, 224 days

drawn from the data on shrinkage obtained by CANMET [34] for concretes incorporating a range of fly ashes (Table 2.11).

Munday et al. [82] reported typical shrinkage-age relationships for fly ash concretes, as shown in Fig. 2.28, and concluded that a general relationship exists between drying shrinkage and equivalent cement content (Fig. 2.29). It was also found that wetting and drying of fly ash concrete results in a cumulative expansion over a number of cycles (Fig. 2.30). It was concluded that overall, the incorporation of fly ash does not significantly affect the drying shrinkage, wetting–drying expansion, or thermal expansion of concrete.

Drying shrinkage of fly ash concrete is affected by the initial moist-curing period. Ravindrarajah and Tam [83] in a study of properties of concrete containing low-calcium fly ash, reported that the drying shrinkage of fly ash concrete was

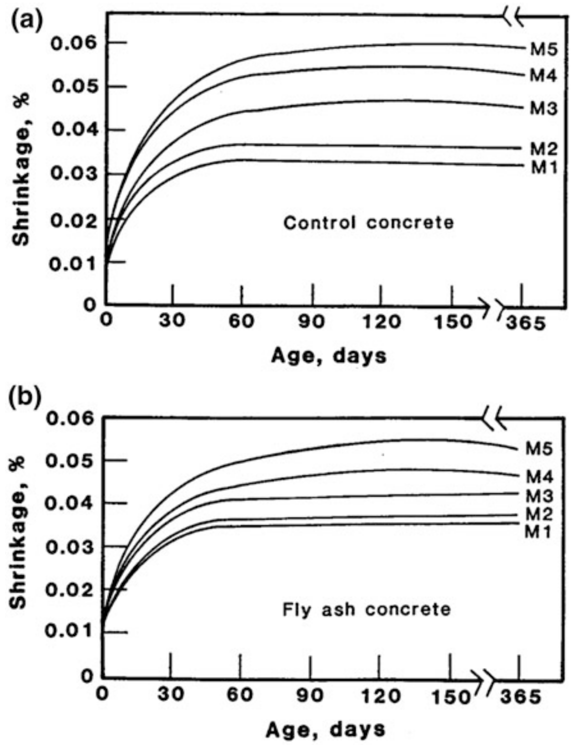


Fig. 2.28 Drying shrinkage of concretes incorporating low-calcium fly ash [82]

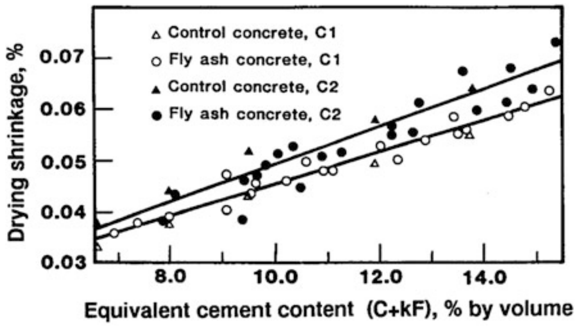


Fig. 2.29 Drying shrinkage of concretes versus equivalent cement content [82]

higher than that of control concrete when the initial moist-curing period was limited to 7 days. However, the difference in drying shrinkage between the two concretes dropped considerably when the initial moist-curing period was increased. In some cases, the drying shrinkage of fly ash concrete was slightly lower than that of the plain concrete.

In the CANMET study [6] of 11 Canadian fly ashes, the drying-shrinkage strain of concrete initially cured for 7 days in water was apparently little affected by the presence of fly ash in the concrete. The strain values for the control and most fly

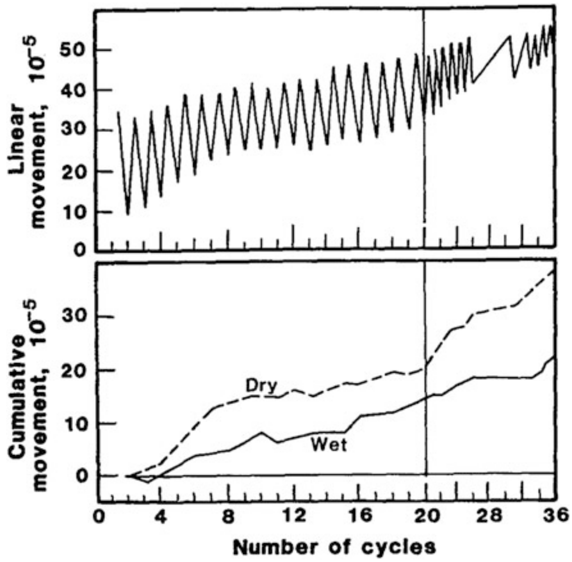


Fig. 2.30 Wetting and drying movements of fly ash concretes [82]

ash concretes were closely grouped together until after 224 days of drying (Fig. 2.31). The only significant deviation from this was for concrete made with lignite fly ash No. 10 (see Table 2.3), in which case the total shrinkage strain was found to exceed the average strain by ~50 %.

Thermal expansion of concrete is mainly affected by the thermal expansion of the coarse aggregate that constitutes its main component. Values for wet limestone and quartzite have been reported to be 4.0 and 11.7 micro-strain per degree Celsius, respectively, and that of cement paste is reported to be 11.0–20.0 micro-strain

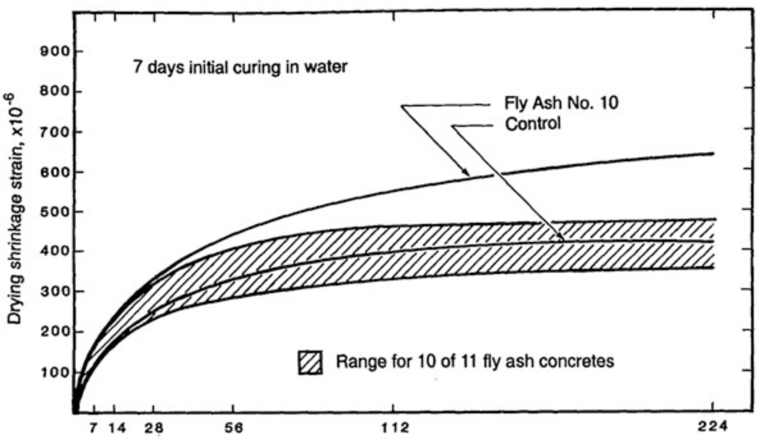


Fig. 2.31 Drying shrinkage strains after initial curing of 7 days in water [6]

per degree Celsius [78]. Gifford and Ward [78] quoted Dunstan as suggesting that fly ash slightly reduces thermal expansion. Their own data indicated an average reduction of 4 % at a fly ash level of 40 %.

Failure of concrete after a period less than the lifetime for which it was designed may be caused by the environment or by a variety of internal causes. External causes may be physical or chemical: weathering, extremes of temperature, Abrasion, or chemical action in the cement, aggregate, or reinforcement components. Internal causes may lie in the choice of materials or in inappropriate combinations of materials and may be seen as alkali-aggregate expansion or other forms of failure. Of all the causes of lack of durability in concrete the most widespread is excessive permeability. Permeable concrete is vulnerable to attack by almost all classes of aggressive agents. To be durable, Portland cement concrete must be relatively impervious.

Increasingly, concrete is being selected for use as a construction material in aggressive or potentially aggressive environments. Concrete structures have always been exposed to the action of sea water. In modern times, the demands placed on concrete in marine environments have increased greatly, as concrete structures are used in arctic temperate, and tropical waters to contain and support the equipment, people, and products of oil and gas exploration and production. Concrete structures are used to contain nuclear reactors and must be capable of containing gases and vapors at elevated temperatures and pressures under emergency conditions. Concrete is increasingly being placed in contact with sulphate and acidic waters. In all of these instances, the use of fly ash as concrete material bas a role, and an understanding of its effect on concrete durability is essential to its correct and economical application.

The following sections of this chapter seek to provide a general view of the present knowledge regarding the durability of fly ash concrete. The subject matter is vast, complex, and as yet incompletely understood. The reader desiring a more detailed treatment of the subject is invited to consult the cited literature.

Effects of Fly Ash on Permeability of Concrete

The movement of aggressive solutions into a concrete mass or the removal from concrete of dissolved reaction products must play a primary role in determining the rate of progress of concrete deterioration caused by chemical attack. Permeability of a concrete mass is, therefore, fundamental in determining the rates of mass transport relevant to destructive chemical action. It should be recognized that all the cementitious hydrates and some of the aggregates from which concretes are made are inherently subject to attack, not only by sulphates, chlorides, acids, and organic agents, but by water alone. That concrete survives aqueous environments at all is attributable to (a) the low equilibrium solubility of the hydrated components and (b) the low rate of mass transfer in well-compacted, cured concrete. Given any combination of cement and aggregate, it is generally observed that the

Table 2.12 Relative permeability of concretes with and without fly ash [84]

Fly ash		W/(C + F) by weight	Relative permeability (%)	
Type	% by weight		28 days	6 months
None	–	0.75	100	26
Chicago	30	0.70	220	5
	60	0.65	1410	2
Cleveland	30	0.70	320	5
	60	0.69	1880	7

Table 2.13 Mixture designations and proportions for concretes examined by Kanitaks [85]

Mixture	Constituents (per m^3)				
	Cement (kg)	Fly ash (kg)	Sand (kg)	Stone (kg)	Water (L)
N	400	–	586	1190	233
M	350	100	519	1213	227

less permeable the concrete. the greater will be its resistance to aggressive solutions or pure water.

A number of investigations have been made of the influence of fly ash on the relative permeability of concrete pipes containing fly ash substituted for cement in amounts of 30–50 %. Davis [84] examined the permeability of concrete pipes incorporating fly ash substituted for cement in amounts of 30-50 %. Permeability tests were made on 150 × 150 mm cylinders at the ages of 28 days and 6 months. The results of these tests are shown in Table 2.12.

It is clear from these data that the permeability of the concrete was directly related to the quantity of hydrated cementitious material at any given time, After 28 days of curing, at which time little pozzolanic activity would have occurred, the fly ash concretes were more permeable than the control concretes. At 6 months, this was reversed. Considerable imperviousness had developed, presumably as a result of the pozzolanic reaction of fly ash.

Kanitakis [85] used an Initial Surface Absorption Test to examine concrete with and without a low-calcium fly ash (CaO = 2.0 wt%) made using the mixture properties shown in Table 2.13. Absorption measurements were made at 7, 17, 28, and 56 days of curing, and the data shown in Fig. 2.32 were obtained.

The author concluded that at early ages, fly ash concrete behaves as a lean-mixture concrete and is, thus, permeable. At later ages, permeability is reduced as the pozzolanic action proceeds.

The rather limited observations on this very important aspect of fly ash concrete are consistent with the view expressed by Manmohan and Mehta [86] that the transformation of large pores to fine pores, as a consequence of the pozzolanic reaction between Portland cement paste and fly ash, substantially reduces permeability in cementitious systems.

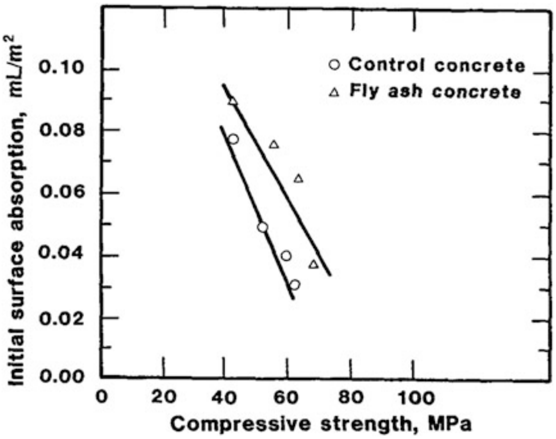


Fig. 2.32 Initial surface absorption of water versus compressive strength of concretes [85]

Diffusion of ions, such as chlorides, that are not specifically bound by the components of concrete is reasonably represented by Fick's diffusion equation [87, 88]

$$dc/dt = D_c\left(d^2C/dX^2\right) \tag{2.1}$$

where C is the ion concentration at a distance *x,* after a time *t;* and D, is the ion diffusion coefficient.

For concrete in offshore structures, Browne [86] reported values for D, of 1–50.0 × 10^{-9} cm^2/s for high-and normal-strength concretes, respectively.

Short and Page [89] reported on the diffusion of chloride ions in solution into Portland and blended cement pastes and found the following values of D, for different cement types:

Type of cement	D_c value (× 10^{-9} cm^2/s)
Normal Portland	44.7
Sulphate-resisting	100.0
Fly ash/Portland	14.7
Slag/Portland	4.1

It was concluded from these data that slag and fly ash cements were more effective in limiting chloride diffusion in pastes than were normal or sulphate-resisting cements.

Permeability to gases, in particular to air and carbon dioxide, is important for some aspects of concrete durability related to carbonation (see below). Kasai et al. [90] examined the air permeability of mortars (moist cured for 1, 3, and 3, **7** days) of blended cements made with fly ash and with blast-furnace slag and concluded the following:

- The air permeability of blended cement mortars is greater than that of Portland cement mortars.
- When early moist curing is extended, the permeability is reduced.

The considerable differences in the strengths at all ages of the mortars examined by these authors, with fly ash mortars being some 20–30 % weaker, suggest that the curing regimes adopted were inadequate to permit any conclusions relevant to the practical behavior of blended cement concretes in the field.

Thomas et al. [91] studied the effect of curing on the permeability to oxygen and water of fly ash concretes designed for equal workability and 28-day compressive strength. The results for oxygen permeability of concretes at 28-days are given in Tables 2.14 and 2.15 respectively. These results confirm the importance of curing, with reductions in curing period resulting in more permeable concrete. Despite exhibiting lower strengths, fly ash concretes moist cured for only 1 day were, generally, no more permeable to water and substantially less permeable to oxygen than similarly cured control concrete. As the period of curing increased, the fly ash concretes became considerably less permeable to water and oxygen than the control concrete. The authors argued that although the increased curing periods recommended in BS8110 for fly ash concrete were justified on the basis of concrete strength, fly ash concrete might require no more curing than control concrete to achieve equal durability, measured by oxygen and water permeability.

Table 2.14 Coefficient of oxygen permeability of concretes after 28 days of storage [91]

Mixture	PFA	Coefficient of oxygen permeability ($\times 10^{-17} m^2$)						
		20 °C, 65 % RH[a]			20 °C, 40 % RH[a]			28 days of water storage
		Curing period			Curing period			
		1 days	3 days	7 days	1 days	3 days	7 days	
A	0 %	24.3	14.8	11.9	27.2	23.8	18.7	3.97
B	15 % M367	21.3	11.6	11.2	12.9	9.50	8.10	2.02
C	30 % M367	9.67	5.85	4.01	15.3	12.2	7.50	2.05
D	50 % M367	18.0	5.26	5.26	16.1	9.53	4.69	0.64
E	30 % M368	6.37	4.64	1.77	–	–	–	1.08
F	30 % M369	18.6	7.51	3.21	–	–	–	1.61

[a] Storage conditions following curing

Table 2.15 Coefficient of water permeability of concretes after 28 days of conditioning [91]

Mixture	PFA	Coefficient of water permeability (× 10^{-13}m/s)						
		20 °C, 65 % RH[a]			20 °C, 40 % RH[a]			28 days of water storage
		Curing period			Curing period			
		1 days	3 days	7 days	1 days	3 days	7 days	
A	0 %	3800	500	320	2200	910	280	1.79
B	15 % M367	3100	270	33	1800	66	60	0.80
C	30 % M367	3800	1100	100	2300	1200	130	0.70
D	50 % M367	3800	130	130	7000	1900	160	0.89
E	30 % M368	1800	36	36	1021	62	5.6	0.63
F	30 % M369	2400	52	52	2000	790	9.5	0.60

[a] Storage conditions following curing

Effects of Fly Ash on Carbonation of Concrete

Calcium hydroxide and, to a lesser extent, calcium silicates and aluminates in hydrated Portland cement react in moist conditions with carbon dioxide from the atmosphere to form calcium carbonate. The process, termed carbonation, occurs in all portland cement concretes. The rate at which concrete carbonates is determined by its permeability, the degree of saturation with water, and the mass of calcium hydroxide available for reaction. Well-compacted and properly cured concrete, at a low water/cement, will be sufficiently impermeable to resist the advance of carbonation beyond the first few millimeters.

If carbonation progresses into a mass of concrete, two deleterious consequences may follow: shrinkage may occur; and carbonation of the concrete immediately adjacent to steel reinforcement may reduce its resistance to corrosion.

In 1968, results from long-term investigations of concrete in Japan [92, 93] indicated that concrete made with blended cements was subject to more rapid carbonation than normal Portland cement concrete. Other investigations [94–96] did not show any appreciable differences in this regard, provided that the strengths of the concretes being compared were equal.

In 1980, Tsukayama et al. [97] reported data from experiments conducted over a long period on fly ash concretes exposed in the field in Japan. They found that the depth of carbonation (termed neutralization by the authors) was related to the quality of the concrete in the following ways:

- A linear relationship was found between water/cement (excluding fly ash) and depth of neutralization (Fig. 2.33).
- At identical water/cement, when fly ash was added, depth of carbonation was found to be slightly decreased (see Fig. 2.33).
- The period of curing in water, after casting, was found to have a substantial influence on concrete exposed indoors. Concrete exposed outdoors was considered adequately cured after about 1 week in water (Fig. 2.34).

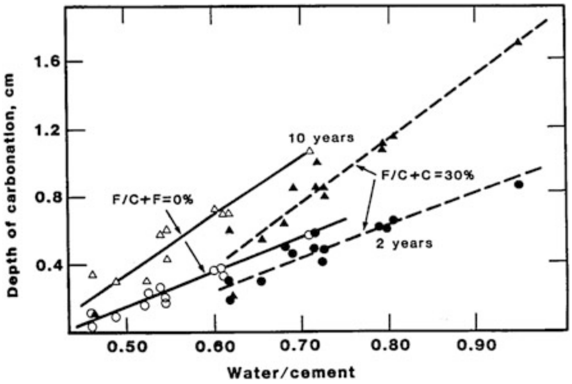


Fig. 2.33 Depth of neutralization (carbonation) versus water/cement of concretes [97]

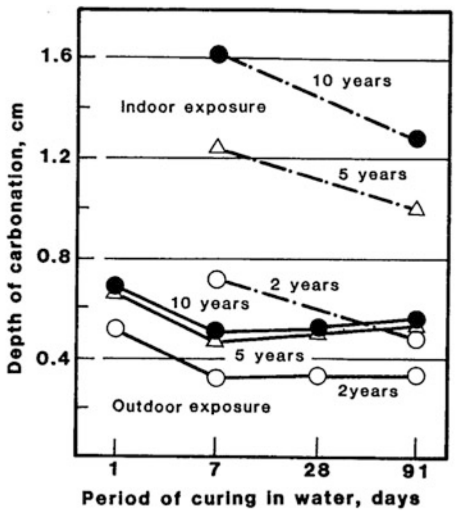


Fig. 2.34 Depth of neutralization (carbonation) versus period of curing of fly ash concretes [97]

Gebauer [98] examined slabs of steel-reinforced concretes with the properties and mixture proportions shown in Table 2.16 the slabs, 100 cm × 50 cm × 7 cm, were formed by compaction and vibration. They were cured for 7 days at 20 °C and 95 % RH. Subsequently, one slab of each composition was placed in an outdoor testing station; control slabs were kept under moist curing conditions (indoor slabs). The compressive strengths of companion prisms were measured at 28 and 365 days.

Tables 2.17 and 2.18 summarize the data from indoor and exposure, respectively.

Gebauer reported that carbonation depth increased as

- Strength and pulse velocity decreased (regardless of composition);
- Water/cement increased;
- Cement content decreased;

Table 2.16 Mixture proportions and properties of concretes [98]

Mix no.	Cement type	Cement (kg/m^3)	W/C	Slump (cm)	Compressive strength (MPa)	
					28 days	1 year
1	Portland #1	300	0.50	3.7	36.7	47.7
2	Portland #1	300	0.55	10.5	32.8	42.3
3	Portland #1	300	0.60	16.0	28.5	38.6
4	Portland #2	300	0.50	2.7	43.2	52.9
5	Portland #2	300	0.55	8.3	37.9	48.0
6	Portland #2	300	0.60	15.0	33.8	43.6
7	Blended #1 10 % ash	300	0.50	5.5	46.4	46.4
8	Blended #1 10 % ash	300	0.55	13.5	42.9	42.9
9	Blended #1 10 % ash	300	0.60	16.0	38.9	38.9
10	Blended #1 20 % ash	300	0.50	8.0	45.2	45.2
11	Blended #1 20 % ash	300	0.55	14.0	39.8	39.8
12	Blended #1 20 % ash	300	0.60	20.0	35.5	35.5
13	Portland #3	350	0.47	3.8	54.8	54.8
14	Blended #3 20 % ash	350	0.47	3.5	55.8	55.8
15	Portland #1	350	0.45	3.3	53.4	53.4
16	Blended #1 20 % ash	350	0.43	4.0	54.8	54.8
17	Blended #1 20 % ash	350	0.46	4.8	54.5	54.5

Table 2.17 Carbonation of concrete slabs stored indoors [98]

Mix no.	Strength (MPa)	Pulse velocity (m/s)	Depth of carbonation (mm)	
			Bottom	Top
1	51.8	4983	0.5	1.0
2	51.5	4885	1.0	2.0
3	46.7	4779	1.0	2.5
4	60.5	5046	0.5	1.0
5	55.5	4970	0.5	1.0
6	50.0	4802	1.0	2.0
7	47.9	4983	1.0	1.5
8	50.3	4897	1.0	1.5
9	42.0	4756	2.0	3.0
10	41.8	4909	1.0	1.5
11	37.5	4837	2.0	2.0
12	35.9	4722	3.0	2.0
13	59.9	5020	0.5	0.5
14	51.7	4995	1.5	1.0
15	62.2	5046	0.5	0.5
16	56.5	5020	1.5	2.0
17	47.5	4958	1.5	2.5

Table 2.18 Carbonation of concrete slabs stored indoors [98]

Mix no.	Strength (MPa)	Pulse velocity (m/s)	Depth of carbonation (mm)	
			Bottom	Top
1	62.0	4945	0.5	1.5
2	57.6	4825	1.0	3.0
3	50.6	4699	1.0	5.0
4	63.1	4921	0.5	1.0
5	61.0	4861	0.5	2.5
6	55.0	4779	1.0	3.0
7	52.7	4897	1.0	3.0
8	48.1	4707	1.0	2.5
9	40.2	4341	2.0	5.0
10	46.7	4873	1.0	5.5
11	40.2	4734	2.0	5.0
12	39.4	4623	3.0	5.5
13	63.9	4945	0.5	1.5
14	53.4	4921	1.5	2.5
15	65.4	4970	0.5	1.5
16	51.6	4995	1.5	2.5
17	51.9	4897	1.5	2.0

- Fly ash content increased.

The primary correlation was between carbonation depth and compressive strength (determined on cores of the slabs, not on test prisms), as is seen in Figs. 2.35 and 2.36.

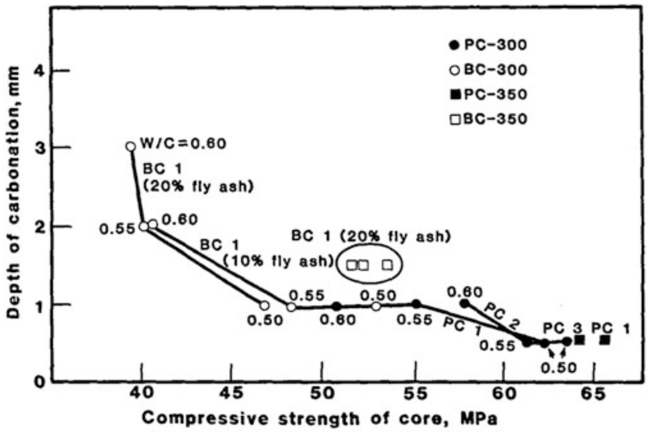


Fig. 2.35 Depth of carbonation versus compressive strength of fly ash concretes (indoor exposure) [98]

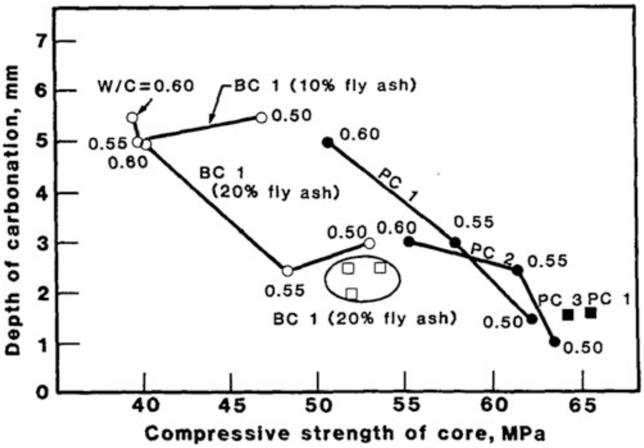


Fig. 2.36 Depth of carbonation versus strength of fly ash concretes (indoor exposure) [98]

The rate of strength development in thin slabs was different for the fly ash concretes and the control concretes. This was not unexpected, because fly ash was incorporated by simple replacement.

Ho and Lewis [99] examined the rates of carbonation of three types of concrete (plain, water-reduced, and fly ash) at equal slump. Accelerated carbonation was induced by storing specimens in an enriched CO_2 atmosphere (4 %) at 20 °C and 50 % RH for 8 weeks. The authors noted that 1 week under these conditions is approximately equivalent to 1 year in a normal atmosphere (0.03 % CO_2).

The data from this study are presented in terms of depth of carbonation versus 28-day compressive strength in Fig. 2.37.

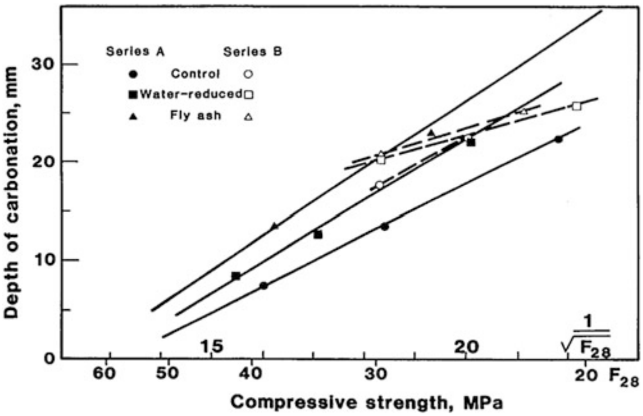


Fig. 2.37 Depth of carbonation versus 28-day compressive strength of fly ash concretes (accelerated testing) [99]

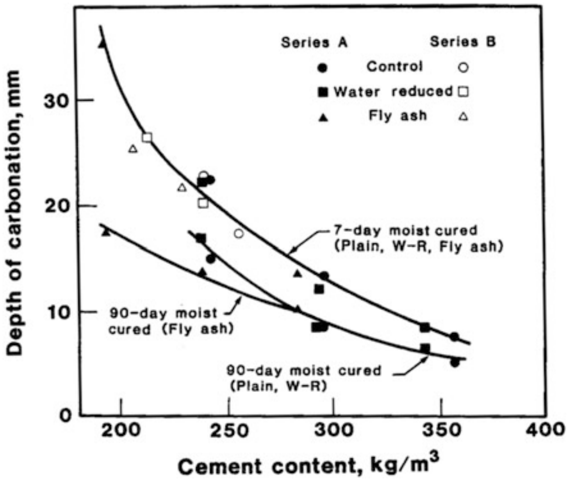


Fig. 2.38 Depth of carbonation versus cement content of fly ash concretes (accelerated testing) [99]

It is clear that there is an inverse relationship between strength and the depth of carbonation and that the fly ash concrete more readily carbonated than the non-fly ash concrete, especially at lower strength (<30 MPa).

Depth of carbonation versus cement content is shown in Fig. 2.38 as a function of the time of moist curing.

The authors concluded as follows:

- Concretes having the same strength and water/cement do not necessarily carbonate at the same rate.
- Based on a common 28-day strength, concrete containing fly ash showed a significant improvement in quality when curing was extended from 7 days to 90 days. such improvement was much greater than that achieved for the plain concrete.
- The depth of carbonation is a function of the cement content for concretes moist cured for 7 days. However, with a further curing to 90 days, concrete containing fly ash showed a slower rate of carbonation than plain and water-reduced concretes.

There is no doubt that these conclusions are consistent with the reported observations. However, the approach taken in this research has a major weakness, the influence of which must not be disregarded. In the accelerated test, concrete specimens that have been moist cured for 7 days and then conditioned in the laboratory for 21 days at 20 °C and 50 % RH are exposed to CO_2 (at elevated pressure) for 8 weeks. The age of the concrete at the start of the test is 28 days. Its maturity, however, is considerably less than an equivalent 28-day moist-cured concrete (although it is arguable that it is closer to the condition of real concrete in most construction situations). The concrete is exposed to carbonation at a rate at least five times that of atmospheric exposure while at the same time being kept at

50 % RH [99]. The disparity between the rate of carbonation and the rate of maturing is extreme and becomes greater the longer the experiment proceeds.

As Butler et al. [100] noted, the accelerated test may be suitable for different cements with different mixture proportions. It is not applicable when comparing concretes made with Portland cement with those made with blended cements because of the slow rate of pozzolanic reactions (Table 2.19).

Nagataki et al. [101] reported the long-term results of experiments carried out since 1969 to investigate the depth of carbonation in concrete with and without fly ash. Table 9.8 shows the depth of carbonation of different concrete mixtures at the ages of 2, 5, 10, and 15 years. The authors concluded that the initial curing period affects the carbonation of concrete cured indoors; hence, it is necessary for fly ash concrete to have a longer curing period in water at early ages. The carbonation of concrete cured outdoors is not affected by the initial curing period in water, provided it is cured in water for a period of 7 days.

Table 2.19 Average depth of carbonation [101]

C + F (kg/m³)	F/(C + F) (%)	Age (years)	Average depth of carbonation (mm)					
			Outdoors[a]				Indoors[a]	
			1 days	7 days	28 days	91 days	7 days	91 days
250	0	2	6.4	3.9	3.4	3.9	7.9	5.2
		5	7.0	5.3	5.9	5.7	13.6	11.7
		10	8.6	6.5	7.0	7.4	18.2	15.2
		15	10.7	7.3	7.6	7.4	22.1	18.3
	30	2	8.9	6.4	5.9	6.2	11.1	7.9
		5	13.1	10.3	10.4	10.8	21.0	16.5
		10	14.1	11.0	11.5	11.8	28.4	21.8
		15	14.9	13.3	12.7	14.6	34.5	27.6
290	0	2	5.0	1.9	2.3	2.7	6.1	4.1
		5	4.3	2.0	2.2	3.5	6.2	6.4
		10	4.1	2.0	2.1	3.8	11.4	10.2
		15	3.7	2.2	4.4	5.4	14.6	13.4
	30	2	6.7	5.1	5.5	4.1	9.3	6.6
		5	7.1	5.9	5.5	5.6	14.5	10.3
		10	7.3	7.1	6.0	5.7	20.2	15.7
		15	9.9	8.2	6.3	6.6	22.3	19.0
330	0	2	0.9	0.2	0.1	0.5	2.2	1.4
		5	2.7	1.2	1.6	1.5	5.7	5.0
		10	1.6	0.8	1.2	1.1	6.2	4.4
		15	0.6	0.2	1.0	1.8	9.0	7.9
	30	2	2.8	1.6	2.1	1.6	5.7	3.8
		5	5.7	2.5	4.3	4.6	10.2	9.4
		10	3.6	2.0	2.3	2.0	12.8	9.8
		15	3.0	2.2	3.3	3.6	15.2	13.9

[a] Initial curing period in water

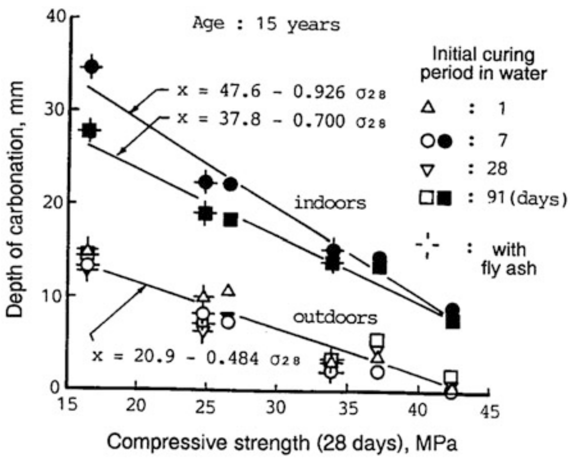


Fig. 2.39 Relation between compressive strength and depth of carbonation [101]

Nagataki et al. [101] found a linear relationship between the compressive strength at 28 days and the depth of carbonation, regardless of fly ash replacement (see Fig. 2.39). This relationship is not valid under changing exposure conditions or initial curing periods in water.

The rate of carbonation can be affected by the type of cement, the environmental conditions, the curing conditions, the water/cement, and the microstructure of concrete. Other published data show that the rate of carbonation is proportional to the water/cement ratio and to the square root of exposure time [102, 103].

Using the results in their work, Nagataki el al. [101] obtained the equation shown below for the rate of carbonation of concretes incorporating fly ash:

$$x = AB\,[\alpha(W/C) - \beta]\,t^{\gamma} \tag{2.2}$$

where x is depth of carbonation (cm); A is the correcting factor; B is the factor for initial curing period in water; ex, α, β are factors for fly ash; W/C is water/cement; t is age (years); and γ is the factor for environmental conditions.

The values of A, B, α, β, and γ, determined under various conditions, are shown in Table 2.20. It is indicated that γ has different values depending on environmental conditions and whether the concrete is cured indoors or outdoors.

Ramezanianpour [104, 105] examined the depth of carbonation of mortars containing some natural and artificial pozzolans under accelerated and long-term

Table 2.20 Coefficients of equation [101]

Exposure condition	F/(C + F) (%)	A	B	α	β	γ
Outdoors	0	0.55		4.211	1.831	
	30	0.77	1	3.311	1.777	0.25
Indoors	0	1.50	1.00 (for 7 days)	1.656	0.622	
	30	1.61	0.78 (for 91 days)	1.445	0.619	0.5

conditions. He found that under all curing and storage conditions the differences between the depth of carbonation of normal Portland cement and that of fly ash mortar mixtures were insignificant. He derived models for the rate of long-term carbonation that took into account the porosity of mortar mixtures and the square root of exposure time.

Ohga and Nagataki [106] investigated the effect of replacement ratio of fly ash, initial curing period in water, and air content on the carbonation phenomenon in concrete. They reported that the carbonation of concrete with fly ash was affected by initial curing conditions and increased with an increase in the replacement ratio of fly ash. They also found that the depth of carbonation of concrete was in proportion to the square root of exposure duration in the accelerated carbonation test.

In general, it appears that good-quality fly ash concrete is comparable to plain concrete in its resistance to carbonation. If concrete is placed at a low cement factor, with insufficient curing (either lack of moisture or low temperature), it should come as no surprise to find that it is not resistant to all forms of chemical and physical aggression, including carbonation [107].

Effects of Fly Ash on the Durability of Concrete Subjected to Repeated Cycles of Freezing and Thawing

It is now generally accepted, other criteria also being met, that air entrainment renders concrete frost resistant. Fly ashes, in common with other finely divided mineral components in concrete, tend to cause an increase in the quantity of admixture required to obtain specified levels of entrained air in concrete. In some instances, the stability of the air or the rate of air loss from fresh concrete is also affected. In general, the observed effects of fly ash on freezing and thawing durability support the view expressed by Larson [108]

> Fly ash has no apparent ill effects on the air voids in hardened concrete. When a proper volume of air is entrained, characteristics of the void system meet generally accepted criteria.

Gebler and Klieger [109] extended their study of air entrainment of fly ash concrete to include an examination of the air-void parameters of hardened concretes cast after initial mixing and after 30, 60, and 90 min. From these experiments, the authors concluded as follows:

> Spacing factors $(\overline{\text{L}})$ of specimens cast over a period of 90 min were essentially constant for the majority of concretes containing fly ash. In addition, the initial spread of results of specific surface and voids per inch was essentially similar for concretes containing Class F or Class C ash. However, when measured on specimens cast at 90 min, concretes with Class F ash exhibited greater variability of results for these air-void parameters than concretes with Class Cash.

Sturrup et al. [110] related the freezing and thawing performance of low-calcium fly ash concretes to carbon content. Accelerated freezing and thawing tests (ASTM C 666, procedure A) and outdoor exposure tests were conducted on concrete specimens containing low-calcium ashes of 5.4, 12.3, and 23 % carbon at 15, 30, 45, and 60 % replacement of cement by weight. Water/(cement + fly ash) was kept constant at 0.6; air content was kept at 6.5 ± 1 %, with the exception of a specimen with the fly ash containing 23 % carbon (air content = 3.6 %).

It was reported that correlation between durability factor, as determined by resonant frequency, and carbon content was poor; correlation with weight loss resulting from freezing and thawing cycling was more definite. This was taken to indicate that surface scaling, rather than internal damage, was the result of frost action on the specimens [111]. This was confirmed by observation of outdoor-exposed specimens [112].

Yuan and Cook [52] reported on the freezing and thawing resistance of concrete incorporating high-calcium fly ash. They examined two series of concrete specimens (non-air-entrained, air-entrained) with 0, 20, 30, and 50 % replacement of cement by weight. The freezing and thawing durability as determined by the relative dynamic modulus is shown in Figs. 2.40 and 2.41 and as determined by weight loss for air-entrained concrete is shown in Fig. 2.42.

- Yuan and Cook made the following resistance of air-entrained concrete is evident with or without fly ash replacement.
- The concrete with 20 % fly ash was found to be more durable than the control.
- As the quality of fly ash in air-entrained concrete was increased to 50 %, more scaling damage was noted after 400 cycles.

Ramakrishnan et al. [37] also examined the freezing and thawing durability of concrete containing a high-calcium fly ash (CaO = 20.1 wt%). Their data for concretes with ASTM type III cement are shown in Figs. 2.43 and 2.44. Weight

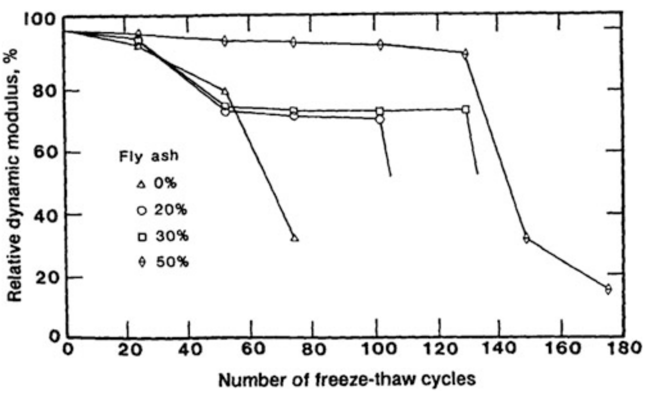


Fig. 2.40 Relative dynamic modulus of elasticity versus number of freezing and thawing cycles for air-entrained fly ash concretes after 14 days of curing [52]

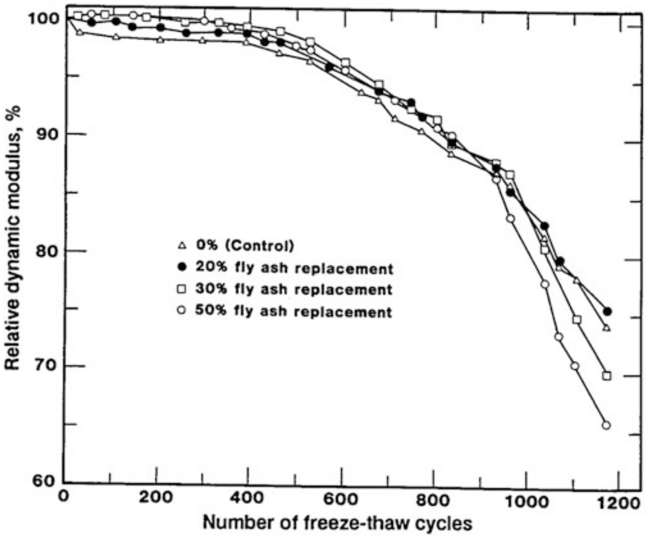
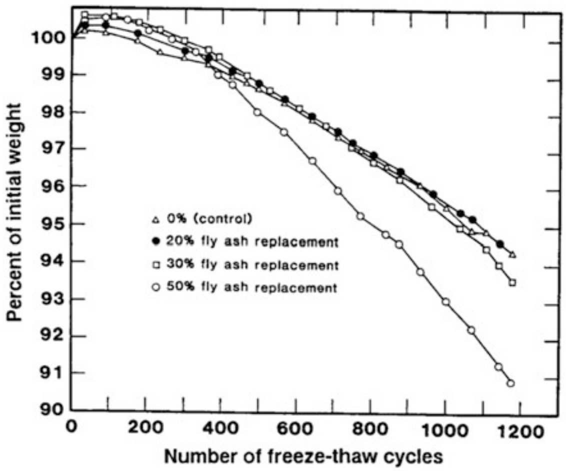


Fig. 2.41 Relative dynamic modulus of elasticity versus number of freezing and thawing cycles for air-entrained fly ash concretes after 14 days of curing [52]

Fig. 2.42 Weigth loss versus number of freezing and thawing cycles for air-entrained fly ash concretes after 14 days of curing [52]



change, pulse velocity development, and dynamic modulus were similar for concretes with and without fly ash.

The freezing and thawing resistance of fly ash concretes incorporating both low- and high-calcium fly ashes was determined in the CANMET study [6]. Table 2.21 shows the durability factors found for specimens made from the concrete described elsewhere in this report.

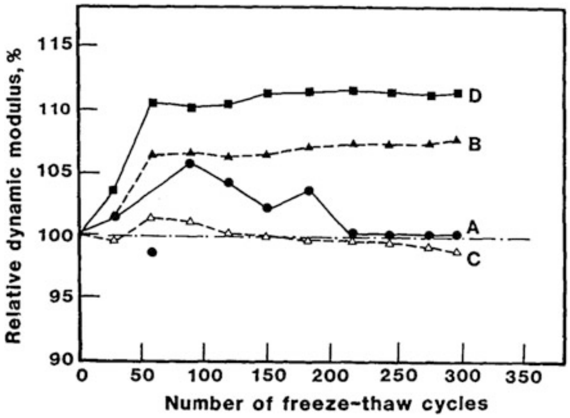


Fig. 2.43 Relative dynamic modulus changes of fly ash concrete under rabid freezing and thawing cycling [37]. *A*, control mix (freeze–thaw cure); *B*, fly ash mix (standard moist cure); *C*, fly ash mix (freeze–thaw cure); *D*, control mix (standard moist cure)

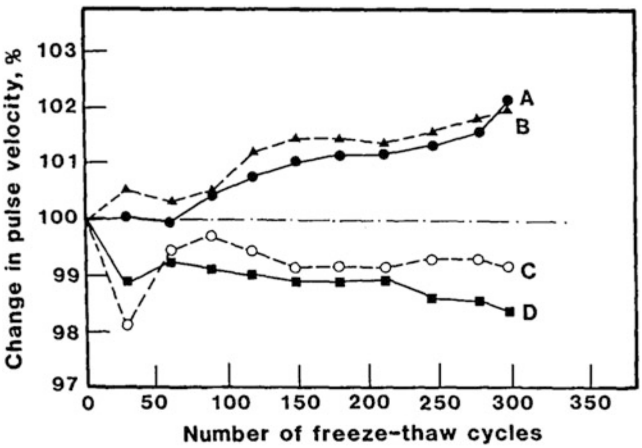


Fig. 2.44 Pulse velocity changes of fly ash concretes under rapid freezing and thawing cycling [37]. *A*, control mix (standard moist cure); *B*, fly ash mix (standard moist cure); *C*, fly ash mix (freeze–thaw cure); *D*, control mix (freeze–thaw cure)

Virtanen [115] compared the freezing and thawing resistance of fly ash, condensed silica fume, and slag concretes. Virtanen's observations on AEA requirement were discussed before. An estimate was made of the relative theoretical service life for each type of concrete as a function of air content (Fig. 2.45), and Virtanen made the following observations:

- The air content has the greatest influence on the freeze–thaw resistance of concrete.

Table 2.21 Freezing and thawing durability factors for fly ash concretes [34]

Mixture no.	Air content (%)	Durability for fly ash concretes[a]
Control 1	6.5	97.7
Control 2	6.4	98.1
F1	6.2	96.4
F2	6.2	98.8
F3	6.2	96.8
F4	6.3	98.8
F5	6.4	97.2
F6	6.5	96.8
F7	6.1	97.6
F8	6.2	96.9
F9	6.4	97.6
F10	6.5	97.2
F11	6.6	95.8

[a] Determined in accordance with ASTM 666

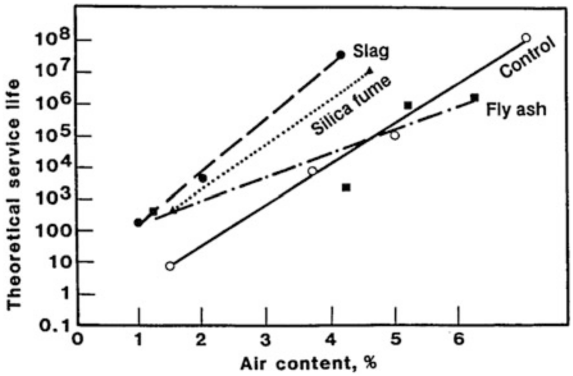


Fig. 2.45 Relationship between theoretical service life and air content of fresh concrete [115]

- Addition of fly ash has no major effect on the freeze–thaw resistance of concrete if the strength and air content are kept constant.
- The addition of blast-furnace slag fly ash may have a negative effect of the freeze–thaw resistance of concrete when a major part of the cement is replaced by them.

Larson [108], discussing some of the difficulties of interpreting the findings of much of the early works on freezing and thawing resistance of fly ash concrete, made the following observation:

Fly ash concrete durability characteristics are influenced and obscured by all the factors operating on ordinary concrete. They are also related to variations in the fly ash itself and perhaps to the associated phenomenon of increased air-entraining-agent requirement. When valid comparisons are made with equal strengths and air contents, however, there are no apparent differences in the freezing and thawing durability of fly-ash and non-fly-ash concretes.

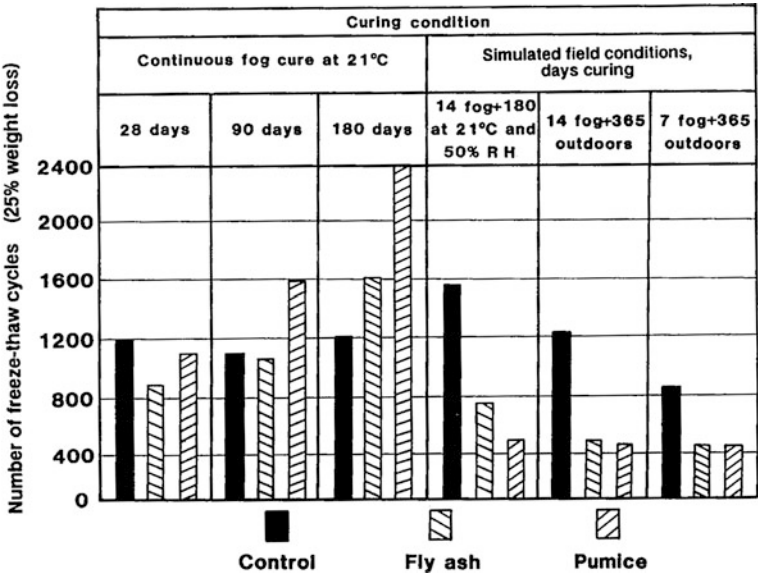


Fig. 2.46 The effect of curing conditions in freezing and thawing durability of concrete containing pozzolans [47]

Elfert [47] noted that the type of curing of specimens used to evaluate freezing and thawing resistance greatly influences the results obtained with fly ash and pozzolan concretes. Figure 2.46 illustrates the differences in results obtained under moist-curing and simulated field condition.

Another aspect of the freezing and thawing testing procedure was criticized by Brown et al. [113] who made the following comments on the freezing and thawing testing of blended cements:

- When blended cements are tested according to ASTM C 666-73, the standard method for measuring the freezing and thawing durability of Portland cement concretes, inferior resistance is usually observed. This is probably because test initiation after only a short curing period does not make proper allowance for the generally lower rate of strength development of blended cements.
- Freezing and thawing studies, when initiated after longer curing periods, have indicated that blended cements, due to development of strengths equivalent or superior to those of Portland cements, also develop superior resistance to freezing and thawing.

These points should certainly be considered when one is reviewing reports of all aspects of the durability of fly ash concrete, not merely its frost resistance.

Johnston [114] studied the freezing and thawing durability of concretes containing up to 42 % ASTM Class C fly ash by weight of cement with various ratios of water to cementitious material. Johnston concluded the following: [116]

- Replacement of cement by Class C fly ashes does not detract from freezing-thawing performance in ASTM C 666, Procedure A, provided the dosage of air-entraining admixture is increased to the point needed to achieve an air void-spacing factor of less than 0.25 mm, and provided water-to-cementitious materials ratio does not exceed about 0.53. At W/C + F values of 0.6 or higher, DF_{300} values show a definite tendency to decrease to below 90 % of their values for equivalent concretes without fly ash.
- For concretes with Class C fly ash, satisfactory performance in ASTM C 666, Procedure A, is not necessarily accompanied by satisfactory scaling resistance in ASTM C 672. They exhibit more severe scaling than control concretes without fly ash at W/C + F as low as 0.53, despite apparently adequate air void spacing factor. However, under field conditions, concrete with the same fly ash, but a lower W/C + F of 0.4, has not scaled noticeably after eight winters of exposure to heavy traffic and deicing salt. Therefore, it appears that the safe upper limit of W/C + F with respect to scaling is no greater than the 0.45 recommended for concrete without fly ash.

Nasser and Lai [117] studied the effects of a lignite fly ash on the resistance of concrete to freezing and thawing. Their results showed that the use of high percentages of fly ash in concrete (35–50 %) reduced its resistance to freezing and thawing even though it contained ~6 % air and was moist cured for 80 days. Nasser and Lai found that concrete containing 20 % fly ash had a satisfactory performance, provided its air content and strength were comparable to those of control concrete.

Klieger and Gebler [118] also evaluated the durability of concretes containing ASTM Class F and Class C fly ashes. Their test results indicated that air-entrained concretes, with or without fly ash, that were moist cured at 23 °C generally showed good resistance to freezing and thawing. For the specimens cured at a low temperature (4.4 °C), air-entrained concretes with Class F fly ash showed slightly less resistance to freezing and thawing than similar concretes made with Class C fly ash.

Klieger and Gebler also carried out the Deicer scaling test of air-retained concretes in the presence of a 4 % NaCl solution. Their results showed that the performance of air-entrained concretes without fly ash was better than that of those with fly ash, regardless of the type of curing. Air-entrained concretes made with either class of fly ash and air cured at 23 °C showed equal results when subjected to NaCl solution during freezing and thawing tests.

Bilodeau et al. [119], in an investigation carried out at CANMET, determined the scaling resistance of concrete incorporating fly ashes. Water/(cement + fly ash) of 0.35, 0.45, and 0.55 were used, and concrete without fly ash and those containing 20 and 30 % fly ash as replacement by mass for cement were made.

Their results showed that the concrete containing $S \leq 30$ % fly ash performed satisfactorily under the scaling test with minor exceptions (see Tables 2.22 and 2.23).

However, the performance of the fly ash concrete was more variable than that of the control concrete. The satisfactory scaling resistance of concrete (scaling residue < 0.8 kg/m^2) is attributed to the adequate air-void system in all cases, even

Table 2.22 Mass of scaling residue after 50 freezing and thawing cycles-series I [140]

Time of moist curing (days)	Time of air drying (weeks)	Mass of scaling residue (kg/m^2)								
		w/(C + F) = 0.35			w/(C + F) = 0.45			w/(C + F) = 0.55		
		Percentage of fly ash			Percentage of fly ash			Percentage of fly ash		
		0	20	30	0	20	30	0	20	30
3	3	0.195	0.504	0.184	0.149	0.160	0.206	0.123	0.282	0.321
	4	0.122	0.237	0.208	0.178	0.200	0.680	0.126	0.281	0.638
	5	0.076	0.128	0.143	0.091	0.243	0.634	1.131	0.734	0.354
	6	0.100	0.074	0.158	0.105	0.306	0.263	0.129	0.255	0.226
7	3	0.154	0.047	0.371	0.135	0.212	0.362	0.160	0.335	0.426
	4	0.147	0.092	0.265	0.158	0.448	0.209	0.172	0.312	0.885
	5	0.098	0.108	0.151	0.114	0.180	0.199	0.119	0.238	0.396
	6	0.192	0.038	0.223	0.169	0.268	0.177	0.118	0.370	0.562
14	3	0.139	0.670	1.094	0.188	0.264	0.409	0.517	0.895	0.705
	4	0.144	0.158	0.449	0.126	0.198	0.202	0.131	0.636	0.625
	5	0.1	0.066	0.493	0.135	0.319	0.839	0.162	0.811	0.613
	6		0.064	0.189	0.117	0.293	0.463	0.286	0.728	0.814

Table 2.23 Mass of scaling residue after 50 freezing and thawing cycle-series II, III, IV, V [140]

Time of moist or membrane curing (days)	Time of air drying (weeks)	Mass of scaling residue (kg/m^2)											
		Mixture series II Mixture nos. 10–12 (membrane cured)			Mixture series III Mixture nos. 13–15 (membrane cured)			Mixture series IV Mixture nos. 16–18 (moist cured)			Mixture series V Mixture nos. 19–21 (membrane cured)		
		Percentage of fly ash			Percentage of fly ash			Percentage of fly ash			Percentage of fly ash		
		0	20	30	0	20	30	0	20	30	0	20	30
3	3	0.129	0.105	0.100	0.072	0.070	0.233	0.194	0.497	0.671	0.215	0.292	0.407
	4	0.069	0.084	0.098	0.062	0.073	0.052	0.225	0.250	0.485	0.253	0.158	0.223
	5	0.087	0.069	0.127	0.057	0.094	0.117	0.105	0.371	0.289	0.266	0.366	0.112
	6	0.062	0.072	0.096	0.097	0.128	0.128	0.176	0.389	0.359	0.240	0.116	0.160
7	3	0.241	0.154	0.111	0.073	0.085	0.097	0.240	1.197	0.527	0.264	0.248	0.203
	4	0.092	0.266	0.136	0.087	0.105	0.164	0.215	0.318	1.041	0.185	0.271	0.374
	5	0.095	0.158	0.174	0.081	0.062	0.157	0.150	0.323	0.491	0.297	0.496	0.174
	6	0.080	0.092	0.201	0.078	0.166	0.162	0.338	0.119	0.392	0.187	0.338	0.325
14	3	0.031	0.096	0.132	0.052	0.205	0.239	0.770	0.157	2.063	0.142	0.350	0.321
	4	0.081	0.119	0.103	0.046	0.064	0.269	0.199	0.549	0.559	0.247	0.450	0.103
	5	0.057	0.103	0.127	0.085	0.099	0.139	0.164	0.318	1.962	0.126	0.130	0.152
	6	0.043	0.154	0.100	0.057	0.258	0.098	0.195	0.337	0.404	0.128	0.273	0.633

Note $W/(C + F) = 0.45$

for fly ash mixtures that have a water/cementitious materials of 0.55 and are moist cured for 3 days.

Carette and Langley [120] studied the performance of fly ash concrete subjected to 50 freezing and thawing cycles in the presence of de-icing salts. They concluded that the incorporation of fly ash in concrete mixtures with ≤30 % replacement of Portland cement did not show significant difference in salt-scaling resistance in the presence of a 4 % calcium chloride solution when examined by visual rating of surface deterioration. In the measurement of weight loss due to surface deterioration, which they believed was a meaningful way to assess surface deterioration, concretes containing fly ash showed greater weigh t loss than control concrete.

Carette and Langley [120] stated that the surface scaling appeared not to be sensitive to the length of time that specimens were moist cured or air dried subsequent to initial moist curing, at least within the periods investigated.

Effects of Fly Ash on the Durability of Concrete Exposed to Elevated Temperatures

The influence of elevated temperatures on the strength of concrete during curing was discussed at some length in the strength section. In recent years, the use of concrete in structures required to withstand elevated temperatures under some circumstances (such as nuclear reactor containment structures) has generated renewed interest in the effects of high temperatures on fly ash and other concretes.

Nasser and Lohtia [121, 122] and Nasser and Marzouk [75, 123] studied plain and fly ash concretes at temperatures ≤230 °C. Carette et al. [124] studied concretes with normal Portland cement, slag, and fly ash at sustained temperatures ≤600 °C. Data from this research are shown in Fig. 2.47. In general, the incorporation of fly ash appears not to influence the behavior of concrete at elevated temperatures. Loss of strength and changes in other structural properties occur at approximately the same temperatures for both types of concrete.

Abrasion and Erosion of Fly Ash Concrete

Under many Circumstances, concrete is subjected to wear by attrition, scraping, or the sliding action of vehicles, ice, and other objects. When water flows over concrete surfaces, erosion may occur. In general, regardless of the type of test performed, the abrasion resistance of concrete is usually found to be proportional to its compressive strength [63]. Similarly, at constant slump, resistance to erosion improves with increased cement content and strength. It may be anticipated that fly ash concrete that is incompletely or inadequately cured may show reduced resistance to abrasion.

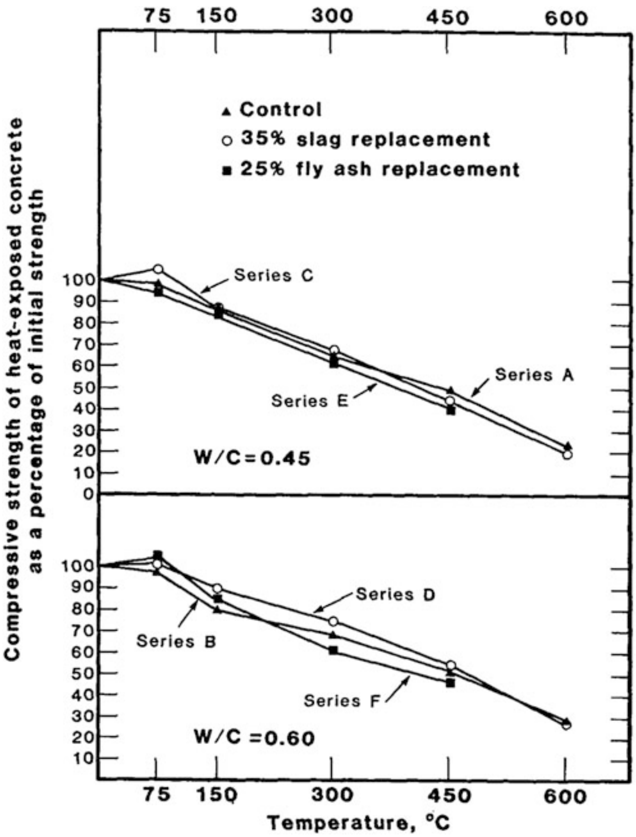


Fig. 2.47 Compressive strength of concretes after 1 month of exposure to various elevated temperatures [124]

Abdun-Nur [69] cited three publications indicating that abrasion resistance may be reduced in fly ash concrete. However, in all of these there is no indication that attempts were made to compare fly ash concrete and plain concrete at equal strength or equal maturity.

Liu [125] examined the abrasion-erosion resistance of concrete using a newly developed underwater abrasion test. One of the concrete mixtures examined by Liu incorporated fly ash at a 25 vol% replacement for Portland cement. Details of the type and origin of the fly ash used were not reported. Performance of the fly ash concrete, cured for 90 days to an average compressive strength of 49 MPa, was compared with that of a concrete of similar mixture proportions containing no fly ash and cured for 28 days to an average compressive strength of 47 MPa.

Little difference in abrasion resistance was found between the two concretes for test periods ≤36 h. At prolonged test times, the performance of the fly ash

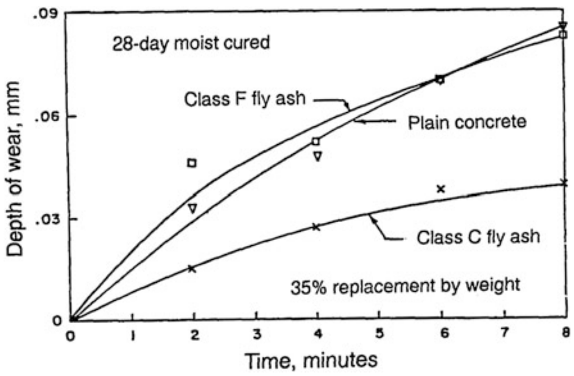


Fig. 2.48 Abrasion resistance of concrete [126]

concrete was inferior to that of the control. After 72 h, the fly ash concrete had lost ~25 % more mass (7.6 % loss) to abrasion-erosion than the control (61 % loss).

Carrasquillo [126] examined the abrasion resistance of concretes containing no fly ash, 35 % ASTM Class C fly ash, or 35 % ASTM Class F fly ash. Specimens tested were cast from concretes having similar strengths, air contents, and cementitious materials contents. As shown in Fig. 2.48, the resistance to abrasion of concrete containing Class C fly ash was greater than that of the concrete containing Class F fly ash or no fly ash. The letter two exhibited approximately equal abrasion resistance; measurement was based on the depth of wear.

Naik et al. [127] carried out an investigation of the compressive strength and abrasion resistance of concrete containing ASTM Class C fly ash. They proportioned concrete mixtures to have cement replacement in the range of 15–70 wt% fly ash. The water/cementitious materials varied from 0.31 to 0.37. Their results showed that the abrasion resistance of concrete containing ≤30 % fly ash was similar to that of the control concrete. However, abrasion resistance of concretes containing ≤40 % fly ash was lower than that of control concrete without fly ash.

Effects of Fly Ash on the Durability of Concrete Exposed to Chemical Attack

Introducing fly ash as a component of concrete has been shown to influence the concrete's resistance to chemical attack. Leaching of calcium hydroxide, acidic dissolution of cementitious hydrates, the action of atmospheric and dissolved carbon dioxide, and the reactivity of cement components to ions in solution are the main causes of deterioration of concrete exposed to chemical action.

Biczok [128] enumerated four conditions related to concrete quality and the constituents of concrete on which the destructive effects of aggressive waters depend:

1. type of cement used and its chemical and physical properties;
2. quality of concrete aggregates and their physical properties and gradation;
3. method used for preparing concrete, the water/cement, the proportion of cement, and the placement; and
4. condition of the surface exposed to the water.

Of these, condition 1 relates strictly to the nature of the cementitious binder used, whereas conditions 2, 3, and 4 apply to one or more aspects of the permeability of concrete.

With regard to cement type, two factors are influential in determining the relative durability of fly ash concrete:

- The chemical composition of the cement, vis-a-vis the cementitious components produced during hydration, has a pronounced influence on resistance to chemical action. The most notable example is the use of low-C_3A (AS 1 M type V) cements as a means of controlling attack by sulphate ions.
- A combination of chemical composition and physical properties, notably fineness, determines the rate at which cement hydration proceeds and, at least for the early life of a structure, must influence its permeability.

Fly ash used as a replacement for Portland cement has an indirect influence on both factors. At early ages, fly ash serves only as an inert component. At later ages, it contributes to the formation of cementitious components but, as Kovacs [129] showed, it does so in a manner that changes the relative proportions of the usual hydrate materials. Finally, it converts some of the calcium hydroxide, which is produced when cement hydrates, to less reactive calcium silicates and aluminates through the pozzolanic reaction. The removal of free calcium hydroxide by reactive combination with pozzolans was shown by Lea [130] to progress as is illustrated in Fig. 2.49, in which the quantities of free $Ca(OH)_2$ in mortars made with and without pozzolan are compared as a function of age.

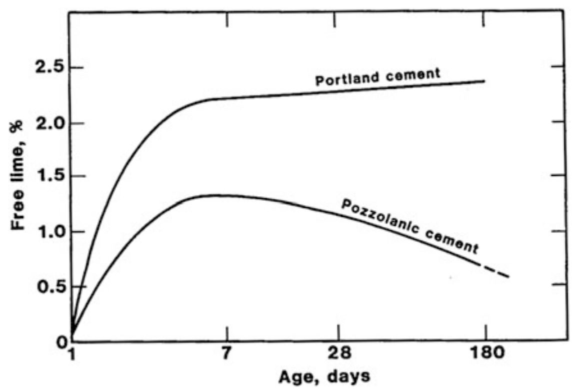


Fig. 2.49 Free lime content of 1:3 cement/sand mortars [130]

It is generally agreed that in concrete this process leads to long-term gains in watertightness, strength, and resistance to aggressive environments.

In recent years, research has been directed at the role played by fly ash in changing the chemical balance of the cementitious components of concrete, either as a factor in concrete durability or with respect to the development of test methods.

Effects of Fly Ash on Sulphate Resistance of Concrete

In 1937, Davis et al. [1] reported that some fly ashes increased the resistance of concrete to sulphate attack, others were ineffective, and some were deleterious and caused increased sulphate deterioration.

In 1967, Dikeou [131] reported the results of sulphate-resistance studies on 30 concrete mixtures made with Portland cement, Portland -fly ash cement, or fly ash. From this work it was concluded that all of the 12 fly ashes tested greatly improved sulphate resistance. The relative order of improvement is shown in Fig. 2.50.

Kalousek et al. [132] reported studies on the requirements of concrete for long-term service in a sulphate environment. From their study, they drew the following conclusions:

- 84 % of the AS1 M types V and II cement concretes without pozzolan showed a life expectancy of <50 years.
- Certain pozzolans very significantly increased the life expectancy of concrete exposed to 2.1 % sodium sulphate solution. Fly ashes meeting present-day specifications were prominent among the group of pozzolans showing the greatest improvements.

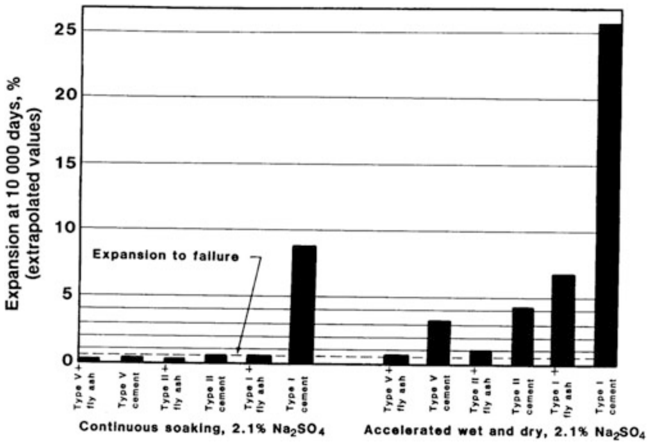


Fig. 2.50 Sulphate expansion of concretes containing 30 % fly ash [131]

- Concretes for long-term survival in a sulphate environment should be made with high-quality pozzolans and a sulphate-resisting cement. The pozzolan should not increase significantly, but preferably decrease, the amount of water required.
- Cement to be used in making sulphate-resisting concrete with pozzolan of proven performance should have a maximum C_3A content of 6.5 % and maximum C_4AF content of 12 % Restrictions of cements to those meeting present-day specifications for type V cement does not appear justified.

The fly ash samples examined by Dikeou [131] and those examined by Kalousek et al. [132] all originated from bituminous coals.

In 1976, Dunstan [133] reported the results of experiments on 13 concrete mixtures made with fly ashes from lignite or subbituminous coal sources. On the basis of this work, he concluded that lignite and subbituminous fly ash concrete generally exhibited reduced resistance to sulphate attack.

Dunstan's work was extended, and in 1980 he published a report summarizing the results of a 5-year study on sulphate attack of fly ash concretes [134]. This report includes a theoretical analysis of sulphate attack and its causes. The basic postulate of Dunstan's thesis is that CaO and Fe_2O_3 in fly ash are the main contributors to the resistance or susceptibility of fly ash concrete to sulphates.

Dunstan noted that as the calcium oxide content of ash increases above a lower limit of 5 % or as the ferric oxide content decreases, sulphate resistance is reduced. To select potentially sulphate-resistant fly ashes (or, more important, fly ashes that can improve the sulphate resistance of concrete), Dunstan proposed the use of a resistance factor *(R)*, calculated as follows:

$$R = (C - 5)/F \tag{2.3}$$

where C is the percentage of CaO; and *F* is the percentage of Fe_2O_3.

Figures 2.51 and 2.52 show the results from two types of laboratory sulphate-resistance tests on samples of concretes containing high-calcium fly ashes with the properties shown in Table 2.24. Figures 2.53 and 2.54 show the results from similar tests on samples of concretes containing low-calcium fly ashes with the properties also shown in Table 2.24. The influences (positive and negative) of fly ash are clearly seen from these data.

The findings of Dunstan's work were summarized in terms of the selection of fly ashes for sulphate-resistant concrete as follows:

R limits[a]	Sulphate resistance
<0.75	Greatly improved
0.75–1.5	Moderately improved
1.5–3.0	No significant change
>3.0	Reduced

[a] At 25 % cement replacement

[b] Relative to ASTM type II cement at a water/cement of 0.45

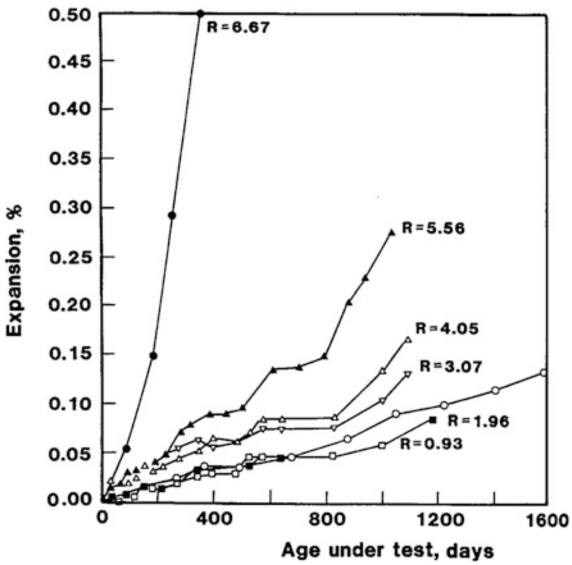


Fig. 2.51 Sulphate expansion of concretes containing high-calcium fly ash (soak test) [134]

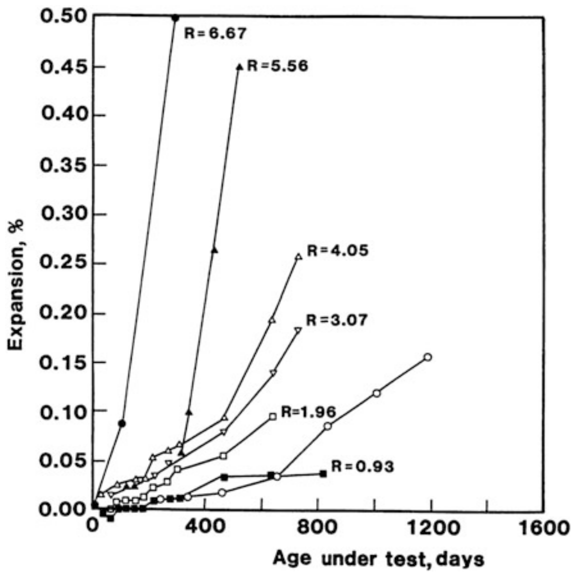


Fig. 2.52 Sulphate expansion of concretes containing low-calcium fly ash (wet-dry test) [133]

The U.S, Bureau of Reclamation incorporated a more conservative version of Dunstan's limits in its revised reprint of the Concrete Manual [135, 136], details of which are given in Table 2.25.

Table 2.24 Characteristics of fly ashes examined by Dunstan [126, 134]

Fly ash no.	Composition (mass %)							
	SiO_2	Al_2O	Fe_2O	CaO	MgO	SO_3	Alkali	LO1
M-6498	46.1	19.0	18.6	8.2	1.3	1.6	0.72	2.0
M-6498	28.1	20.0	4.1	32.0	6.4	3.8	0.68	0.2
M-6498	34.7	24.8	4.2	26.1	5.2	1.4	0.81	0.2
M-6498	37.2	15.6	5.6	24.3	11.3	0.9	0.07	0.3
M-6498	37.1	11.8	7.3	21.8	5.6	2.6	4.23	0.3
M-6498	31.1	17.1	7.9	25.3	8.1	3.3	1.35	1.1
M-6498	51.8	27.2	2.0	10.7	2.1	0.7	0.86	1.2
M-6498	49.6	25.7	3.0	11.3	2.1	0.7	1.20	1.3
M-6498	61.4	23.4	3.7	7.0	1.2	0.5	0.81	2.5
M-6498	32.8	19.6	4.1	28.0	5.5	3.4	1.54	0.5
M-6498	36.9	18.1	4.7	24.0	4.8	2.8	1.86	0.6
M-6498	41.1	17.9	4.9	20.2	4.4	2.2	2.21	0.8
M-6498	45.7	18.4	5.3	15.5	3.8	1.6	2.83	0.9
M-6498	51.5	24.5	5.7	10.2	2.1	0.9	0.96	1.2
M-6498	34.7	24.8	4.2	26.1	5.2	1.4	0.81	0.2

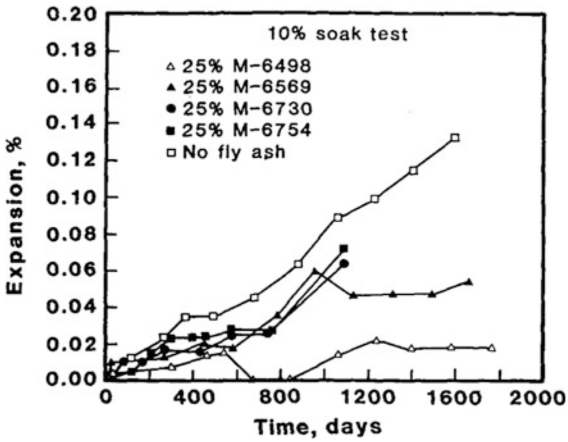


Fig. 2.53 Sulphate expansion of concretes containing low-calcium fly ash (10 % soak test) [133]

Dunstan [137] examined the *R* value as an advance indicator of potential sulphate resistance of concretes containing fly ash after >12 years of testing. The sulphate-resistance test results indicated that the *R* value remained a good indicator of potential sulphate resistance of fly ash concretes. For concrete containing 15–25 % fly ash with an *R* value of <3, the sulphate resistance would be as good as or better than that of a concrete with the same cement and without fly ash.

Tikalsky et al. [138] reported the effect of 24 different fly ashes on the sulphate resistance of fly ash concretes. They found that except for some fly ashes, Dunstan's R factor could provide a good indication of the effect of fly ashes on the sulphate resistance of concrete. Some fly ashes that contained calcium oxide at

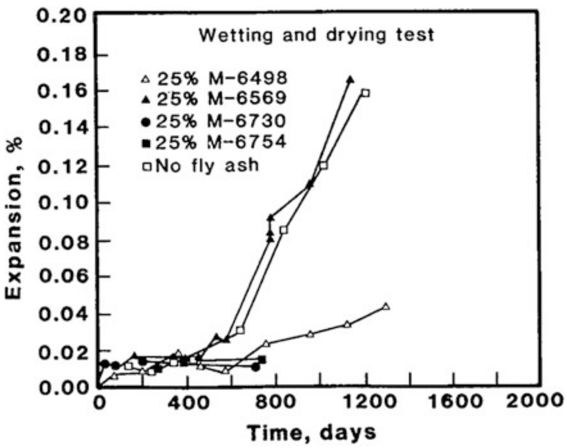


Fig. 2.54 Sulphate expansion of concretes containing low-calcium fly ash (wet-dry test) [133]

Table 2.25 US Bureau of Reclamation cementitious materials options for sulphate resistance [135]

I Positive sulphate attack (0.1–0.2 %, or 150–1500 ppm)
A Type II cement
B Type II cement plus class N, F, or C pozzolan with R < 2.5
C Type IP (MS) cement with R < 2.5
II Sever sulphate attack (0.2–2 %, or 1500–10000 ppm)
A Type V cement
B Type V cement plus class N, F, or C pozzolan with R < 2.5
C Type II cement plus class N, F, or C pozzolan with R < 2.5
D Type IP (MS) cement
with R < 2.5 if C_3A is < 5.0
with R < 1.5 if C_3A is < 5.0–8.0
III A Type V cement plus class N, F, or C pozzolan with R < 1.5
B Type II cement plus class N, F, or C pozzolan with R < 0.75
C Type IP (MS) cement
with R < 1.5 if C_3A is < 5.0
with R < 0.75 if C_3A is < 5.0–8.0

10–25 wt% did not conform to the general trend defined by Dunstan's R factor. In their investigation, the effect of a given ash replacement level of cement within the range of 25–45 vol%.

Mather [139] reported data from two studies at the laboratories of the U.S. Army Corps of Engineers. Various pozzolans were being investigated for their influence on sulphate resistance of concrete. The data presented were obtained from exposure of mortars to 0.352 M Na_2SO_4 solution. Care was taken in the experiments to expose the mortar bars to the sulphate solution only after they had reached approximately equal maturity as determined by measurements of compressive strength on companion mortar cubes.

Three non-sulphate-resisting cements, with C_3A contents of 14.6 % (cement RC-756), 13.1 % (cement RC-714), or 9.4 % (cement RC-744), were used. Ten pozzolans were examined: one condensed silica fume, one volcanic glass, three fly ashes of subbituminous origin, one bituminous fly ash, and four fly ashes from lignite coals. It is unfortunate that the chemical and physical properties of these materials were not recorded in this preliminary report of the study.

The pozzolans were incorporated in mortars by replacement of 30 vol. % of portland cement.

Figures 2.55, 2.56, 2.57 and 2.58 show the results obtained from the experiments reported by Mather [139]. The ranking of effectiveness in reducing sulphate expansion was found to be, from best to worst, as follows: condensed silica fume, volcanic glass, subbituminous fly ash (three examples), bituminous fly ash, and lignite fly ash (four examples).

Mather summarized the findings of the study as follows:

> What seems to be suggested (by the results) IS that a pozzolan of high fineness, high silica content and highly amorphous silica is the most effective pozzolan for reducing expansion due to sulphate attack on mortars made with non-sulphate resisting cements…. The pozzolans that resulted in poorer performance… were in 6 of 7 cases fly ashes produced by the combustion of lignite.

It might be added that the ranking of subbituminous ashes as better than the one bituminous ash examined is in direct contradiction with the findings of Dunstan [133, 134]. However, in the absence of specific properties of the ashes examined

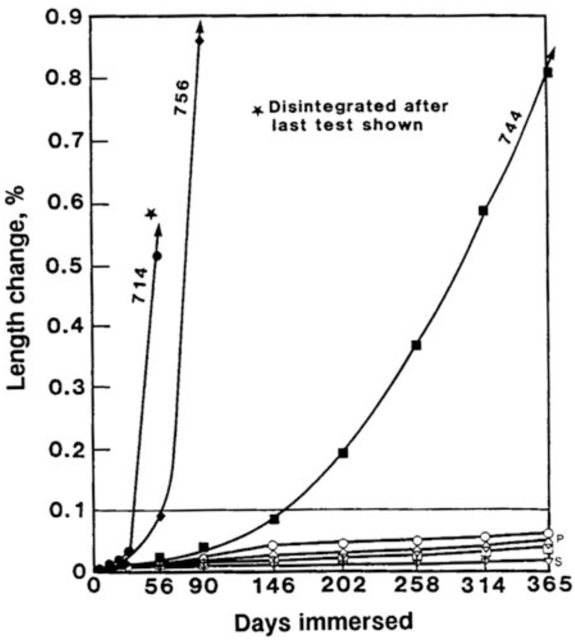


Fig. 2.55 Effect of condensed silica fume and volcanic glass pozzolan on the expansion of mortar prisms incorporating non-sulphate-resisting cement in sulphate solution [139]. *P*, replacement of cement by pozzolan; *S*, 30 % replacement of cement by condensed silica fume; *714*, cement with calculated C_3A = 13.1 %; *756*, cement with calculated C_3A = 14.6 %; *744*, cement with calculated C_3A = 9.4 %

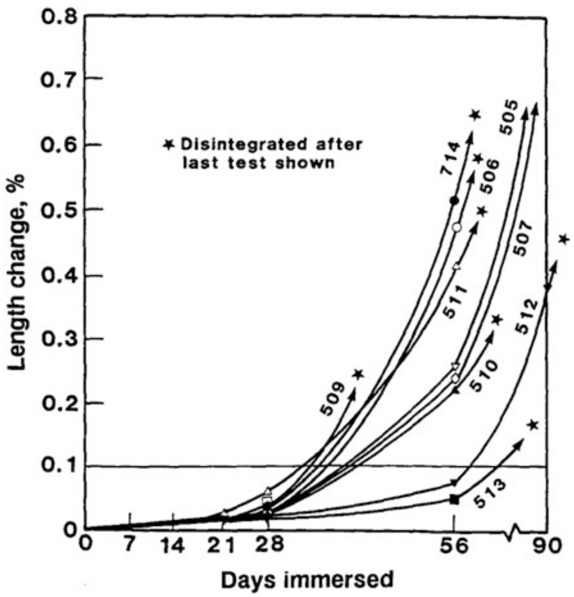


Fig. 2.56 Effect of fly ash on the expansion of mortar prisms incorporating non-sulphate-resisting cement in sulphate solution [139]. *Curve 714* represents cement with calculated $C_3A = 13.1$ %; remaining curves represent replacement of cement *714* by 30 % of eight different, but unidentified, fly ashes

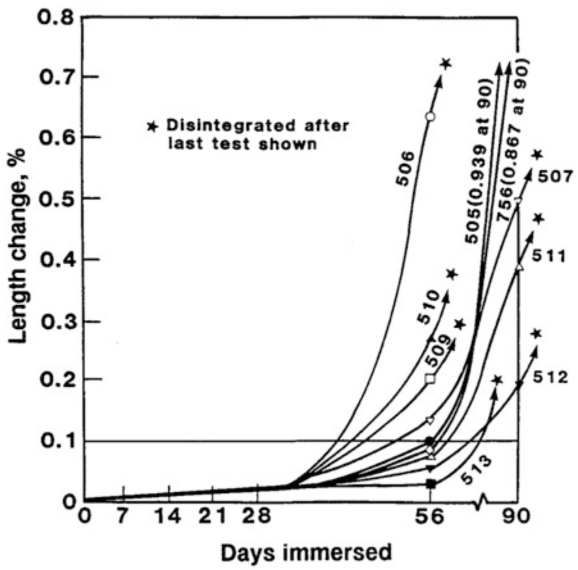


Fig. 2.57 Effect of fly ash on the expansion of mortar prisms incorporating non-sulphate-resisting cement in sulphate solution [139]. *Curve 756* represents cement with calculated $C_3A = 14.6$ %; remaining curves represent replacement of cement *756* by 30 % of eight different, but unidentified, fly ashes

and without comparable data from mortars made with other fly ashes, it would be inadvisable to draw further conclusions from this report. Clearly, the influence of fly ash on the sulphate resistance of concrete is not completely understood, and much more research is needed to establish guidelines on this important aspect of concrete durability.

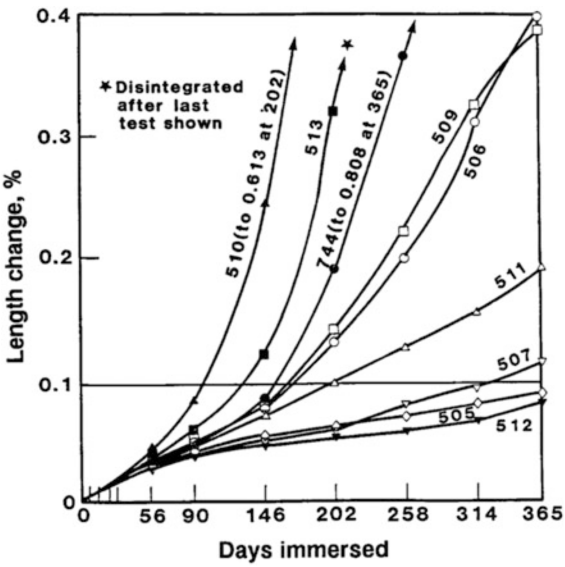


Fig. 2.58 Effects of fly ash on the expansion of mortar prisms incorporating non-sulphate-resisting cement in sulphate solution [139]. *Curve 744* represents cement with calculated $C_3A = 9.4$ %; remaining curves represent replacement of cement *744* by 30 % of eight different, but unidentified, fly ashes

Effects of Fly Ash on Alkali-Aggregate Reaction in Concrete

Shortly after Stanton [140] discovered that alkali-aggregate reactions (AAR) caused expansion and damage in some concretes, he reported that the effects could be reduced by adding finely ground reactive materials for the concrete mixture. Subsequently, a variety of natural and artificial pozzolans and mineral admixtures, including fly ash, were found to be effective in reducing the damage caused by AAR. As discussed below, the effectiveness of fly ash (and other mineral admixtures) in reducing expansion due to AAR appears to be limited to reactions involving siliceous aggregates. A form of AAR, known as alkali-carbonate reaction, has been reported and has been shown to be relatively unresponsive to the addition of pozzolans.

The damage caused by AAR. As discussed below, the effectiveness of fly ash (and other mineral admixtures) in reducing expansion due to AAR appears to be limited to reactions involving siliceous aggregates. A form of AAR, known as alkali-carbonate reaction, has been reported [141] and has been shown to be relatively unresponsive to the addition of pozzolans [142].

It is not within the scope of this review to consider numerous complex aspects of AAR; these matters are the subject of much current research and are poorly understood. Rather, consideration here is limited to some aspects directly relevant to the selection of fly ash as a means to reducing expansion caused by alkali-silica reaction.

Table 2.26 Minimum percentage replacement of fly ash for the effective control of expansion [143]

Replacement material	Minimum replacement for effectiveness (vol%)		
	14 days	6 months	Average
Fly ash I	46	36	41
Fly ash II	48	36	42
Fly ash III	52	36	44
Fly ash IV	45	34	40

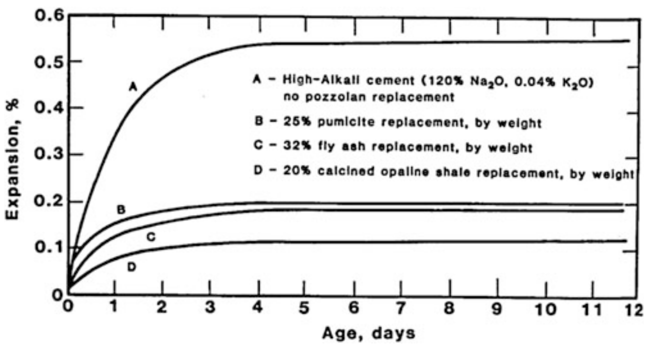


Fig. 2.59 Effect of pozzolans on reducing expansion of mortars made with a high-alkali cement and crushed Pyrex^{TM} glass [47]

The effectiveness of fly ash in the control of the alkali-silica reaction has been widely reported. Pepper and Mather [137] reported the minimum percentage replacement (by volume) of cement by fly ash required to reduce expansion in test specimens by 75 %. Their results are shown in Table 2.26. Elfert [47] reported data of a similar nature from work carried out at the U.S. Bureau of reclamation (Fig. 2.59).

While it is clear that some fly ashes are effective in reducing expansion due to AAR, it is questionable whether the early strength losses caused by replacement of 40-50 % of the cement by low-calcium fly ash would be tolerable for more than a limited number of applications. Similar levels of replacement using high-calcium fly ashes may be more acceptable.

During a study of alkali-reactive aggregates in Nova Scotia, Duncan et al. [144] showed effective suppression of expansion of expansion by replacement of moderate-alkali cement (0.71 % as Na_2O) with a little as 25 % fly ash. Some data are shown in Fig. 2.60.

In other studies, the following factors have been identified as particularly important:

- The concentration of soluble alkali in the system;
- The type of aggregate; and
- The quality of fly ash used.

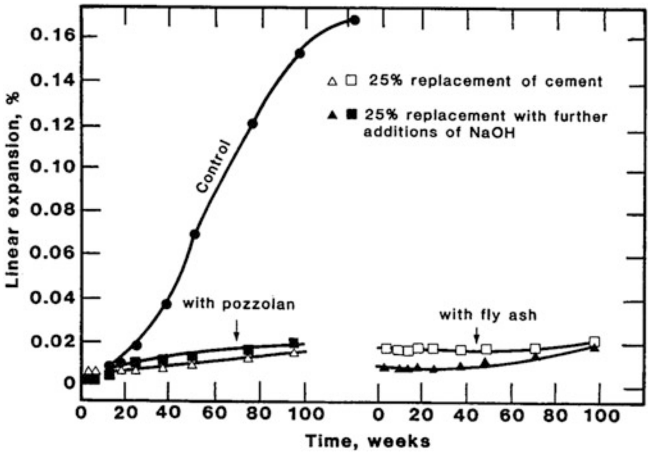


Fig. 2.60 Expansion of concrete prisms made with metagreywacke aggregate and 25 % cement replaced with pozzolan [144]

It is now generally accepted that, with regard to alkali-silica reactivity, it is the concentration of soluble alkali, rather than the total alkali content of the system, that affects expansion. Figure 2.61 shows the relationship between water-soluble alkali content and the time required for cracking in concrete containing Beltane opal as aggregate, as reported by Hobbs [145].

In general, Hobbs estimated that the lower limit of alkali concentration at which mortar test specimens exhibit excessive cracking was 3.4 kg/m^3 as acid-soluble alkali [146]. This is equivalent to 2.5 kg/m^3 as water-soluble alkali [145].

The source of alkali (Na_2O or K_2O) is not considered important. Thus, soluble alkali from fly ash is regarded as being as deleterious as that from Portland cement. High-calcium fly ashes, for example, contain large amounts of soluble alkali sulphates, which have been reported to increase the rate of deterioration through “the alkali-silica reaction” [147].

Not all aggregates are susceptible to the alkali-silica reaction, nor do all susceptible aggregates behave in the same way. The alkali-silica reaction is a long-term process that has been found to occur most commonly with aggregates that contain non-crystalline or cryptocrystalline silica.

Aggregates and their mineralogical constituents known to react with alkalis in concrete include the following [148]:

- silica materials -opal, chalcedony, tridymite, and cristobalite;
- zeolites, especially heulandite;
- glassy to cryptocrystalline rhyolites, dacites, andesites, and their tuffs; and
- certain phyllites.

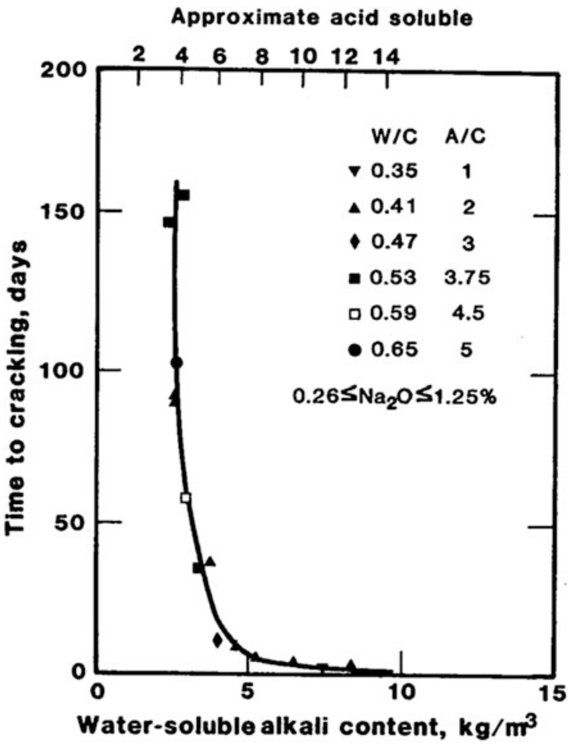


Fig. 2.61 Variation in time to cracking with water-soluble alkali content at the most critical alkali/Beltane opal ratio [145]

In Britain, the main reactive component of aggregates susceptible to alkali-silica reactivity has been found to be chert (flint) [149]. In South Africa, studies have been made on hornfels of the Malmesbury Group [150].

Much of the experimental work reported in the literature has been directed to the study of very reactive, porous, opaline aggregates, such as the Beltane opal from California and Pyrex™ glass. Both aggregates are generally more reactive than many of the natural aggregates encountered in practice, and this should be considered when the reported data are evaluated for practical applications.

As with most other aspects of fly ash use, ashes from different sources have significantly different effects on alkali-silica reactivity. As was noted above, some high-calcium fly ashes have been found in the laboratory to be ineffective or deleterious in relation to alkali reactivity.

In studies using Beltane opal, Hobbs [151] reported the expansion data shown in Fig. 2.62 for fly ashes with the chemical compositions summarized in Table 2.27.

The following conclusions were drawn by Hobbs from these experiments:

- The partial replacement of a high-alkali cement by fly ash reduced the long-term expansion due to alkali-silica reaction but, even when 30 or 40 % of the cement was replaced, most of the blended cement mortars cracked at earlier or similar ages as the Portland cement mortars.

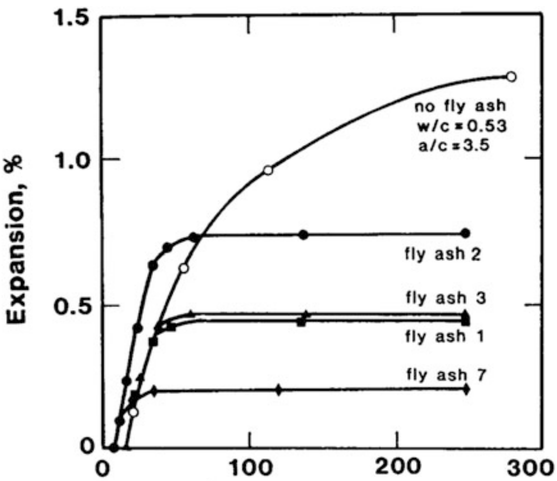


Fig. 2.62 Variation in expansion with age for specimens where part of the aggregate was replaced with fly ash [151]

Table 2.27 Composition and properties of fly ashes examined by Hobbs [151]

Composition (wt%)	Fly ash no.			
	1	2	3	7
SiO_2	50.02	51.48	46.58	49.72
Fe_2O_3	9.02	8.70	14.24	5.22
Al_2O_3	26.83	28.08	25.22	32.45
CaO	1.48	1.27	4.10	2.77
MgO	0.93	0.93	0.95	2.41
SO_3	0.79	1.15	1.29	0.53
LOI	3.43	1.74	1.84	3.24
Na_2O (total)	0.88	1.13	0.80	0.38
Na_2O (water sol.)	0.07	0.10	0.08	0.02
K_2O (total)	3.90	3.85	2.35	1.40
K_2O (water sol.)	0.07	0.11	0.04	0.02

- The effectiveness of the fly ashes in reducing the long-term expansion varied widely. It is suggested that the effectiveness of the (fly ashes) may be dependent upon their alkali content or fineness.
- Where part of the cement was replaced by fly ash, the lowest mortar alkali content, expressed as equivalent Na_2O, at which cracking was observed was 2.85 kg/m^3. This figure relates only to the acid soluble alkalis contributed by the Portland cement and compares with a figure of 3.5 kg/m^3 for a Portland cement mortar.
- If it is assumed that fly ash acts effectively like a cement with an alkali content of 0.2 % by weight, the lowest alkali content at which cracking was observed was 3.4 kg/m^3.

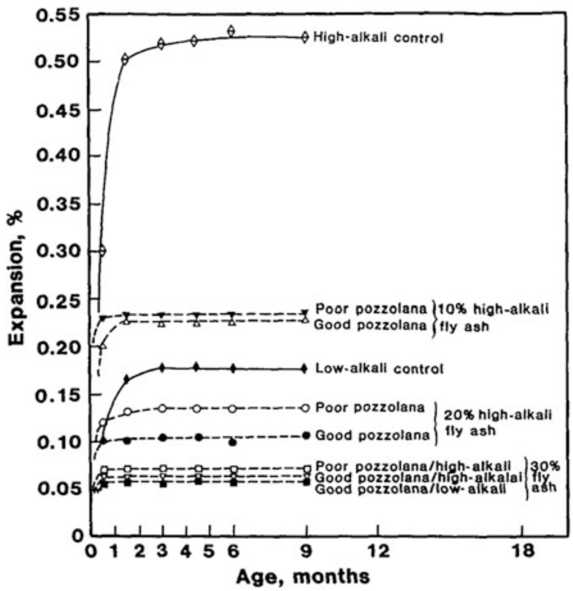


Fig. 2.63 Expansion of mortar bars containing high-alkali cement and fly ash with Pyrex aggregate [149]

- Both fly ashes and granulated blast-furnace slags act as alkali diluters, slags being more effective in reducing damage due to alkali-silica reaction than fly ashes.
- From the above it may be concluded that, when the aggregate to be used contains a reactive constituent, and when the concrete is to be exposed to external moisture, damage due to alkali-silica reaction is unlikely to occur if the acid-soluble equivalent Nap content of the concrete is below 3 kg/m^3. In calculating the alkali content of the concrete, granulated blast· furnace slags may be assumed to contain no available alkalis but fly ash should be assumed to have an available alkali content of 0.2 % by weight.

After conducting experiments using Pyrex glass, Nixon and Gaze [149] presented the data shown in Fig. 2.63 and drew the following conclusions:

- When Pyrex glass is used as the reactive aggregate, the partial replacement of a high alkali Portland cement by fly ash or by granulated blast-furnace slag produces a significant reduction in expansion of mortar bars at all replacement levels tested (10, 20 and 30 percent fly ash). The reductions are greater than could be accounted for by simple dilution of the alkali content of the Portland cement.
- Weight for weight the fly ashes are more effective (than granulated slag) in reducing expansion….
- Only small differences were found between the effectiveness of different fly ashes. These differences could best be correlated with a measure of the pozzolanicity of the ash. The ashes with lower alkali content did, on the whole,

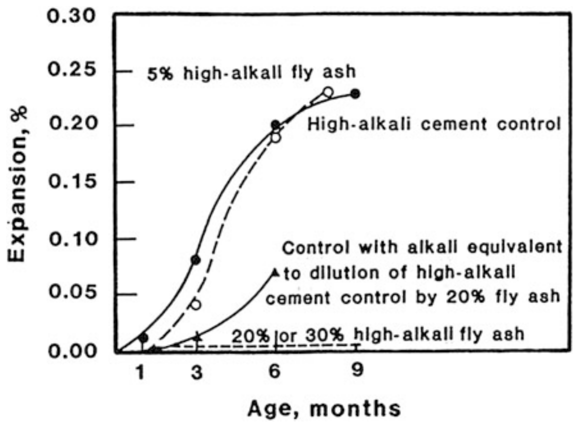


Fig. 2.64 Expansion of concrete prisms containing high-alkali cement and fly ash with 30 % flint or quartz aggregate [152]

seem to perform slightly better than those with high alkali (content) but this effect was secondary to the pozzolanicity. The available alkali content of the ashes gave no better correlation with the observed expansions than did the total alkali content….

Nixon and Gaze [152] also reported on studies using chert aggregate in fly ash concrete and published the data shown in Fig. 2.64.

Oberholster and Westra [150] studied alkali-silica reactivity of the Malmesbury Group aggregates and examined, among many additives, a low-calcium fly ash. Oberholster and Westra reported the fly ash to be more effective in reducing expansion than would be expected from a simple dilution of alkali content.

The study by Oberholster and Westra [150] included an examination of concrete prisms in which the fly ash effectively suppressed expansion at cement replacement levels of ≥20 % on an equal volume basis.

Stanton [140], Porter [153], and Pepper and Mather [143], in early studies of the use of fly ash to reduce expansion caused by alkali-silica reactions, noted that small additions of fly ash to mortars containing an opal aggregate may increase expansion, whereas lager amounts may reduce expansion. The general form of the relationship between ash quantity and expansion observed by these researchers is illustrated in Fig. 2.65.

In another study, Hobbs [154] reported that replacing 5 wt% of Portland cement by four fly ashes, a ground granulated slag, or limestone fines had little effect on the expansion of mortar bars tested at a critical alkali/silica.

Dunstan [148] examined 17 fly ashes of both bituminous and subbituminous origin, with Pyrex™ glass as an aggregate. Dunstan suggested that the expansion–fly ash replacement relationship takes the form shown in Fig. 2.66 and that the amount of fly ash corresponding to the pessimum point (the point of maximum expansion) is related to the CaO content: as CaO increased with fly ash replacement, so the pessimum point increased. This suggests that high-calcium fly ashes would show an increased contribution to expansion at the levels of replacement

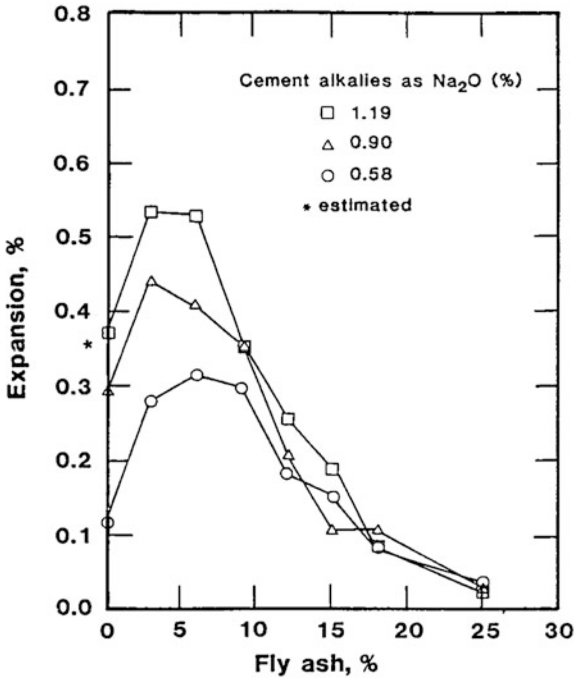


Fig. 2.65 Effect of cement alkali and fly ash on alkali-aggregate reaction [148]

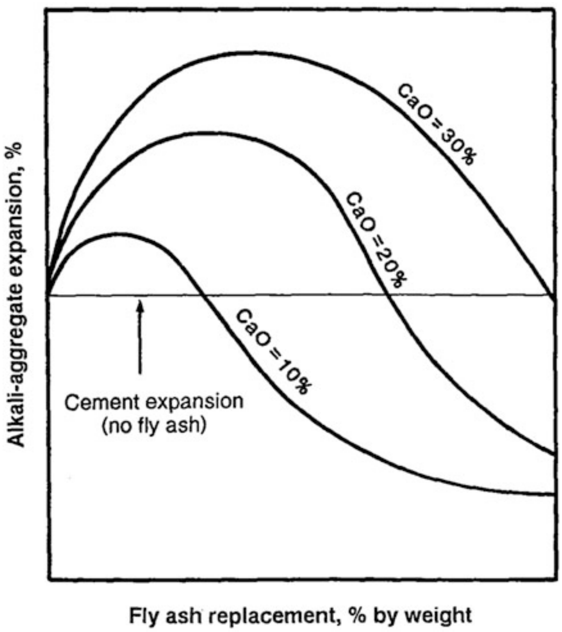


Fig. 2.66 Theoretical expansion due to alkali-aggregate reaction [148]

normally used with low-calcium fly ashes and would only become effective in retarding expansion caused by alkali-silica reactions at higher replacement levels.

Farbiarz and Carrasquillo [155] investigated the effectiveness of using fly ash in concrete to reduce the damage to concrete caused by alkali-aggregate reaction. Their results showed that the addition of fly ash can effectively reduce alkali-aggregate expansions. Nevertheless, for fly ashes with >1.5 % alkali content there was a pessimum limit for the percentage of fly ash below which no beneficial effect was achieved. This limit is inherent to each particular fly ash.

Carrasquilo and Snow [156] reported the alkali-aggregate reaction of mortar mixtures made with ASTM Class C and Class F fly ashes having available alkali contents of 0.57–4.35 %. Based on their test results, the following general conclusions were drawn:

- For mixture proportions with or without fly ash, mortar-bar expansion increases as the alkali content of the cement increases.
- The replacement of a portion of cement with fly ash effectively reduces the expansion in mortar bars caused by alkali-aggregate reaction, regardless of aggregate reactivity and the chemical composition of the cement, provided an adequate replacement with fly ash is used.
- The available alkalis in fly ash do participate in the alkali-aggregate reaction in concrete. In general, it was found that for similar mixture proportions, mortar-bar expansion increases as the alkali content of the fly ash increases.
- The CaO content of fly ash does not seem to have a significant effect on alkali-aggregate reaction in concrete.
- When the available alkali content of fly ash is <1.5 %, its beneficial effect in preventing expansion due to alkali-aggregate reaction increases as the percentage of cement replaced increases, regardless of the class of the fly ash, the alkali content of the cement, the alkali content of the fly ash, and the aggregate reactivity.
- When the available alkali content of fly ash is >1.5 %, there is a minimum percentage of cement replacement below which the fly ash causes expansion greater than that caused by a mixture without fly ash and above which the fly ash causes smaller expansions. This minimum is known as the pessimum limit.
- Minimum percentage of cement replacement rather than a maximum allowable available alkali content of fly ash could provide an adequate guideline for the use of fly ash to prevent damage of concrete due to alkali-aggregate reaction.

Nagataki et al. [157] examined eight different ASTM Class F fly ashes for controlling alkali-aggregate reaction of concretes made with Pyrex™ as an aggregate and with a replacement ratio of fly ash of 0–30 wt% of cement. The expansion of their mortar prisms depended on the type and the replacement ratio of fly ash. The expansion value was independent of equivalent sodium oxide content in fly ash but correlated with the concentration of soluble alkali ions in fly ash. Nagataki et al. suggested that the use of finer silicon dioxide and fly ash containing a higher amount of amorphous silica, together with a higher replacement ratio of fly ash, can control the alkali-aggregate reaction. They proposed a method to

Table 2.28 Mix proportions, properties of fresh concrete, and 28-day strength results [158]

Mix series	Total cementitious content (kg/m^3)	Fly ash (%)	Alkali concrete (eq Na_2O) Total (kg/m^3)	Alkali concrete (eq Na_2O) From cement (kg/m^3)	Reactive sand content[a] (%)	Total w/b[b]	Wet density (kg/m^3)	CF[c]	28-d Strength (MPa)
A	741	–	7.9	7.9	20	0.30	2444	0.69	68.6
B	735	5	8.7	7.5	20	0.30	2411	0.73	71.0
C	737	20	11.3	6.3	20	0.29	2398	0.68	67.7
D	740	30	13.1	5.5	20	0.28	2391	0.67	70.9
E	600	–	6.4	6.4	20	0.36	2421	0.86	65.7
F	599	–	6.4	6.4	30	0.36	2420	0.89	67.7
G	598	20	9.2	5.1	30	0.34	2394	0.91	66.5
H	603	30	10.6	4.5	30	0.34	2398	0.92	65.8

[a] As percentage of total aggregate
[b] Water to binder ratio
[c] Compacting factor

evaluate the expansion of mortar containing fly ash based on amorphous silicon dioxide content, replacement ratios, and mean diameter of fly ash.

Thomas et al. [158] studied the effect of fly ash on alkali–silica reaction in concrete containing natural UK aggregate. Mixture proportions and properties of fresh and hardened concretes are given in Table 2.28. Petrographic examinations showed that concrete containing either no fly ash or 5 % fly ash exhibited considerable expansion and cracking caused by alkali-silica reaction (see Fig. 2.67). However, concretes containing 20–30 % fly ash showed little expansion (<0.03 %) and no cracking after 7 years of exposure.

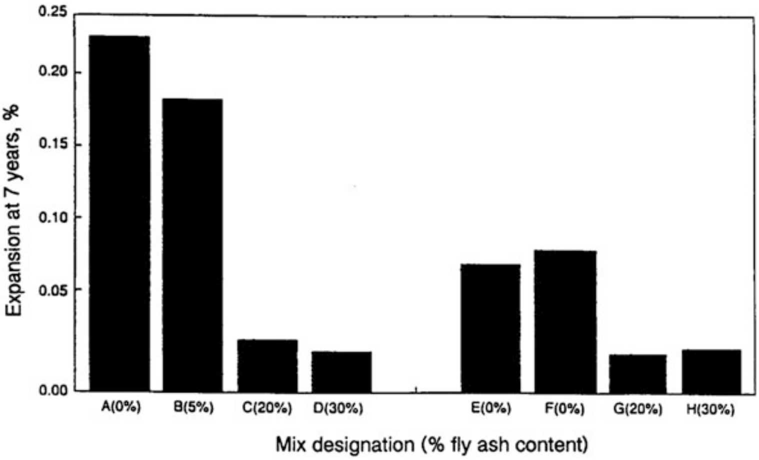


Fig. 2.67 Expansion of concrete prisms (75 mm × 75 mm × 200 mm) after 7 years of external exposure [158]

In summary, the following points may be made:

- There are substantial published data to show that low-calcium fly ashes are effective in reducing expansion caused by alkali-silica reactions when the fly ashes are used at a replacement level in the range of 25–30 %.
- The use of high-calcium ashes has received less attention; hence, the background information relevant to their use is less well developed. If they are to be used, there is some indication that effective replacement levels may be higher than those for low-calcium ashes.
- The mechanism and details of control of expansion caused by alkali-silica reactions are not fully understood, and there remains much research to be carried out before a satisfactory understanding can be developed.

Effects of Fly Ash on the Corrosion of Reinforcing Steel in Concrete

Recently, an issue of concern has been the corrosion of steel reinforcement in fly ash concrete structures exposed to chloride ions from deicing salts or sea water.

If the concrete cover over steel reinforcement is sufficiently thick and impermeable, it will normally provide adequate protection against corrosion. The protective effect of the concrete cover is of both a physical and a chemical nature and functions in three ways:

- It provides an alkaline medium in the immediate vicinity of the steel surface.
- It offers a physical and chemical barrier to the ingress of moisture, oxygen, carbon dioxide, chlorides, and other aggressive agents.
- It provides an electrically resistive medium around the steel members.

Under alkaline conditions (pH higher than ~ 11.5), a protective oxide film will form on a steel surface, rendering it passive to further corrosion.

When concrete carbonates (see Effects of Fly Ash on Carbonation of Concrete in this chapter) and the depth of carbonation reaches the steel–concrete boundary, passivation may be reduced and corrosion may occur if sufficient oxygen and moisture reach the metal surface. Chlorides or other ions may also undermine the protective effect of passivation and encourage corrosion.

The Reunion international des laboratories d'essais et de recherches sur les materiaux et 1es constructions (RILEM) Technical Committee on Corrosion of Steel in Concrete [159] made the following statements, which give perspective to this issue:

- The efficiency of the (concrete) cover in preventing corrosion is dependent on many factors which collectively are referred to as its "quality". In this context, the "quality" implies impermeability and a high reserve of alkalinity which satisfies both the physical needs and chemical requirements of the concrete

cover. If the concrete is permeable to atmospheric gases or lean in cement, corrosion of the reinforcement can be anticipated and good protection should be attempted by the use of dense aggregate and a well compacted mix with a reasonably low water/cement.
- If chloride corrosion is excepted, it is now usually agreed that carbonation of concrete cover is the essential condition for corrosion of reinforcement.

As discussed in Effects of Fly Ash on Carbonation of Concrete in this chapter, the issue of carbonation of fly ash concrete has received some attention in recent years. However, it is our opinion that the carbonation of fly ash concrete is not a matter of concern, provided attention is paid to obtaining adequate impermeability in the concrete mass.

In 1950, the question was raised [160] whether the sulphur-containing components of fly ash could corrode the reinforcing steel in fly ash concrete. Gilliland [161] noted that most of the sulphur in fly ash is present as sulphate and, therefore, would have an effect similar to the sulphate components in Portland cement. Further, he pointed out that corrosion of steel is greatly affected by pH; at the high pH prevailing in concrete, corrosion rates would be expected to be slow. Ryan [162] presented further information on the same point and drew the following conclusions:

- Sulphur compounds in fly ash are usually so limited by specifications that they are not materially different in the concrete, whether fly ash is used or not. Moreover, the alkaline condition in the concrete is unfavourable to a sulphate attack on steel.
- Carbon in fly ash would appear by theoretical considerations to be much more significant in concrete than is sulphur. The actual effect should be investigated. However, if it is kept under 3 percent in the fly ash, its percentage in the concrete becomes so small that if it is well dispersed, its effect on the electrical conductivity of the concrete, and therefore upon the corrosion of the steel, should be quite minor.

These conclusions seem to be generally acceptable in the light of reported research that has shown that fly ash concrete does not decrease the corrosion protection of steel reinforcement, compared with normal concrete [163–165]. Larsen et al. [166, 167] found that the inclusion of fly ash in concrete increased corrosion protection.

In regard to the quality of the concrete cover over steel and to the points raised by the RILEM Technical Committee on Corrosion of Steel in Concrete (see above) [159], fly ash may influence both permeability and the alkalinity of the system.

The permeability of fly ash concrete and the related issue of carbonation were discussed in the first two sections of this chapter. It is sufficient here to recall that properly proportioned fly ash concrete subjected to adequate curing should in general be less permeable at later ages than the corresponding plain concrete. The danger of permeability lies in the premature exposure of fly ash concrete to

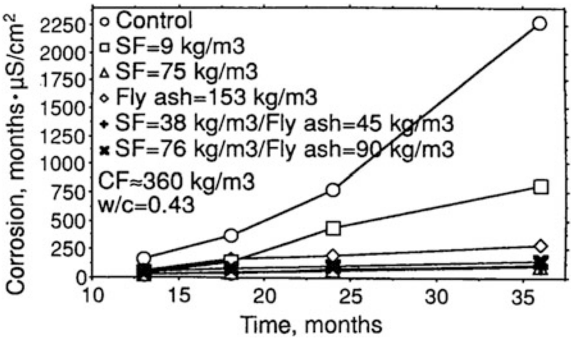


Fig. 2.68 Total corrosion versus time for reinforcing steel in concretes at W/C = 0.43, exposed to 3 % NaCl, as a function of pozzolan additions [169]. *SF*, Silica fume; *CF*, Cement factor

aggressive agents, as a result of either inadequate proportioning, incomplete curing, or poor fly ash quality.

It has been suggested that because the pozzolanic reaction consumes calcium hydroxide as it progresses, this may cause a decrease in the pH of the pore water in fly ash cement paste. The pore solutions in hydrated cement are highly alkaline; as Diamond [168] has shown, this results from the presence of sodium and potassium ions rather than from the presence of calcium hydroxide. In studies of two fly ash cement systems, Diamond [168] showed that the alkalinity is determined almost entirely by the dissolution of sodium and potassium salts from cement; at quite early ages, the concentration of calcium in solution is reduced to very low levels. In the samples studied by Diamond, pore-solution pH was reduced from 13.75 in a control system to ~13.55 in the presence of fly ash.

Berke et al. [169] reported the long-term effects of fly ash and silica fume on chloride ingress, electrical resistivity, microstructure, and corrosion of steel reinforcement in concrete. Figure 2.68 shows the corrosion of steel reinforcement in concrete with 0.43 water/cementitious materials after 3 years of exposure to 3 % NaCl. It can be seen that the steel reinforcement in control concrete and in concrete with 9 kg/m^3 silica fume is corroding after 3 years. Concretes containing fly ash were effective in lowering the corrosion rates. However, at a higher water/cementitious materials (W/C = 0.52), fly ash concretes showed higher corrosion rates than the other concretes.

Effects of Fly Ash on Concrete Exposed to Sea Water

The deterioration of concrete in marine environments is a complex subject and cannot be treated adequately here. This discussion has been limited to an examination of some of the aspects of using fly ash in marine concrete, focusing on the rather limited, directly applicable published data and some extrapolations from many reports on the behavior of plain concrete in the sea.

Exposure of concrete to the marine environment subjects it to an array of severely aggressive factors, including most of those discussed in the preceding sections of this chapter.

Concrete in the tidal zone is the most severely attacked, subjected as it is to alternating wetting and drying; wave action; abrasion by sand and debris; frequent freezing and thawing cycles; and corrosion of reinforcement all occurring in a chemically aggressive medium. Permanently immersed concrete is less severely affected [170, 171].

Very little direct observation of fly ash concrete in sea water has been reported in the literature, although research in this area is in progress [172].

In 1978, CANMET [173, 174] started a long-term project on the performance in a marine environment of concretes incorporating supplementary cementing materials. The test specimens are exposed to repeated cycles of wetting and drying and to ~100 freezing and thawing cycles per year.

Even under exposure to severe marine conditions, concretes incorporating 25 % fly ash from a bituminous source were in satisfactory condition after 10 years. The only exceptions were the specimens with a water/(cement + fly ash) of 0.60. It was concluded that fly ash concrete at 25 % cement replacement level (by mass) can be satisfactory under such conditions of exposure, provided the water/cementitious materials is ≤ 0.50.

Ohga and Nagataki [175] evaluated the effectiveness of fly ash for controlling alkali-aggregate reaction in the marine environment. They measured the expansion of mortars made with high-and low-alkali cements. The alkali content in the mixture was adjusted by adding NaCl or NaOH. The specimens were then exposed to humid air, distilled water, and NaCl solution. Figure 2.69 shows that the

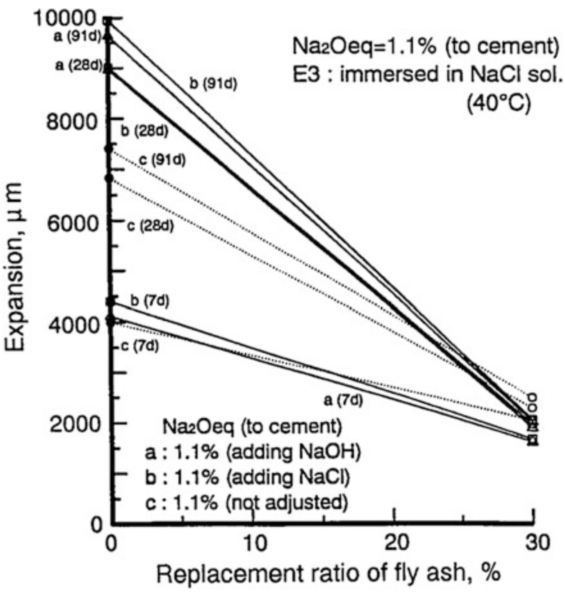


Fig. 2.69 Effect of replacement ratio of fly ash on the expansion of mortar at 40 °C [175]. Concrete in the sea is subjected to the aggressive influences discussed above

Table 2.29 Potential influence of aggressive on fly ash concretes in sea water

Form of attack	Influence of fly ash	Conditions
Wetting–drying	None	If proportioning and curing are adequate
Freezing-thawing	None	If proportioning, air entrainment, and curing are adequate
Sulphate	Improved by low-calcium ash	
Alkali-aggregate reaction	Expansion reduced	
Corrosion of steel	None	If proportioning and curing are adequate
Permeability	Improved at late ages	If proportioning and curing are adequate
Magnesium salts	Not known	

expansion due to alkali-aggregate reaction can be controlled, even in a marine environment, if an adequate amount of a suitable fly ash is used.

Table 2.29 gives a profile of the ways in which fly ash concrete might be affected by exposure to sea water.

Whereas permeability is considered the major factor affecting the durability of concrete in sea water, it is evident that fly ash has the potential to contribute to a number of aspects of concrete durability in the marine environment. It is clear also that this is an aspect of fly ash concrete behavior that is greatly in need of research.

Recent Development on the Durability of Fly Ash Concretes

In recent years most of the researches have been concentrated on the durability of fly ash concretes in severe environments. Corrosion of reinforcement due to chloride penetration and carbonation of concretes containing fly ash has been investigated at longer ages.

The capacity of binding chloride ions in fly ash concrete under marine exposure was investigated [176]. The free and total chloride contents in concrete were determined by water and acid-soluble methods, respectively. In order to study the effects of W/B ratios, exposure time, and fly ash contents on chloride binding capacity of concrete in a marine site, a class F fly ash was used as a partial replacement of Type 1 Portland cement at 0, 15, 25, 35, and 50 % by weight of binder. Water to binder ratios (W/B) were varied at 0.45, 0.55, and 0.65. Concrete cube specimens of 200 mm were cast and placed into the tidal zone of a marine environment in the Gulf of Thailand. Consequently, acid-soluble and water-soluble chlorides in the concrete were measured after the concrete was exposed to the tidal zone for 3, 4, 5, and 7 years. It was found that the percentage of chloride binding capacity compared to total chloride content increased with the increase of fly ash in the concrete. The percentage of chloride binding capacity significantly decreased within 3–4 years after the concrete was exposed to the marine environment, and then its value was almost constant. The research also showed that the W/B ratio does not noticeably affect the chloride binding capacity of concrete.

In another study concrete specimens were produced by using fly ash at 0, 15, 30 and 45 % ratios replaced by CEM I 42.5 R cement. The specimens were moist cured for 28 and 56 days and then remained in two different conditions which are air and water. Physical, mechanical, and durability properties of the produced concrete were determined. Chloride ion permeability test was carried out on concrete specimens. Reinforced concrete specimens were evaluated under accelerated corrosion technique. It was seen that corrosion currents decreased and deterioration occurrence time took longer due to the moist curing at series which were cured for 28 and 56 days. The lowest initial corrosion current values and the longest deterioration occurrence times were obtained concretes containing 30 and 45 % fly ash replacement and cured in water. Results showed that specimens having no fly ash additive had high chloride permeability. It was found that all of the series had low chloride permeability due to use of 15 % fly ash replacement. The use of 30 and 45 % fly ash showed great reductions in chloride permeability of specimens cured for 28 and 56 days in water. Based on their results, it was concluded that 15 % replacement of fly ash with cement was an optimum value for durability enhancement against corrosion. Durability of reinforced concretes containing fly ash significantly increased when 56 day moist curing was applied [177].

Recently a research was focused on investigating the durability of concretes containing fly ash and silica fume exposed to combined mode of deterioration. For this purpose, the chloride ion diffusivity of concrete was evaluated before and after 300 freeze–thaw cycles [178].

It was found that the coefficient of chloride ion diffusivity increased as water to cementitious material ratio and air content increased. When a proper curing was provided, all concrete showed good durability factor regardless of amount of air content.

Test results clearly showed that the coefficient of chloride ion diffusivity for all concretes increased after freeze–thaw cycles. However, fly ash concrete showed good resistance to chloride ion diffusivity before and after freeze–thaw cycles when low w/cm as well as a proper curing and air content were provided. This was attributed to the adsorption of chloride ion to C–S–H layers and the improved microstructure by the pozzolanic reaction. Higher coefficient of chloride ion diffusivity were observed for fly ash concrete than plain concrete when w/cm was 0.6 and air content was 2 %.

In order to study the effect of fly ash on alkali silica mitigation of concrete, 45 concrete blocks (915 mm × 915 mm × 815 mm or 350 mm cubes) containing alkali-silica reactive aggregates, and various levels of high-alkali cement and fly ash were placed on an outdoor exposure site in S.E. England for a period of up to 18 years. The reactive aggregates used included a variety of flint sands and a crushed greywacke combined coarse and fine aggregate. Length-change measurements were conducted periodically throughout this period. All concrete blocks without fly ash showed excessive expansion and cracking within 5–10 years of production and in many cases the ultimate expansion exceeded 1.0 % after 15–18 years. Fly ash used at replacement levels of 25 and 40 % was effective in significantly reducing expansion and cracking with all three flint aggregates at all levels of alkali. Of the 27 blocks containing fly ash and flint sand only two blocks showed evidence of damage after 16–18 years. The expansion of these blocks was significantly lower than similar blocks with the same Portland cement content without fly ash. None of the blocks with greywacke aggregate and fly ash exhibited cracking (expansion data were not available for these blocks). Collectively the data confirm that fly ash, when used at levels of 25–40 %, does not effectively contribute alkalis to the alkali-silica reaction [179].

Durability of special concretes such as high strength and high performance concretes, self consolidating concretes containing fly ash have been investigated by a number of researchers. In a recent study, durability properties of high strength concrete utilizing high volume Class F fly ash sourced from Western Australia have been investigated [180]. Concrete mixtures with fly ash as 30 and 40 % of total binder were used to cast the test specimens. The compressive strength, drying shrinkage, sorptivity and rapid chloride permeability of the fly ash and control concrete specimens were determined. The 28-day compressive strength of the concrete mixtures varied from 65 to 85 MPa. The fly ash concrete samples showed less drying shrinkage than the control concrete samples when designed for the same 28-day compressive strength of the control concrete. Inclusion of fly ash reduced sorptivity and chloride ion permeation significantly at 28 days and reduced further at 6 months. In general, incorporation of fly ash as partial replacement of cement improved the durability properties of concrete.

In an experimental program properties of self consolidating concrete (SCC) made with Class F fly ash were investigated. The mixtures were prepared with five percentages of class F fly ash ranging from 15 to 35 %. Properties investigated were self consolidating parameters such as slump flow, J-ring, V-funnel, L-box and U-box, strength properties such as compressive and splitting tensile strengths, and durability properties (deicing salt surface scaling, carbonation and rapid chloride penetration resistance). SCC mixes developed 28 day compressive strength between 30 and 35 MPa and splitting tensile strength between 1.5 and 2.4 MPa. The carbonation depth increased with the increase in age for all the SCC mixes. Maximum carbonation depth was observed to be 1.67 mm at 90 days and 1.85 mm at 365 days for SCC with 20 % fly ash content. Also, the pH value for all the mixes was observed to be greater than 11. Deicing salt surface scaling weight loss increased with the increase in fly ash content except for the mixture containing 15 % fly ash. At 365 days age, the weight loss was almost consistent for all percentages of fly ash. SCC mixes made with fly ash exhibited very low chloride permeability resistance less than 700 and 400 Coulombs at the age of 90 and 365 days, respectively [181].

Application of Fly Ash in Concrete

For most civil engineering applications, the decision to use fly ash in concretes will depend on the availability of materials, local concrete practice, and, most importantly, economics. However, some types of special concretes require fly ash or other mineral by-products to attain specific properties. In particular, high-strength concretes (>60 MPa at 28 days) and roller-compacted mass concretes both depend on the use of fly ash for their structural and economic success.

High-Strength Concrete

High-strength concretes can be classified broadly into three groups:

- concretes with a compressive strength of 50–70 MPa, used over the
- past 10 years in a number of construction applications;
- concretes with a compressive strength of 70–100 MPa; and
- concretes with a compressive strength of >100 MPa.

Although field-placeable concrete in the strength range of 70–120 MPa is now commercially available, the major documented uses of high-strength concrete in Building applications have been for 85 MPa concretes in the major cities of Canada and the United States. Thus, for the present time, use of fly ash in high-strength concrete must be restricted to the lower end of the above strength range.

The most important reasons for using high-strength concrete are the following:

- to minimize the size of concrete structural members in buildings;
- to obtain more rapid production cycles in the precast and prestressed
- concrete industry; and
- to obtain high strength and high modulus of elasticity in structural members built to withstand large stresses.

In general, the production of high-strength concrete requires the use of mixtures with low water/cement but with sufficient workability to permit placement in a heavily reinforced structure. To meet these requirements, the following factors are usually considered important [182–184];

- use of high cementitious contents (550 kg/m^3) at slumps of 75–100 mm;
- stringent selection of cement and aggregates;
- use of low water/cement, attained through water-reducing agents and
- superplasticizers and
- use of pozzolans, such as fly ash and silica fume, and blast-furnace slag.

Fly ash in high-strength concrete provides at least two benefits:

- a good-quality fly ash generally permits a reduction in the water
- content of a concrete mixture, without loss of workability

Table 2.30 Mixture proportions and properties of fresh high-strength concretes [182]

	Quantity/m^3	
	Water tower place	River plaza
Materials		
Cement (kg)	383.7	385.6
Fine aggregate (kg)	464.9	471.7
Stone (kg)	1403.5	1300.7
Water (kg)	136.1	149.7
Water-reducing admixture (ml)	751.1	1271.5
Fly ash (kg)	45.4	45.4
Properties		
Slump (mm)	115	115
Air content (%)	–	1.5
Unit weight	2433	2383

Table 2.31 Compressive strengths of high-strength concrete [182]

Age (days)	Compressive strength (MPa)					
	Water tower place			River plaza		
	Air[a]	Moist	Cores	Yard	Job site	Cores
7	–	52.7	–	–	50.4	46.5
28	6301	64.8	–	71.3	64.9	55.8
56	–	72.9	–	77.5	72.4	73.7
90	64.9	–	–	80.2	78.7	72.1
180	63.5	–	–	91.1	–	–
368	66.9	–	–	–	–	–
730	61.8	–	79.7	–	–	–

[a] 7 days moist curing followed by curing at 50 % RH, 21 °C

- fly ash produces increased strength at later ages of curing, which cannot be achieved through the use of additional Portland cement.

Typical mixture proportions for high-strength concrete used in two structures built in the Chicago area during the 1970s are given in Table 2.30, and the compressive-strength values obtained with these mixtures are given in Table 2.31. Concrete mixtures with strengths of 55 MPa and incorporating fly ash and using similar proportions have been used in construction in the Toronto area [88].

Cook [185] reported on a comprehensive investigation of concretes in the strength range of 50–75 MPa (28 days) made using a high-calcium fly ash ($CaO = 30.3$ wt%). Tables 2.32 and 2.33 illustrate how fly ash can contribute to the strength development of high-strength concretes and the flexibility in the selection of mixture proportions that can be used to obtain essentially similar concretes. Table 2.32 presents the concrete properties attained by using different

Table 2.32 Mixture proportion and properties of fresh and hardened high-strength concrete at a constant ash/cement ratio [185]

Nominal cement content (kg/m^3):	279	335	390	446	502
Material					
Cement (kg/m^3)	282	341	396	449	501
Fly ash (kg/m^3)	71	85	99	112	131
Limestone (kg/m^3)	1144	1147	1141	1130	1121
Sand (kg/m^3)	735	643	578	513	454
Water (kg/m^3)	148	157	161	169	179
W/R admixture (mL/m^3)	696	851	967	1083	1238
Properties of fresh concrete					
Slump (mm)	102	102	114	102	95
Unit weight	2379	2373	2376	2373	2374
W/(C + F)	0.42	0.37	0.33	0.30	0.28
F/C	0.25	0.25	0.25	0.25	0.26
Compressive strength (MPa)					
7 days	44.3	48.1	53.1	55.1	59.3
28 days	54.6	62.7	67.4	72.7	70.2
56 days	61.0	68.0	75.7	75.9	78.0
90 days	63.3	68.9	75.0	75.7	75.0
180 days	67.8	76.9	83.6	86.6	85.3

Table 2.33 Mixture proportions and properties of fresh and hardened high-strength concretes at various ash/cement ratios [185]

	Mixture no.			
	1	2	3	4
Materials				
Cement	320	281	279	245
Fly ash	80	120	71	105
Limestone	1127	1127	1127	1127
Sand	698	702	769	720
Water	151	142	148	145
Admixture[a]	–	–	–	–
Mix properties				
Slump (mm)	102	95	83	108
W/(C + F)	0.38	0.36	0.42	0.41
F/(C + F)	0.20	0.30	0.20	0.30
Compressive strength (MPa)				
7 days	44.9	44.0	42.0	40.5
28 days	56.6	55.8	52.7	52.3
56 days	58.6	61.9	56.8	58.8
180 days	68.9	74.4	70.5	71.6

[a] Quantities not reported

quantities of cementitious materials at a constant ash/cement ratio (0.25). As the cement factor was increased, sand content and the water/cementitious materials were reduced. Strength at 28 days was controlled over a range of 55–70 MPa. The data in Table 2.33 show the effect on strength of increasing fly ash content from 20 to 30 % for two basic concrete mixtures.

Naik et al. [186] examined three concrete mixtures incorporating fly ash to achieve nominal strengths of 70 MPa. In one of the mixtures, they used ASTM Class C fly ash as a partial replacement for cement. Water-reducing, retarding admixture and a superplasticizer were also added to the concrete to lower the water/cementitious materials and to achieve a slump of 150 mm. Details of the mixture proportions and the result of the compressive-strength results at various ages are given in Table 2.34.

Naik et al. [186] also showed that high-strength concretes containing mineral admixtures had a dense matrix and, hence, a high resistance to chloride-ion penetration, especially at later ages.

The use of three classes of "classified fly ash" (classified by air-separation method as having maximum particle diameters of 20 pm) as concrete admixtures was investigated by Ukita et al. [187]. The compressive strength of concrete mixtures with 30 % replacement of cement with fly ash reached 92 MPa for a water/cementitious materials of 0.27 %. In their research, Ukita et al. showed that the use of classified fly ash reduced water requirement, improved workability, enhanced strength and water tightness, and increased resistance to alkali–silica reaction in the concrete [188].

Table 2.34 Concrete mixture proportions and strength data for high-strength concrete [186]

Nominal strength (MPa)	70
Cement (ASTM type I) (kg/m^3)	355
Fly ash (ASTM Class C) (kg/m^3)	207
Water (kg/m^3)	180
Water/cementitious materials	0.3
Sand (saturated surface dry) (kg/m^3)	712
Coarse aggregate (12.5 mm max. crushed limestone) (kg/m^3)	978
Slump (mm)	150
Entrapped-air content (%)	0.3
Retarding admixture (ASTM type A) (kg/m^3)	1
Superplasticizer (ASTM type F) (kg/m^3)	7.3
Compressive strength on 100 mm × 200 mm cylinders (MPa)	
7 days	58.0
28 days	69.6
91 days	83.8
365 days	93.9

Roller-Compacted Concrete

In the 1970s, a method for the construction of dams, termed roller compaction, was proposed [189–192]. The method, which in many ways is more related to the procedures used in geotechnical engineering than to conventional concrete practice, depends on the placement of layers of a low-workability concrete in the interior of a dam and its compaction using vibrator rollers.

The ACI [193] described roller-compacted concrete (RCC) as a dry concrete material that is consolidated by external vibration by vibratory rollers. It differs from conventional concrete in its required consistency: for effective consolidation, RCC must be dry enough to support the weight of the placement equipment but fluid enough to permit distribution of the paste throughout the mass during mixing and compaction.

Roller-compacted concrete must satisfy four requirements:

- It must have a high density, with a minimum of air voids.
- The layers of concrete must bond together [186].
- The generation of heat in the dam must be minimized.
- To resist thermal cracking, the hardened concrete must have a high capacity to withstand tensile strains.

Three types of materials have been investigated and used for RCC:

- cement-stabilized, soil-like materials;
- lean concrete, with a cementitious-materials content of 100–150 kg/m^3, of which 30 % may be fly ash; and
- rich concrete, with a cementitious-materials content of 180–270 kg/m^3, of which 60–80 % may be fly ash.

RCC can be made from any of the basic types of Portland cement in combination with pozzolans. In regard to proportioning, the principal difference between the selection of the relative quantities of the cementitious components in RCC, compared with more conventional concretes, is the use of large quantities of fly ash. The principal function of fly ash in RCC is to provide a large volume of fine material to occupy the space between larger particles, which could otherwise be accomplished only with the use of additional cement.

RCC normally needs to have a high paste content. Dunsan [194] showed that as paste/mortar falls below 0.35–0.38, the density of the compacted mass is significantly reduced. Below this level of paste content, some of the voids in the fine aggregate are not being filled. To obtain maximum density, the paste content must be increased; however, to attain this by the addition of Portland cement results in two serious disadvantages:

- The rate of heat evolution increases, and the possibility of thermal cracking becomes greater.
- The cost of the concrete may not be economical.

Table 2.35 Mixture proportions for some roller-compacted concretes [97]

Source	Max. aggregate size (cm)	Mix data (kg/m^3)				
		Cement	Pozzolan	Water	Fine aggregate	Coarse aggregate
1	7.6	56	77	77	660	1649
2	11.4	139	0	80	618	1774
3	7.6	139	0	86	683	1691
4	7.6	139	0	83	676	1602
5	7.6	42	78	83	676	1602
6	3.8	75	164	89	745	1426
7	3.8	45	178	84	727	1438
8	3.8	116	139	103	657	1438

Table 2.36 Properties of some roller-compacted concretes [97]

Source	Age (days)	Compressive strength (MPa)	Shear strength (MPa)	
			Mass	Joint
1	138	23	4	2
2	72	26	5	1
3	66	23	6	–
4	120	23	6	3
5	120	16	4	1
6	90	26	–	3
7	90	18	2	2
8	90	41	–	–

To obtain maximum density in RCC, the desired approach is to use large volumes of fly ash to increase the paste content.

Pozzolanic activity is somewhat secondary: strength in RCC can develop over long periods after placement. ACI Committee 207 reported the following [193]:

Where there is a deficiency in fines [in RCC] a pozzolan does not have to be highly reactive to be effective. Thus, many fly ashes whose reactivity, due to insufficient particle fineness, would not meet….ASTM specifications would be suitable for most roller compaction applications.

Typical RCC mixture proportions and the corresponding strength data, as reported by ACI Committee 207, are shown in Tables 2.35 and 2.36.

As in more conventional mass concrete, fly ash helps reduce the rate of heat evolution in RCC and, hence, extent of temperature rise.

Permeability of RCC used in the Upper Stillwater Dam was reported to be equal to, or less than, that of conventional mass concrete [193]. Both AEA and water-reducing admixtures have been used at normal dosages in RCC. ACI Committee 207 [187] stated that these admixtures are effective in reducing the vibration time for fill consolidation. However, the effectiveness of AEA in RCC and the appropriate dosage rates are as yet not fully established.

The use of RCC is not restricted to mass structures such as dams. It has been employed to replace riprap for erosion control of floodway sill in Alaska, as a foundation rock protection, in a lock floor, and in other structures [196].

As Joshi [197] pointed out, RCC are closely related to the family of stabilize materials commonly used for pavements and other applications. The use of RCC and lean concrete containing large amounts of fly ash has been extensively studied for pavement construction in the United Kingdom. Sherwood and Potter [198] reported studies of ash-modified lean concrete for use in road bases. They suggested that ash-modified lean concrete performs as well as conventional lean concrete, provided the development of thermal and shrinkage cracks was similar, and that it could withstand repeated traffic-induced stress at early ages.

Dunstan [194] reported on field applications of lean concretes containing high amounts of fly ash and drew the following conclusions:

- A considerable material cost saving (>20 %) was achieved.
- Good-quality control over the batching process is required to maintain consistency of material.
- It is difficult to obtain satisfactory levels of air entrainment in concrete incorporating large quantities of fly ash.
- Very little early age cracking was seen in the base materials.
- A fly ash that did not conform to British Standard specifications was found to be adequate, with no deleterious effects.

The Electric Power Research Institute (EPRI) of the United States began a program in 1984 involving six new demonstration projects. The demonstration projects were structured to show the environmental and technological acceptability of ash use in road construction in a controlled and monitored segment of a highway. The project of most interest to the concrete-design community was the one completed in North Dakota, in which a Class C fly ash was used to replace 70 % of the cement in a concrete pavement.

Naik et al. [199] reported the results of research performed in developing and using high volumes of ASTM Class C and Class F fly ash concrete mixtures for pavement construction. They concluded that the high-volume fly ash concrete incorporating ASTM Class F or Class C fly ash can be used to produce high-quality pavements with excellent performance.

With regard to air entrainment, Oliverson and Richardson [195] noted that research on the freezing and thawing durability of RCC is needed. Certainly, given the well-known difficulties associated with air entrainment of some fly ash concretes, considerable research in this area is required if RCC is to find use under the climatic conditions to which most pavement concrete is exposed in Canada.

Torii and Kawamura [200] studied the engineering properties and durability of dry, lean-rolled concrete containing fly ash, and they concluded as follows:

- The use of fly ash with cement in dry, lean-rolled concretes contributed to the improvement of the compaction of the concrete mixtures.

- Dry, lean-rolled concretes with fly ash showed relatively high strength development at later ages, compared with those without fly ash, when they were cured in water. Therefore, the curing conditions significantly influenced the strength development of dry, lean-rolled concretes made using fly ash.
- Low drying shrinkage of dry, lean-rolled concretes with fly ash was advantageous in the prevention of cracks in pavements.
- Resistance of dry, 1ean-rolled concretes with fly ash to freezing—thawing cycles was less than, or equal to, that of dry, lean concretes without fly ash.

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