Chapter 2
Fly Ash

Kosmas Sideris, Harald Justnes, Marios Soutsos and Tongbo Sui

Abstract Fly ash is an industrial by-product deriving from electricity generating plants. It is the by-product of burning coal or lignite. Fly ash is one of the first artificial admixtures used for the production of concrete since the first decades of the 20th century. Its chemical and mineralogical composition mainly depends on the relevant properties of the raw material used as well as on the type of furnace and the way it is collected. Fly ash may have beneficial effects on both the fresh and hardened properties of concrete mixtures. This chapter provides an extensive report on the use of fly ash in concrete. Reference is made to the regulatory framework governing the application of fly ash, mainly in Europe and America, to factors affecting the quality of the product and to the effects of different fly ashes on fresh and hardened characteristics of concrete.

Keywords Fly ash · Pozzolans · Supplementary cementitious materials Sustainability · Transport properties

K. Sideris (✉)
Laboratory of Building Materials, Department of Civil Engineering,
Democritus University of Thrace, University Campus, Xanthi GR 67100, Greece
e-mail: kksider@civil.duth.gr

H. Justnes
SINTEF Building and Infrastructure, Richard Birkelandsvei 3, 7465 Trondheim, Norway
e-mail: Harald.Justnes@sintef.no

M. Soutsos
School of Natural and Built Environment, Queen's University, Stranmillis Road,
Belfast BT9 5AG, UK
e-mail: m.soutsos@qub.ac.uk

T. Sui
Sinoma Research Institute, Sinoma Int'l, CNBM, 16 Wangjing North Road,
100102 Chaoyang District, Beijing, China
e-mail: suitongbo@sinoma.com.cn

N. De Belie et al. (eds.), *Properties of Fresh and Hardened Concrete Containing Supplementary Cementitious Materials*, RILEM State-of-the-Art Reports 25,
https://doi.org/10.1007/978-3-319-70606-1_2

2.1 Overview, Production of Fly Ash, Pre- and Post-blending, Uses in Concrete

Fly ash, also known as pulverized fuel ash, is produced from burning pulverized coal in electricity generating plants. During combustion, mineral impurities in the coal (clay, feldspar, quartz, and shale) fuse in suspension and float out of the combustion chamber along with exhaust gases. As the fused material rises with the gas flow, it cools and solidifies into spherical glassy particles called fly ash. It is a fine grained, powdery particulate material that is collected from the exhaust gases by electrostatic precipitators or bag filters.

Depending upon the collection system, varying from mechanical to electrical precipitators or bag houses and fabric filters, more than 90% of the ash from the flue gases is retrieved in the form of fly ash. Fly ash accounts for 75–85% of the total coal ash, and the remainder is collected as bottom ash or boiler slag (Fly Ash and Coal Conversion By-Products 1988).

Fly ash produced from thermal power plants is a variable material because of several factors. These factors include (Siddique and Khan 2011):

(i) type and mineralogical composition of the coal;
(ii) degree of coal pulverization;
(iii) type of furnace and oxidation conditions; and
(iv) the manner in which fly ash is collected, handled and stored before use.

Since no two utilities or plants may have all these factors in common, fly ash from various power plants is likely to be different. Fly ash properties may also vary within the same plant because of load conditions over a 24-hour period. Fly ash particle size primarily depends upon the type of dust collection equipment. It is generally finer than Portland cement. Diameter of fly ash particles usually ranges between 1–150 μm. The chemical composition of fly ash is determined by the types and relative amounts of incombustible material in the coal used. Depending upon the source and makeup of the coal being burned, the components of fly ash vary considerably, but all fly ash includes substantial amounts of silicon dioxide (SiO_2) (both amorphous and crystalline), aluminium oxide (Al_2O_3) calcium oxide (CaO) and ferric oxide (Fe_2O_3), both being endemic components in many coal bearing rock strata. Use of fly ash in concrete was first reported by Davis et al. (1937).

2.2 List of Relevant Standards

ASTM C618 (2015) categorizes fly ashes into the two categories as shown in Table 2.1. Class F fly ashes are usually of lower CaO content. They are normally produced from burning anthracite or bituminous coal. This class of fly ash exhibits

Table 2.1 Requirements for fly ash for use as a mineral admixture in Portland cement concrete (Data taken from ASTM C618-2015)

Requirements	Fly ash classification	
	F	C
Chemical requirements SiO_2+AlO_3+Fe_2O_3, min (%)	70.0	50.0
SO_3, max (%)	5.0	5.0
Moisture content, max (%)	3.0	3.0
Loss of ignition, max (%)	6.0	6.0
Physical requirements. Amount retained when wet sieved on 45-µm sieve, max (%)	34	34
Pozzolanic activity index, with Portland cement at 28 days, min (%) of control	75	75
Pozzolanity activity index with lime at 7 days, min (MPa)	5.5	–
Water requirements, max (%) of control	105	105
Autoclave expansion or contraction, max (%)	0.8	0.8
Specific gravity, max variation from average	5	5
Percentage retained on 45 µm sieve, max variation, percentage points from average	5	5

pozzolanic property but rarely, if any, self-hardening property. They are predominantly (70%) non-crystalline silica, which is the determining factor for pozzolanic activity. Their crystalline minerals are generally composed of quartz, mullite, and spinels magnetite (Gomes et al. 1999). Class C fly ashes are generally produced from lignite or sub-bituminous coal. This class of fly ash has both pozzolanic and varying degree of self-cementitious properties. Most Class C fly ashes contain more than 15% CaO, but some Class C fly ashes may contain as little as 10% CaO. Class C fly ashes contain predominantly calcium alumino-silıca glass which is highly reactive. Crystalline phases in Class C ash include: quartz, lime, mullite, gehlenite, anhydrite, and cement materials such as C_3A, C_2S and C_4A_3S.

In Europe, the use of high-calcium fly ashes HCFA(s) blended directly into concrete is not defined by a specific regulative frame as in the case of siliceous fly ashes where there is the standard EN 450-1:2005, but there are definitions in European standards for cement (www.ecoba.com 2007, EUROGYPSUM-ECOBA-VGB 2005). Therefore, the only way of utilizing HCFA as an acceptable mineral admixture is to follow limits according to standard EN 197-1 (2013), where HCFA(s) are symbolized by (W)—calcareous fly ashes. Logically, the main limits in the quality of HCFA(s) are related to the quality of produced cement with a specified replacement level of clinker with HCFA.

In Greece, after long term working period of a relevant Scientific Committee, the Hellenic Specification for the Use of HCFA in Unreinforced Concrete or Cement

Products was approved by the State and put in force in October 2007 (Hellenic technical specifications 2007). Two categories of HCFA are specified in this standard: the EIT1 with R45 $\leq$ 45% and SO_3 $\leq$ 7% and EIT2 with R45 $\leq$ 30% and SO_3 $\leq$ 5% and CaO free $\leq$ 3%. EIT refers to unprocessed while EIT refers to processed high calcium fly ash. In Poland, national certifications for the use of HCFA in concrete and road construction have also been issued. In addition, different processing methods of HCFA have been used for improving their quality, such as: sieving for reducing grain size and unburnt carbon content, slaking for reducing hot lime undesirable effect, milling and slaking for increasing fineness, reduction of free lime content and homogenization of HCFA (Papayianni 2010a, b).

2.3 Environmental Sustainability

While the production of energy from coal does produce about 25% of the CO_2 released by the humans globally (World coal Institute 2003), the impact of this can be reduced if beneficial use is made of its by-product, fly ash. Hence, increasing the use of fly ash in construction works can yield significant technical, environmental and economic benefits and such use would contribute considerably to sustainable development. Fly ash has been widely used for numerous applications and no environmental problem resulting from its use has ever been reported (Camoes et al. 2003).

For conventional structural applications, fly ash as a cement constituent in concrete is well accepted. This is due to several factors, including: better consistency during the fresh stage, and superior durability with respect to chloride resistance; coupled with lower material cost. Fly ash concrete also decreases environmental impact by reducing the amount of cement used, thus consuming less energy and releasing fewer greenhouse-gas emissions than conventional Portland cement concrete (Manmohan and Mehta 1981). Utilization of fly ash in cement and concrete has significant environmental benefits such as (Siddique and Khan 2011):

- Increasing the service life of concrete roads and structures by improving concrete durability,
- Reduction in energy use and greenhouse gas and other adverse air emissions when fly ash is used to replace or displace manufactured cement,
- Reduction in amount of coal combustion products that must be disposed in landfills, and
- Conservation of other natural resources and materials.

Making blended cements with fly ash also makes the cement plant utilize their limestone source longer and postpone building new cement plants.

2.4 Fresh Properties of Fly Ash

2.4.1 Size, Shape and Colour

Fly ash particle size is finer than ordinary Portland cement. Fly ash consists of silt sized particles, which are generally spherical in nature and their size typically ranges between 1 and 100 μm. These small glass spheres improve the fluidity and workability of fresh concrete. Fineness is one of the important properties contributing to the pozzolanic reactivity of fly ash. Fly ash colour depends upon its chemical and mineral constituents. It can be tan to dark gray. Tan and light colours are generally associated with higher lime content, and brownish colour with the iron content. A dark gray to black colour is attributed to elevated unburned carbon (LOI) content. Fly ash colour is usually very consistent for each power plant and coal source (Siddique and Khan 2011).

2.4.2 Fineness

Fineness of fly ash is most closely related to the operating condition of the coal crushers and the grindability of the coal itself. Fineness of fly ash is related to its pozzolanic activity. For fly ash use in concrete applications, fineness is defined as the percent by weight of the material retained on the 45 μm (#325) sieve. ASTM C618 (2015) limits the maximum amount of fly ash retained on the 45 μm (#325) mesh sieve on wet sieving as 34%. Generally, a large fraction of ash particles is smaller than 3 μm in size. In bituminous ashes, the particle sizes range from less than 1 to over 100 μm. A coarser gradation can result in a less reactive ash and could contain higher carbon content.

2.4.3 Specific Gravity

The specific gravity is related to shape, color and chemical composition of fly ash particles. In general, specific gravity of fly ash may vary from 1.3 to 2.8. Canadian fly ashes have specific gravity ranging between 1.94 and 2.94, whereas American ashes have specific gravity ranging between 2.14 and 2.69 (Siddique and Khan 2011).

2.4.4 Pozzolanic Activity

The property of low calcium fly ashes possessing little or no cementing value by themselves, to react with calcium hydroxide (usually from cement hydration) in the presence of water and produce highly cementitious water insoluble products, is called pozzolanic reactivity. The meta-stable silicates present in self-cementitious high calcium fly ash react with calcium ions in the presence of moisture to form water insoluble calcium-alumino-silicate hydrates.

The pozzolanic activity of a fly ash depends on its: (1) fineness; (2) calcium content; (3) structure; (4) specific surface; (5) particle size distribution; and (6) LOI content (Joshi 1979). Several investigators have reported that when fly ash is pulverized to increase fineness, its pozzolanic activity increases significantly. However, the effect of increase in specific surface area beyond 600 m^2/kg is reported to be insignificant (Joshi 1979).

2.4.5 Particle Morphology

Fly ash particles consist of clear glassy spheres and a spongy aggregate. Several morphological investigations have been carried out on particle shape and surface characteristics of various types of fly ashes using scanning electron microscope (SEM) and energy dispersive x-ray analysis (EDXA) (Diamond 1985; Mehta 1988). Scanning electron micrographs of different fly ashes show the typical spherical shape of fly ash particles, some of which are hollow. The hollow spherical particles are known as cenospheres or floaters as they are very light and tend to float on water surface. Cenospheres are unique free flowing powders composed of hard shelled, hollow, minute spheres. Cenospheres are made up of silica, iron and alumina. Cenospheres have a size range from 1 to 500 μm. Colours range from white to dark gray.

Sometimes fly ashes may also contain many small spherical particles within a large glassy sphere, called pherospheres. The exterior surfaces of the solid and hollow spherical particles of low-calcium oxide fly ashes are generally smooth and better defined than those of high-calcium oxide fly ashes which may have surface coatings of material rich in calcium (Mehta 1988).

2.4.6 Moisture

Any amount of moisture in Class C fly ash may cause hardening from hydration of its cementitious compounds. Even surface spraying may cause caking. To prevent caking and packing of the fly ash during shipping and storage and to control uniformity of fly ash shipments, a 3.0% limit on moisture content is specified in ASTM C618 (2015). Therefore, it is important that such ashes are kept dry before being mixed with cement.

2.4.7 Chemical Composition

Chemical composition of fly ashes include silica (SiO_2), alumina (Al_2O_3), and oxides of calcium (CaO), iron (Fe_2O_3), magnesium (MgO), titanium (TiO_2), sulphur (SO_3), sodium (Na_2O), and potassium (K_2O), and Loss of ignition (LOI). Amongst these, SiO_2 and Al_2O_3 together make up about 45–80% of the total ash. The sub-bituminous and lignite coal ashes have relatively higher proportion of CaO and MgO and lesser proportions of SiO_2, Al_2O_3 and Fe_2O_3 as compared to the bituminous coal ashes. Table 2.2 presents the chemical analysis of different American fly ashes (ACI 226 1987).

2.4.8 Mineralogical Characteristics (References)

Mineralogical characterization determines the crystalline phases that contain the major constituents of fly ash. Fly ashes usually have 15–45% crystalline matter. The high-calcium ashes contain larger amounts of crystalline matter ranging between 25 and 45% (McCarthy et al. 1988).

Although high-calcium Class C ashes may have less glassy or amorphous material, they do contain certain crystalline phases such as anhydrite ($CaSO_4$), tricalcium aluminate ($3CaO{\cdot}Al_2O_3$), calcium sulpho-aluminate ($C_4A_3\underline{S}$) and very small amounts of free lime (CaO) that participate in producing cementitious compounds (Siddique and Khan 2011). Also, glassy phase in Class C ashes is usually more reactive. The glassy particles in Class C fly ashes contain large amounts of calcium, which possibly makes the surface of such particles highly strained, and probably, this is the reason for the highly reactive nature of Class-C fly ashes (Papayianni-Papadopoulou 1981; Papayianni 2010a, b).

Anhydrite ($CaSO_4$) is formed from the reaction of CaO, SO_2 and O_2 in the furnace or flue. Quantity of anhydrite increases with the increase in SO_3 and CaO contents. It has a significant role in hydration behavior of fly ash because it participates along with tricalcium aluminate and other soluble aluminates to produce ettringite and calcium sulphoaluminate hydrate (Papayianni-Papadopoulou 1981;

Table 2.2 Composition of Class F and Class C fly ashes (data taken from ACI 226 1987)

Parameter (%)	Class F fly ash	Class C fly ash
Silicon dioxide	45–64.4	23.1–50.5
Calcium oxide	0.7–7.5	11.6–29.0
Aluminum oxide	19.6–30.1	13.3–21.3
Iron oxide	3.8–23.9	3.7–22.5
Sodium oxide	0.3–2.8	0.5–7.3
Magnesium oxide	0.7–1.7	1.5–7.5
Potassioum oxide	0.7–2.9	0.4–1.9
Loss on ignition	0.4–7.2	0.3–1.9

Table 2.3 Concentration range of minerals in bituminous fly ashes (data taken from Alonso and Wesche 1992)

Minerals	Concentration (%)
Mulite	6.5–9.0
Hematite	1.1–2.7
Magnetite	0.8–6.5
Quartz	2.2–8.5
Free CaO	Up to 3.5

Papayianni 1996; Papayianni 2010a, b; Mehta 1986a, b). Tricalcium aluminate ($3CaO{\cdot}Al_2O_3$) is one of the most important crystalline phases to identify and quantify the fly ash because it contributes to ettringite formation, and also in self-hardening reactions as well as disruptive sulfate reactions in hardened concrete.

Periclase is the crystalline form of magnesium oxide (MgO). Presence of this form of MgO in fly ash affects the soundness of the resulting concrete through its expansive hydration to brucite, $Mg(OH)_2$ (Papayianni-Papadopoulou 1981; Mehta Mehta 1986a, b). Crystalline iron oxide, ferrite spinel and/or hematite are generally found in all fly ashes. In most of the fly ashes, about 0.33–0.50% of iron is present as crystalline oxide. The reactivity of fly ash is, however, dependent on the Fe_2O_3 content in the glassy phase (Siddique and Khan 2011). The concentrations of important minerals found in bituminous coal fly ashes, as reported by Alonso and Wesche (1992) are given in Table 2.3.

2.5 Effect of Fly Ash on the Fresh Properties of Cement and Concrete

Fresh concrete is a concentrated suspension of particulate materials of different densities, particle sizes and chemical composition in a solution of lime and other compounds. Fresh concrete properties include workability, air-entrainment, bleeding and segregation, pump ability, compactability, and finishability. In fresh concrete, fly ash plays an important role in the fluidity of concrete.

2.5.1 Workability

The spherical shape and glassy surface of most fly ash particles, usually finer than cement, permit greater workability or slump for equal water–cement ratios.

Lane and Best (1982) concluded that the use of fly ash as partial replacement of cement usually reduces the water content for a given consistency. With proper proportioning of the concrete, cohesion and plasticity are adequate, and bleeding is reduced. Helmuth (1987) has reported that if the water reduction were due to the spherical shape of the fly ash particles or the lack of chemical reactivity, the water reduction would progressively increase with increase in fly ash content.

Brown (1982) conducted several studies with fly ash replacing cement and fine aggregate at levels of 10–40% by volume. He concluded that for each 10% of ash substituted for cement, the compacting factor or workability changed to the same order as it would by increasing the water content of the mix by 3–4%. When fly ash was substituted for sand or total aggregate, workability increased to reach a maximum value at about 8% ash by volume of aggregate. Further substitution caused rapid decrease in workability.

Yuan et al. (1982) showed that the water demand decreased by adding 15 and 20% fly ash and increased when fly ash content was higher than 20%. This was attributed to the increase in water demand from the introduction of additional specific surface and porous grains, and the decreased deflocculation resulting from the adsorption of fine grains of fly ash on cement clusters. Owens (1979) reported that with the use of fly ash containing large fraction of particles coarser than 45 μm or a fly ash with high amount of unburnt carbon, exhibiting loss on ignition more than 1%, higher water demand was observed. Water demand was noticeably increased to maintain the desired level of fluidity. The effect of coarse fly ash particles on the water demand of concrete mixtures is clearly shown in Fig. 2.1.

At a given content of cementitious materials in concrete the addition of fly ash generally reduces water demand and improves workability. However, some fly ashes may increase the water demand by up to 5% (Gebler and Klieger 1986). Jiang and Malhotra (2000) have studied the effect of 8 different fly ashes on the water demand, and the experimental results are given in Table 2.4. At a given fly ash content of 55% by mass of cementitious materials, 8.8–19.4% reduction in the water demand was achieved depending on the quality of the fly ashes. The

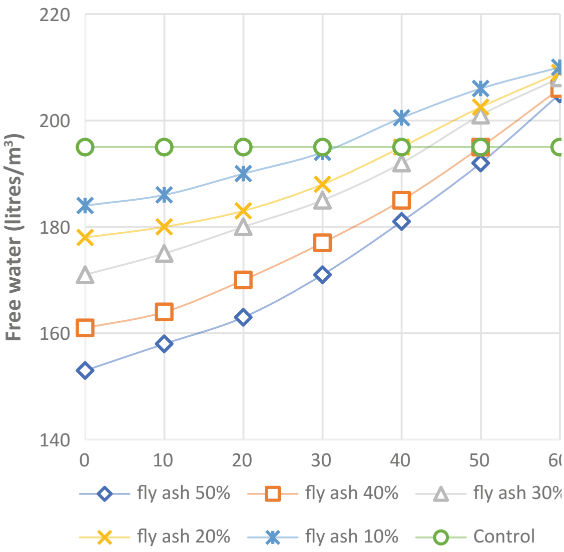

Fig. 2.1 Influence of coarse particles of fly ash on the water required for equal workability in concrete (data taken from Owens 1979)

Table 2.4 Reduction in the water demand due to the addition of different fly ashes (data taken from Jiang and Malhotra 2000)

Fly ash	Fly ash-to-cementitious material ratio	Water-to-cementitious material ratio	Reduction in water demand, %
–	0	0.43	–
F1	55	0.38	11.2
F2	55	0.39	8.8
F3	55	0.37	14.1
F4	55	0.35	17.6
F5	55	0.34	18.8
F6	55	0.38	9.4
F7	55	0.38	10.6
F8	55	0.34	19.4

reduction of the water demand is often attributed to the spherical shape and plain surface of fly ash particles, called "ball-bearing effect" and also to the improved grain size composition, called "filling effect". Due to the electrical charges of fly ash, the finer fly ash particles are adsorbed on the surface of cement particles. If enough fine fly ash particles are present to cover the surface of cement particles, the cement particles will become deflocculated and the water demand for a given workability will be reduced (Roy 1987). In this manner, fly ash has similar action on the water demand as plasticizers (Helmuth 1987).

The effect of fly ash on the water demand is determined mainly by its fineness, grain size composition, shape and carbon content. The increase in fineness generally results in a reduction of the water demand, which is attributed to the improved grain composition of the cement and fly ash mixture (Efes 1980). The spherical particle of fly ash contributes to the "ball bearing effect" and therefore has a positive effect on reducing the water demand (Braun and Gebauer 1983). High carbon content in fly ash has a negative effect on the workability due to the water absorption by porous carbon particles (Neville 1995).

The effect that fly ash has on the fresh properties of concrete mixtures strongly depends on its chemical composition (Low calcium or high calcium ash) and the fineness of the ash. According to Papayianni (2010a, b) the role of high calcium fly ash (HCFA) in the rheology of fresh concrete is governed by the fact that these fly ashes more or less take part in the hydration reaction of cementitious systems as soon as they are mixed with water. Regarding the water demand of HCFA concrete mixtures, it could be said that the issue of Abdun Nur (1961) about HCFA improving the workability is not verified in all cases. Moderately cementitious HCFAs (with relatively low CaO and SO_3 content) usually do not greatly affect the water required for a given workability, while the highly cementitious fly ashes (high content in CaO, Al_2O_3 and SO_3) increase the water demand. This extra water does not have so close relation to HCFA carbon content nor to the coarse fragment of grains >45 μm, but rather to the presence of free lime, calcium aluminates and

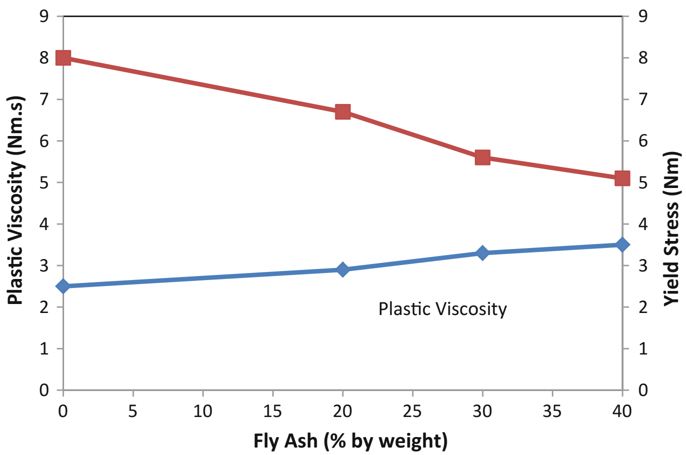

Fig. 2.2 Influence of fly ash content on plastic viscosity and yield stress of concrete (data taken from Khan 2010)

calcium sulfoaluminates (concentrated in fine particles) which are rapidly hydrated by binding a great number of H_2O molecules in their phase.

In order to develop a theoretical concept and understanding of the rheology of fresh fly ash concrete, Tattersall and Banfill (1983) suggested mathematical expressions relating the yield value (τ) and the plastic viscosity (μ) to the volumetric proportions of concrete mix constituents, in terms of Bingham model. Yield stress and plastic viscosity varied with volumetric proportions of concrete mix constituents, water-to-cement ratio, replacement levels of cement/aggregate with fly ash, and fineness of fly ash. An increase in the volume of the paste at a constant ratio of ash to total cementitious material resulted in an increase in plastic viscosity. Apparently because of fine particle size and smooth glassy texture as well as spherical shape, fly ash acts to plasticize concrete at a given water content when used as partial replacement of cement or fine aggregate. Khan (2010) reported that the incorporation of 20, 30 and 40% fly ash increased the plastic viscosity of concrete whilst the yield stress of concrete reduced with increase in fly ash content, see Fig. 2.2.

2.5.2 Bleeding and Segregation

Incorporation of fly ash in mortar or concrete significantly reduces the bleeding and segregation. This is due to the lubrication effect of the glassy spherical fly ash particles and the increased ratio of solids to liquid which make the concrete less prone to segregation and improve concrete pumpability. Figure 2.3 shows the bleeding rate of fly ash concrete compared to that of control concrete (CEGB 1967).

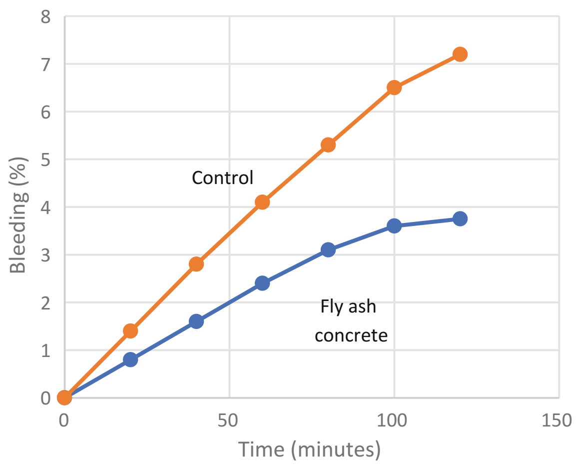

Fig. 2.3 Relative bleeding of control and fly ash concretes (data taken from CEGB 1967)

Joshi and Lohtia (1993) used Alberta fly ashes in making high-volume fly ash concrete mixes, and concluded that fly ash concrete mixes were more cohesive than control mixes. During the slump test, the fly ash concrete mixes subsided more slowly and gradually than the control mixes which exhibited abrupt fall or subsidence.

In general, concrete containing fly ash is cohesive and has reduced bleeding and segregation. The addition of fly ash can, therefore, solve the excessive bleeding problem particularly in concretes which are deficient in fine aggregates. Figure 2.3 shows a comparison of the bleeding of concretes with and without fly ash. The reduced bleeding is due to the reduced water demand by the addition of fly ash. Gebler and Klieger (1986) have reported the correlation between the reduced bleed water and the reduced water demand. Another reason is that finer fly ash provides a greater surface area of solid particles for a given workability (Idorn and Henriksen 1984).

2.5.3 *Setting Time*

With the addition of water to concrete, hydration reaction starts and the cement paste begins to stiffen accompanied by heat release. The rate of stiffening of cement paste is expressed in terms of setting time. Generally, the effect of fly ash on the setting time depends upon the characteristics and amount of fly ash used.

The interacting effects of fly ash with other chemical and mineral admixtures may also influence the setting of concrete. Investigations have revealed that the addition of low-calcium Class F fly ashes result in retarding the cement setting. High-calcium fly ashes, generally low in carbon and high in reactive and/or cementitious components sometimes exhibit the opposite behavior, i.e. reduced

Table 2.5 Properties of some Canadian fly ashes (data from Carette and Malhotra 1984)

Fly ash source	Type of coal	Major chemical compounds (% by weight)					
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	LOI
1	Bituminous	47.1	23.0	20.4	1.21	1.17	2.88
2	Bituminous	44.1	21.4	26.8	1.95	0.99	0.70
3	Bituminous	35.5	12.5	44.7	1.89	0.63	0.75
4	Bituminous	38.3	12.8	39.7	4.49	0.43	0.88
5	Bituminous	45.1	22.2	15.7	3.77	0.91	9.72
6	Bituminous	48.0	21.5	10.6	6.72	0.96	6.89
7	Sub-bituminous	55.7	20.4	4.61	10.7	1.53	0.44
8	Sub-bituminous	55.6	23.1	3.48	12.3	1.21	0.29
9	Sub-bituminous	62.1	21.4	2.99	11.0	1.76	0.70
10	Lignite	46.3	22.1	3.10	13.3	3.11	0.65
11	Lignite	44.5	21.1	3.38	12.9	3.10	0.82

setting time. Not all Class C fly ashes cause rapid setting. Ramakrishan et al. (1981) reported an increase in setting time with the use of high-calcium fly ash in concrete. Lane and Best (1982) concluded that the influence of fly ash on setting time is less than the influence due to cement fineness, water content, and ambient temperature. Carette and Malhotra (1984) studied the effect of Canadian fly ashes on the fresh concrete properties. Fly ashes were collected from 11 different sources. Cement was replaced with 20% fly ash in all the mixes. The w/b ratio was equal to 0.40 for all mixtures. Chemical properties of fly ashes are given in Table 2.5 and fresh concrete properties in Table 2.6.

Table 2.6 Properties of concrete with Canadian fly ashes (data from Carette and Malhotra 1984)

Mix No	Cement (kg/m^3)	Slump (mm)	Air (%)	Bleeding (%)	Setting time (h:min)	
					Initial	Final
Control	295	70	6.4	2.9	4:10	6:00
F1	236	100	6.2	3.1	4:50	8:00
F2	237	102	6.2	4.6	7:15	10:15
F3	237	100	6.2	5.1	5:20	8:10
F4	238	110	6.3	4.3	6:20	8:25
F5	237	65	6.4	2.7	5:15	8:55
F6	238	75	6.5	2.6	4:30	6:50
F7	239	100	6.1	2.9	4:15	6:20
F8	236	115	6.2	5.6	5:10	7:30
F9	236	100	6.4	4.4	5:25	9:00
F10	237	130	6.5	2.5	4:45	7:00
F11	237	140	6.6	0.6	4:00	6:05

Rodway and Fedirko (1989) studied the setting times of concretes made with varying percentages (0, 56, 68 and 76%) of fly ash of the total cementitious material. High fly ash concrete mixes exhibited increasingly greater initial setting times of 22–42.5 h with increasing fly ash content from 56 to 76% compared to 7.6 h for the control mix without fly ash. They observed that delays appeared to be related to the problem of compatibility between cementitious materials and superplasticizer used to maintain workability. Sivasundram et al. (1990) investigated the setting time of high-volume fly ash (HVFA) concrete mixes, and concluded that the initial setting time of 7.50 h was comparable to that of the control concrete, whereas the final setting time was extended by about 3 h as compared to that of the control concrete. Joshi et al. (1993) examined three different sub-bituminous Alberta coal ashes at replacement levels of 40–60% by cement weight to produce superplasticized and air entrained concretes. They observed that fly ash concrete achieved an initial setting time of 5–11 h as compared to about 5 h for neat Porltand cement concretes. The final setting time varied from 10 to 13 h compared to 7 h for control mixes without fly ash.

2.5.4 *Chemical Admixture Interaction*

Ng and Justnes (2016) studied the influence of 5 different plasticizers on cementitious paste in which the OPC was replaced by siliceous (Class F) fly ash (FA) in increments of 20–60% by mass and with a constant water-to-powder ratio of 0.36. The plasticizers were lignosulfonate (LS), naphthalene sulfonate-formaldehyde condensate (NSF) and 3 different polycarboxylate ethers (PCEs). The flow resistance (FR) of the pastes decreased steadily with increasing replacement of OPC by FA in spite of increased total volume of solids resulting from the density of FA being lower than OPC. The decrease in FR is due to the spherical nature of FA and

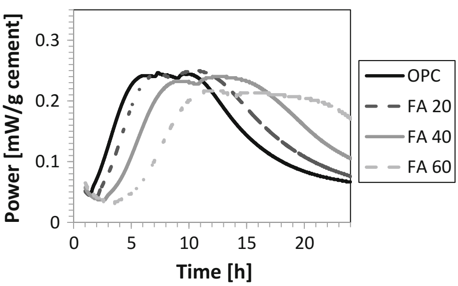

Fig. 2.4 Heat of hydration (Power) evolution for cementitious pastes with 0 (OPC), 20 (FA20), 40 (FA40) and 60% (FA60) replacement of OPC with FA. All pastes are plasticized by 0.2% dry NSF of powder mass (data taken from Ng and Justnes 2016)

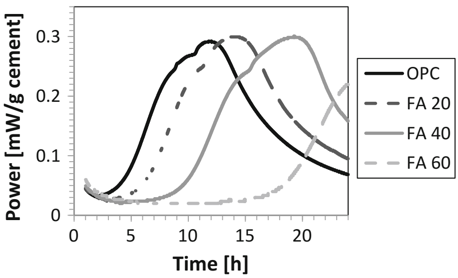

Fig. 2.5 Heat of hydration (Power) evolution for cementitious pastes with 0 (OPC), 20 (FA20), 40 (FA40) and 60% (FA60) replacement of OPC with FA. All pastes are plasticized by 0.2% dry PCE of powder mass (data taken from Ng and Justnes 2016)

the low reactivity of the glass phase at this early stage. Furthermore, there is much lower interaction of the plasticizers with FA than with cement, so the effective plasticizer-to-cement ratio is increasing and thereby also increasing the retardation of the cement as illustrated in Figs. 2.4 and 2.5 for NSF and one PCE, respectively. Hence, the required plasticizer dosage for equal flow and/or acceptable setting time has to be reduced when cement is replaced by Class F FA. The situation may be different for Class C FA depending on its C_3A content etc.

2.6 Early Age Strength Development

Figure 2.6 shows the effect of temperature on the strength development of fly ash concrete grade 40. At an early age, in all mixes, the strength development of PC and FA concretes at higher curing temperatures is faster than at lower curing temperatures. This is attributed to an increase in the hydration rate. However, at a later age, the strength achieved at higher curing temperatures was reduced. The later age strength of Portland cement was much more detrimentally affected by higher curing temperatures than that of fly ash concretes, the so-called “crossover” effect. Furthermore, this effect appeared earlier for Portland cement concretes than FA concretes. The crossover effect is significantly delayed with increasing cement replacement by fly ash (Elsageer 2011; Hatzitheodorou 2007; Soutsos et al. 2016). The later age strengths of the 30 and 45% fly ash concrete samples cured at 30 and 40 °C, i.e. other than those cured at 50 °C, did not significantly get affected by the high early age curing.

The strength development under all curing temperatures relative to achieved standard 20 °C cured specimens for 32-day strength is shown in Fig. 2.7. The ratio of the strength development at all curing temperatures of fly ash concretes was slightly below the equivalent PC concrete up to the age of 4 days, except from the

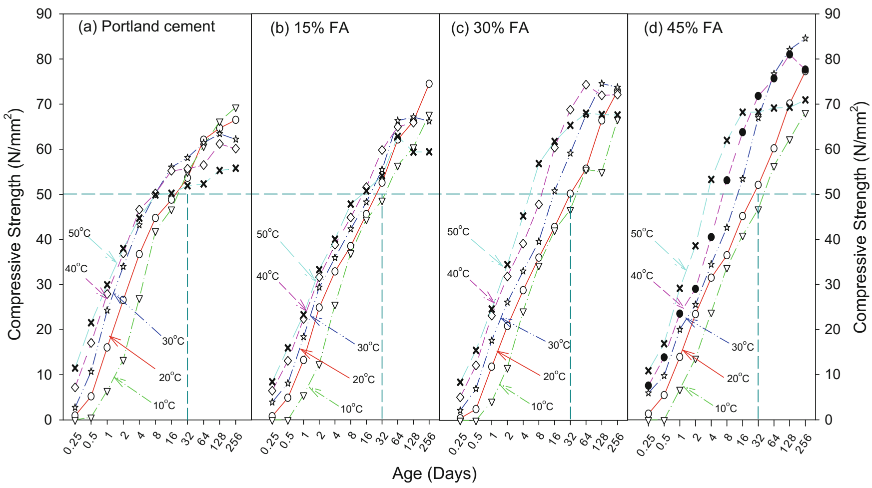

Fig. 2.6 Strength development of PC and FA concrete under 10, 20, 30, 40 and 50 °C curing temperatures (grade 40) (data from Elsageer 2011)

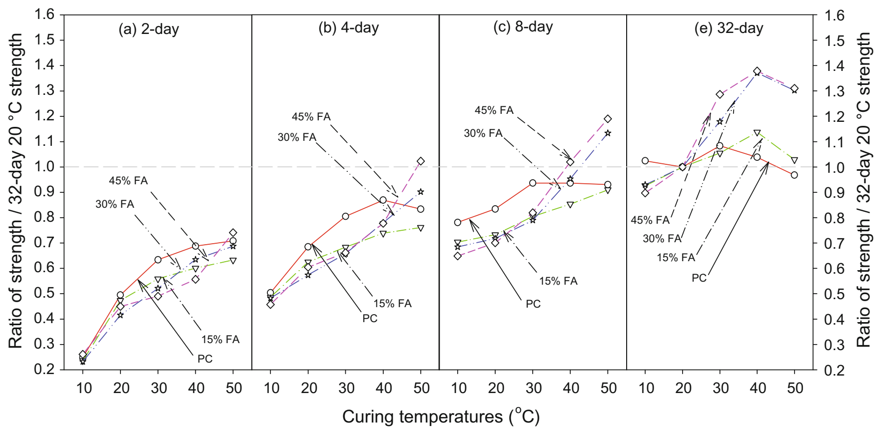

Fig. 2.7 Relative strength of all concrete mixes (grade 40) (data taken from Elsageer 2011)

45% FA concrete that reached more than 100% of its 32-day strength at 20 °C at the age of 4 days. It can be also seen that the 45% FA concrete cured at 40 °C is capable of reaching the 32 days standard 20 °C cured strength within just 8 days. On the other hand, 30% FA concrete reached more that 100% of the 32 days standard cured strength within 8 days, only when cured at 50 °C.

The strength development of all the concretes under adiabatic conditions is shown in Fig. 2.8 (Elsageer 2011). Higher early age strength was achieved for all

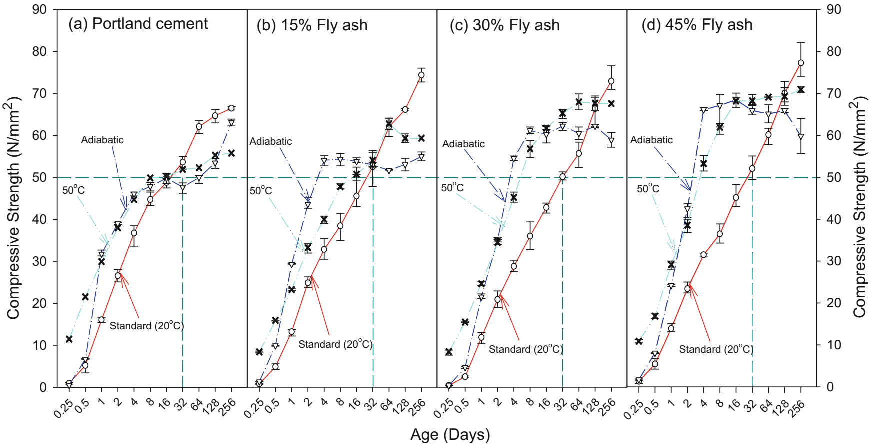

Fig. 2.8 Adiabatic, standard and 50 °C strength development of PC and PFA concrete (grade 40) (data taken from Elsageer 2011)

concretes, compared to the standard cured strength; however, at later age the strength development was detrimentally affected by the high adiabatic curing temperature, i.e. the strength development was lower in comparison with the samples cured under standard curing condition. It can be observed that the fly ash concretes benefited from the adiabatic temperatures more than Portland cement concrete. The greatest strength benefit appears to take place within the first 4 days. At this age, i.e. 4 days, all fly ash concrete had achieved more that 100% of their 32-day standard strength, but the strengths levelled off from this age onwards. The peak temperatures of these concretes are reached after 3 days and therefore, a more pronounced improvement in strength at 4 days is observed.

A comparison of the strength development of FA concretes to PC concrete at standard and adiabatic curing conditions is shown in Fig. 2.9. The early age strengths at standard curing are slightly lower as levels of cement replacement with FA increased, for example, the strength of 30% FA at 1-day was 73% of the strength of the Portland cement concrete. Nevertheless, from the age of 64-days onwards, the strength is higher as the levels of cement replacement with fly ash increase. The strength development of FA concretes benefits considerably more from the adiabatic temperature rise than the PC concrete. However, at later age, the adiabatic temperature rise is responsible for a levelling off of strength gain for all the concretes. For example, as shown in Fig. 2.9b, at 2 days, 15 and 45% fly ash concretes had greater strength than PC concrete and the greater improvement was observed at the age of 4 days. From the age of 4 days onwards, the strength rations drop continuously with age and the ratios are higher as the percentage of fly ash increases.

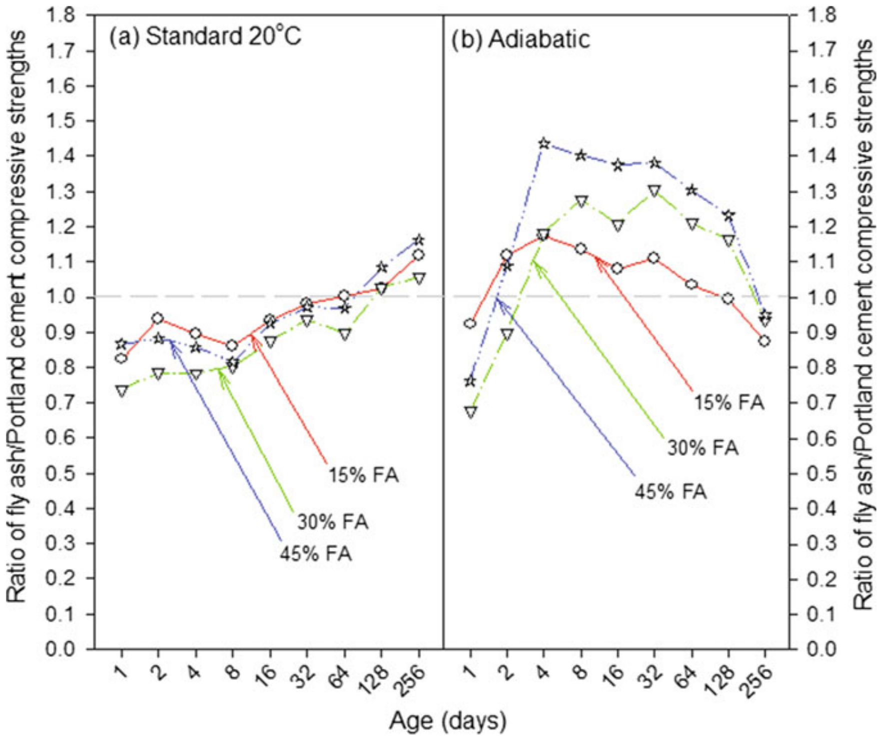

Fig. 2.9 Ratio of fly ash/Portland cement compressive strength development and standard and adiabatic curing regimes (grade 40) (data taken from Elsageer 2011)

2.7 Heat of Hydration, Rate of Reaction (Influence of Temperature and Curing, Maturity Functions)

The rate of heat output generation is highly dependent on temperature and time, i.e. it increases at higher temperatures for Portland cement and Portland cement/fly ash mixes. The use of fly ash reduces the amount of heat generated when compared to that of Portland cement (Papayianni-Papadopoulou 1981; Elsageer 2011; Hatzitheodorou 2007; Poole et al. 2010), thus potentially reducing the risk of thermal cracking in concrete and this can be the main reason for its use in concrete.

The binder mortars' isothermal heat output results in W/kg are plotted on log scale to highlight the differences at early ages. Figure 2.10 indicates that the higher the temperature, the earlier and sharper the heat of hydration peak appears. In all mortars and under all curing regimes, the peak of PC was higher than all levels of FA and the heat decreased gradually with the increase of the level of FA.

Higher temperature accelerates the reactions of fly ash to a greater extent than in the case of Portland cement alone. As a consequence, the behaviour of concrete

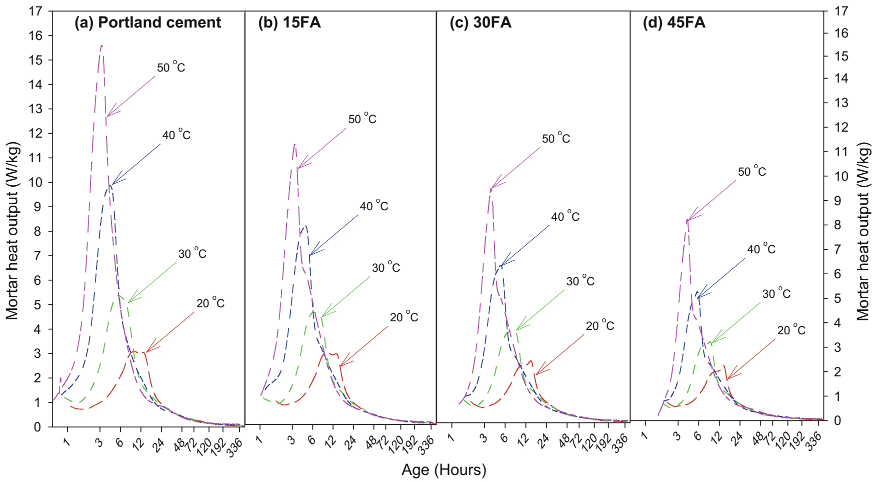

Fig. 2.10 Heat output per kg of binder of mortar (grade 40) (data taken from Elsageer 2011)

containing fly ash may be different in massive concrete elements from the behaviour in small concrete elements. This is relevant to the strength development of fly ash concrete.

For mass concrete projects the performance of the concrete designs should be tested using the local materials to ensure their performance regarding temperature and strength development. Adiabatic tests may be used for this purpose. The adiabatic temperature histories are shown in Fig. 2.11 for Grade 40 concretes (Elsageer 2011). The maximum temperature rise was highest for the PC concrete, which is 49 °C from the casting temperature of 16.7 °C and slightly lower for concrete with 15% fly ash. The maximum temperature rise was reduced in the concretes with 30% and 45% fly ash. The rate of temperature was higher and the maximum temperature was reached in a longer time as the level of fly ash increased. The temperature development in concrete blocks is not only affected by their size but also by the ambient temperature at the time of casting. Strength grade and level of replacement by fly ash both affect the temperature increase in the concrete. Figure 2.12 shows the DETR project blocks (Soutsos et al. 2016) that were cast to determine the ratio of in situ strength (determined from cores) to companion cubes cast and cured alongside the blocks. A unique ratio does not exist as the strengths will be affected by the different temperature histories depending whether it is winter or summer. Winter temperatures allow more heat dissipation from the concrete blocks and the lower reaction rate of fly ash assists in obtaining lower peak temperatures. The differences in peak temperatures between the PC and fly ash mixes increase with winter conditions (Fig. 2.13).

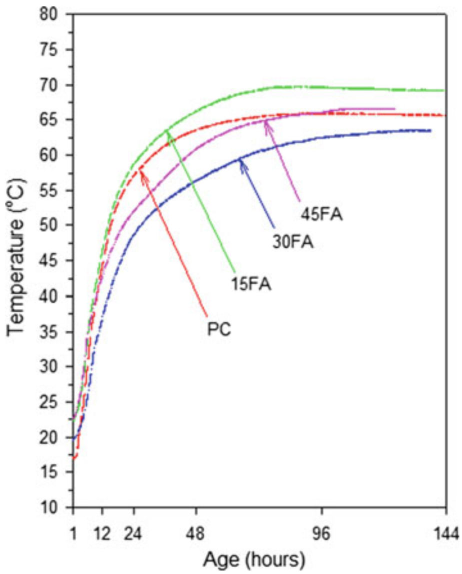

Fig. 2.11 Adiabatic temperature rise of grade 40 concretes (data from Elsageer 2011)

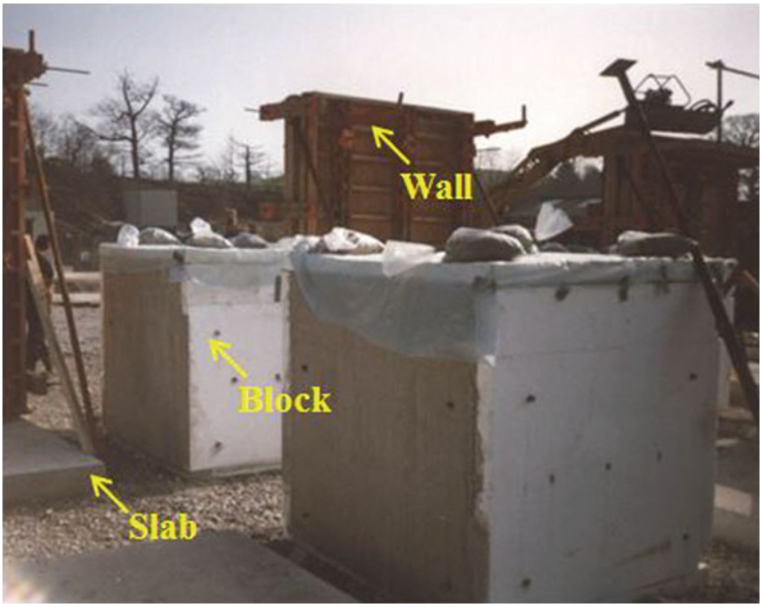

Fig. 2.12 The DTI Concrete Core project (photo from Soutsos et al. 2016)

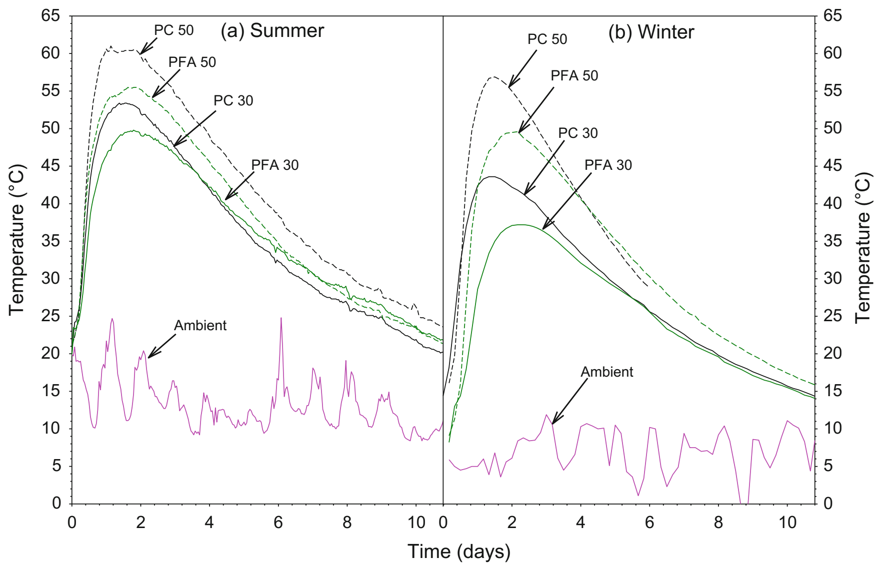

Fig. 2.13 Temperature development in concrete blocks containing 30% fly ash during summer and winter (30 and 50 MPa concretes) (data from Soutsos et al. 2016)

2.8 Compressive Strength

The pozzolanic reaction of fly ash affect the compressive strength of concrete mixtures by different ways. Mehta (1986a, b) has identified these as:

- the reaction is slow, so that the rates of both heat liberation and strength development are correspondingly slow
- the reaction consumes lime rather than producing it
- the reaction products are efficient in filling up space and subdividing pores.

The rate of strength development depends upon the following factors (Siddique and Khan 2011):

- fly ash characteristics such as its chemical and mineralogical composition, fineness, and pozzolanic reactivity
- type of cement (in particular alkali content, but also fineness)
- replacement level of cement with fly ash
- mixture proportions
- ambient temperature
- curing environment reference.

When aggregates or cement are replaced by low-calcium fly ash (up to a certain level, Pmax) higher strengths are observed. In the former case the strength enhancement is significantly higher and obvious 2–3 weeks after the mixing, whereas in the latter case the enhancement is much lower and obvious after 3 months. The final strength gain is roughly proportional to the content of active silica in the concrete volume. (Papadakis 1999).

High calcium fly ashes start their contribution to strength development almost from the onset of Portland cement hydration (Siddique and Khan 2011). Some high-calcium fly ashes, with calcium oxide content more than 15%, result to compressive strength increase as early as 3 days after mixing because of their self hardening and pozzolanic properties (Siddique and Khan 2011; Papayianni 2010a, b).

Because of its fineness as well as pozzolanic reactivity, fly ash in concrete significantly improves the density of cement paste and the micro-structure of the transition zone between the binder matrix and the aggregate (Siddique and Khan 2011; Papadakis 2000a, b). As a result of the continual process of pore refinement, due to the inclusion of fly ash hydration products in concrete, a gain in strength development with curing age is achieved. When high-calcium fly ashes are used, the strength development with time is usually different from the one observed when using low calcium fly ashs. The self-hardening reactions in the high calcium fly ashes are likely to occur within the same time frame as the normal Portland cement hydration reactions, giving equal or sometimes greater strengths at early ages (Papayianni-Papadopoulou 1981; Mehta 1986a, b; Sideris 1996; Papadakis 2000a, b; Siddique and Khan 2011). The pozzolanic activity of such cementitious fly ashes further enhances strength at later ages (Sideris 1996; Papadakis 2000a, b; Papayianni 2010a, b).

Lane and Best (1982) observed that proportioning fly ash concrete on strength basis requires a replacement ratio greater than one-to-one by mass so that the fly ash in effect replaces some of the fine aggregate. When fly ash replaces cement on a one-to-one basis, the rates of hardening and strength gain at early ages are reduced. In order to take into consideration the reactivity of fly ash on the compressive strength of concrete mixtures the concept of fly ash efficiency factor was introduced by EN 206-13 (EN206 2013). The efficiency factor (or k-value) is defined as the part of the fly ash in a pozzolanic concrete, which can be considered as equivalent to Portland cement, having the same properties as the concrete without SCM (obviously $k = 1$ for Portland cement). The quantity of the fly ash in the mixture can be multiplied by the k-value to estimate the equivalent cement content, which can be added to the cement content for the determination of the water/cement (W/C) ratio, minimum required cement content etc. (Papadakis and Tsimas 2002). According to EN 206 (2013), when a fly ash conforming to EN 450 is used a k-value of 0.4 is permitted for concrete containing cements CEM I and CEM II-A conforming to EN 197-11. Papadakis and Tsimas (2002) reported that the pulverized high calcium fly ashed used in their research performed k-values ranging from 0.9 to 1.4.

Carette and Malhotra (1984) studied the effect of Canadian fly ashes on the compressive strength of concrete mixes. Cement was replaced with 20% fly ash in all the mixes. Compressive strength was measured up to the age of 365 days, and results are given in Table 2.7. It can be seen from this table that compressive strength of all tested mixtures continued to increase with age, indicating pozzolanic reaction of fly ashes.

Table 2.7 Compressive strength of hardened concrete (data taken from Carette and Malhotra (1984))

Mix No	Compressive strength (MPa)			
	7 days	28 days	91 days	365 days
Control	23.4	30.6	34.9	39.2
F1	18.4	25.7	31.4	38.3
F2	16.9	25.2	34.8	37.0
F3	14.4	21.0	27.6	34.4
F4	17.8	23.3	32.3	36.9
F5	20.1	28.0	33.9	44.3
F6	18.4	24.8	31.8	39.2
F7	16.7	24.1	29.1	35.7
F8	17.9	27.7	29.0	40.4
F9	16.7	24.9	31.1	35.6
F10	19.2	28.5	33.7	39.7
F11	21.1	29.4	35.3	40.1

Mehta (1994) reported that no significant contribution to strength development was noticed up to 7 days with the use of low-calcium fly ash in concrete. At 28 days and beyond, most fly ashes at the replacement levels of up to 30% by cement weight exhibited strength gain in concrete and the strength generally equalled that of control concrete.

Haque et al. (1988) concluded that for concrete mixes with 40–75% bituminous fly ash replacing cement, the increase in flexural strength was slightly less than the increase in compressive strength between 28 and 91 days of curing. Klieger and Perenchio (1972) found that concrete made with Type-I cement [EN 197-1(2013)] partially replaced with fly ash had lower strength than the control (neat Type_I cement) at all ages up to 3 years. Lower casting and initial-curing temperatures resulted in higher strengths at later ages for both types of concretes. Korac and Ukraincik (1983) found that the early-age strengths of 50% fly ash concrete were lower than the controls; after 90 days strengths were comparable.

Erdoğdu and Türker (1998) studied the effect of particle size of high and low calcium fly ash on the compressive strength of mortar. Fly ashes were sieved from the 125, 90, 63, and 45-µm sieve by a sieve-shaker. Six different size groups, including the all-in ash, were investigated by combining the materials retained on each sieve. They were; material retained on 125 µm sieve, material having 125–90, 90–63, and 63–45, and material passing 45-µm sieve. For strength tests, mixtures composed of 25% fly ash and 75% Portland cement, by weight, were prepared. Tests were conducted up to the age of 90 days, and results are given in Table 2.8. It is evident from these results that (1) mortars with high-calcium ash exhibited higher strengths than mortars with low-calcium ash at all ages; (2) the finer the size of a fraction then the higher was the compressive strength.

Table 2.8 Compressive strength results of the mortars (data taken from Erdoğdu and Türker 1998)

		Compressive strength (N/mm^2)			
		2 days	7 days	28 days	90 days
25% High + 75% PC	All-in ash	27.6	36.7	46.7	55.7
	Above 125 μm	19.2	26.6	31.2	33.2
	125–90 μm	22.6	27.6	35.0	38.4
	90–63 μm	24.8	31.3	35.4	42.6
	63–45 μm	26.6	35.1	41.4	47.5
	Under 45 μm	32.0	43.0	55.8	64.6
25% Low + 75% PC	All-in ash	23.5	33.2	39.6	47.4
	Above 125 μm	17.9	24.4	26.7	29.9
	125–90 μm	21.6	29.2	32.0	37.1
	90–63 μm	22.6	29.6	34.9	40.6
	63–45 μm	23.8	33.5	37.4	46.8
	Under 45 μm	26.6	37.3	43.4	57.2
100% PC 32.5		38.0	44.4	51.6	58.2

Siddique (2003) studied the effect of partial replacement of fine aggregate (sand) with varying percentages of Class F fly ash on the compressive strength of concrete up to the age of 365 days. Fine aggregate (sand) was replaced with five percentage levels (10, 20, 30, 40, and 50%) of Class F fly ash by weight. Control mix (without fly ash) was proportioned to have a 28-day cube compressive strength of 26.4 MPa. Compressive strength results are shown in Fig. 2.14.

Based on the results shown in Fig. 2.14, it was concluded that (1) compressive strength of fine aggregate (sand) replaced fly ash concrete specimens was higher

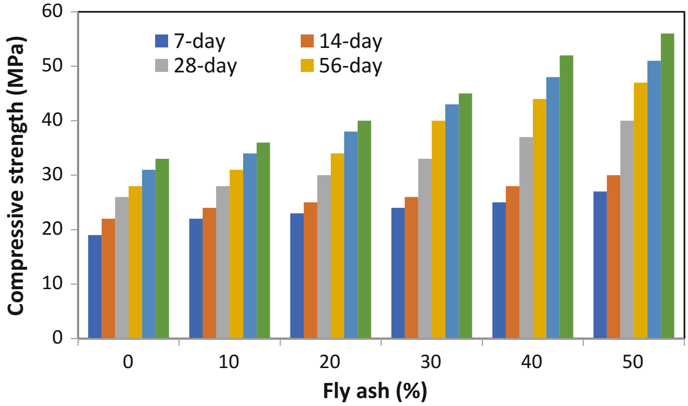

Fig. 2.14 Compressive strength versus fly ash percentage (data taken from Siddique 2003)

than the plain concrete (control mix) specimens at all the ages. The strength difference between the fly ash concrete specimens and plain concrete specimens became more distinct after 28-days; (2) compressive strength continued to increase with age for all fly ash replacement levels; and (3) The maximum compressive strength occurs with 50% fly ash content at all ages. It was 40 MPa at 28-day, 51 MPa at 91-day, and 55 MPa at 365-day.

Demirboğa et al. (2007) investigated the role of high-volumes of Class C fly ash on the compressive strength of concrete. Cement was replaced with 0, 50, 60, and 70% fly ash. Compressive strength of concrete mixtures was determined at the ages of 3, 7, 28 and 120 days. The researchers reported that:

(i) fly ash reduced the compressive strength of tested mixtures at all tested ages and at all replacement levels
(ii) strength reductions were very high at the early ages of hydration, but the percent of strength reduction decreased as the hydration age increased
(iii) cement paste containing fly ash showed a steady reduction in strength at 3, 7, 28 and 120 days as a function of replacement percentage.

Chindaprasirt et al. (2007) studied the effect of fly ash fineness on the compressive strength of concrete. Three fly ash finenesses: coarse, medium and fine were used. The coarse fly ash was 100% original fly ash (100FA). The medium fly ash was the 45% fine portion of the original fly ash (45FA). The fine fly ash was the 10% fine portion of the original fly ash (10FA). Three concrete mix series viz. a low, a normal/medium and a high strength concrete mix series were made. For the low- and normal-strength concrete, the water-to-cement ratios of 0.54 and 0.48, respectively, were used for Portland cement mixes. For the high strength concrete, the water-to-cement ratio was kept low with the use of a superplasticizer. The fly ash dosage of 30% by weight of binder was used for all fly ash concrete mixes. The strengths of fly ash concrete were higher than those of the Portland cement concrete in the same group. For the normal-strength concrete, the 28-day strength of the PC2 concrete was 49 MPa, whereas those of fly ash concretes were between 44 and 52 MPa. For the high strength concrete, the strength of the PC3 concrete was 80 MPa, whereas those of the fly ash concretes were between 71 and 84 MPa. For the low strength concrete series, the strength of PC1 concrete was lower than the fly ash concrete owing to a very large reduction in the water content of the fly ash concrete. The reduction in the water content, the good dispersing and the filling effect of the fly ash contributed to the relatively good strength development of the fly ash concrete in this series. With the use of finer fly ash, the water content was further reduced and the strength of concrete enhanced further.

In general, the replacement of cement by fly ash has a retarding effect on the early-age strength development of concrete and a positive effect on the later-age strength. However, some highly reactive fly ashes, especially Class C fly ashes, could increase the compressive strength even at early ages. Figure 2.15 shows the strength development of concrete with different fly ashes (Whiting 1989).

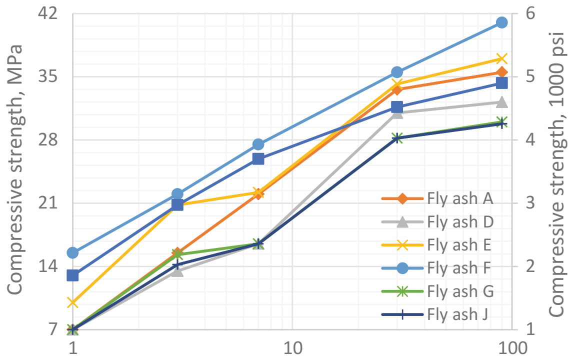

Fig. 2.15 Compressive strength of concrete containing 307 kg/m^3 of cementitious materials, where 25% of cement was replaced by fly ash. Fly ashes A, F are G were class C, and fly ashes D, E and J were class F (data taken from Whiting 1989)

Beside the mix composition of concrete and the properties of aggregates and the curing conditions, the strength of concrete containing fly ash is determined by the pozzolanic reactivity of fly ash. The chemical composition of fly ash strongly affects its pozzolanic reactivity. The major components in fly ash contributing to the reactivity are silicates and aluminates contained in the glass phase (Wesche 1991). In general, Class C fly ash has a higher reactivity than Class F fly ash, and this results in different performance in terms of strength development (Neville 1995). The fineness of fly ash is another important factor affecting the reactivity. Many researchers (Costa and Massazza 1983; Ravina 1980) reported a direct correlation between the fineness of fly ash and its reactivity as well as the strength development of the concrete containing it. Grinding fly ash increases the fineness, which has a positive effect on the reactivity (Jaturapitakkul et al. 2004). However, the grinding destroys the spherical particles of fly ash and results in an increase in the water demand (Monzo et al. 1995), which possibly causes an adverse effect on the strength development.

Papayianni (2010a, b) used two high calcium lignite fly ashes for the production of concrete mixtures in cement replacement levels from 50 to 100%. She reported that plain concrete mixtures with only raw fly ash (100% replacement) developed 7-and 28-days compressive strength of 2.5 and 5.0 MPa, respectively. When processed fly ash was used the mixtures developed comparable strength values with the reference mixture produced with CEM II 32.5N cement from the age of 7 days, see Fig. 2.16.

Sideris et al. (1997) used two high calcium lignite fly ashes at replacement levels of 10 and 30% for the production of concrete mixtures with limestone or silicate aggregates. They concluded that only the 10% fly ash mixtures developed 28 day strength comparable with the one measured in the reference mixture. However at the ages of 60 days and beyond all fly ash mixtures gained significant strength values (Fig. 2.17).

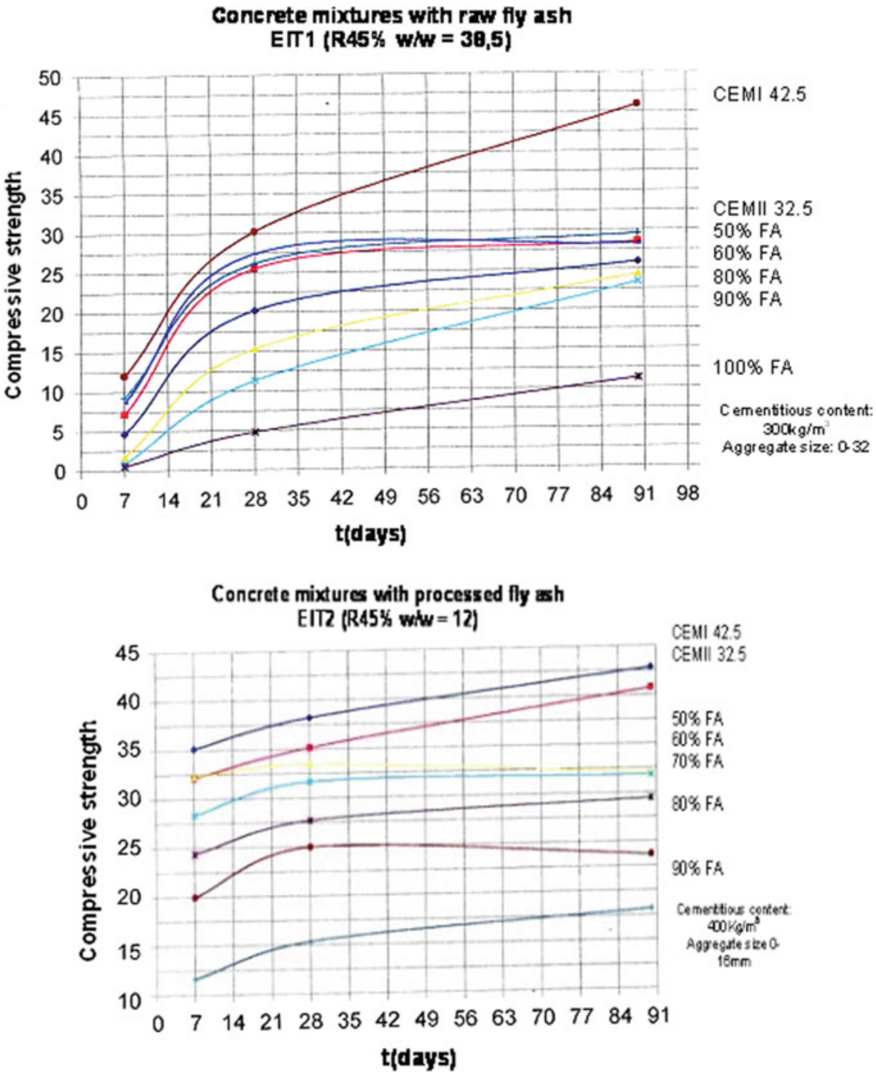

Fig. 2.16 Compressive strength development of concrete mixtures produced with raw (EIT1) and processed (EIT2) high calcium lignite fly ashes (data taken from Papayianni 2010a, b)

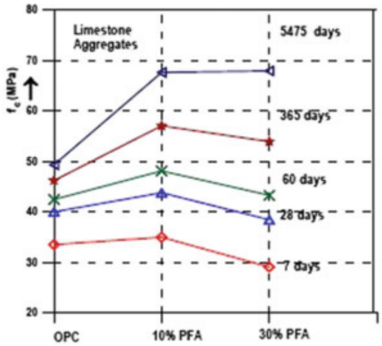

Figure 5: Compressive strength of different PFA concretes for various hydration ages.

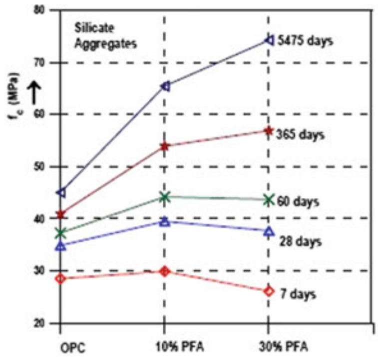

Figure 6: Compressive strength of different PFA concretes for various hydration ages.

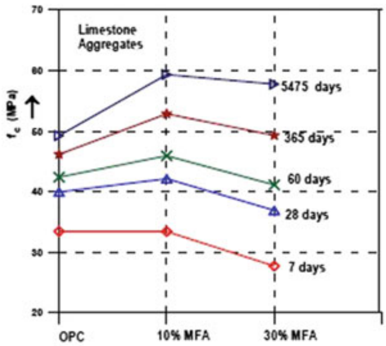

Figure 7: Compressive strength of different MFA concretes for various hydration ages.

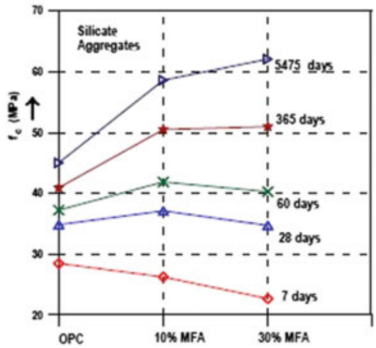

Figure 8: Compressive strength of different MFA concretes for various hydration ages.

Fig. 2.17 Compressive strength development of mixtures produced with high calcium lignite fly ashes at different replacement levels. Total cementitious content: 300 kg/m^3, w/c ratio = 0.60 (data taken from Sideris et al. 1997)

2.9 Tensile Strength

Carette and Malhotra (1984) studied the effect of Canadian fly ashes on the flexural strength of concrete mixes up to the age of 91 days. According to the results of this research, flexural strength continued to increase with age. The researchers attributed this trend to pozzolanic action of fly ash.

Siddique (2003) investigated the effect of partial replacement of fine aggregate (sand) with varying percentages of Class F fly ash on the splitting tensile strength and flexural strength of concrete. Fine aggregate was replaced with five levels of percentages (10, 20, 30, 40, and 50%) of Class F fly ash by weight. A reference mix (PC concrete) was designed with a 28-day compressive strength of 26 MPa. Tests were performed up to the age of 1 year (365 days). Siddique (2003) concluded that:

- splitting tensile strength, and flexural strength of fine aggregate (sand) replaced fly ash concrete specimens was higher than OPC concrete (reference mix) specimens at all the ages. However, the strength differential between the fly ash concrete specimens and OPC concrete specimens became more distinct after 28-days
- both splitting and flexural strengths continued to increase with age for all fly ash percentages
- fly ash concrete mix with the higher content of 50% performed best at all tested ages having the maximum measured values.

2.10 Transport Properties

In ordinary Portland cement concrete, calcium hydroxide formed during hydration of Portland cement can be leached out over a period of time (Siddique and Khan 2011). This creates channels available for the ingress of water and deleterious salt solutions. When fly ash is incorporated in the mixture, it reacts with the calcium hydroxide to produce calcium silicate and aluminate hydrates of the same or similar type that are formed in the normal hydration of cement (Papayianni-Papadopoulou 1981; Mehta Mehta 1986a, b; Papadakis and Tsimas 2002; Siddique and Khan 2011). Thus pozzolanic reaction consumes calcium hydroxide and converts it to water insoluble hydration products. The reactions reduce the risk of leaching calcium hydroxide, pozzolanic products fill capillaries and reduce diffusion to aggressive fluids such as chloride or sulfate solutions. It is clear therefore that addition of fly ash results in pore refinement since it transforms bigger pores into smaller ones due to the formation of pozzolanic reaction products concomitant with the progress of cement hydration (Sideris 1996; Siddique and Khan 2011). Since permeability of concrete is related to the volume of pores larger than 100 Å in the hydrated paste, incorporation of fly ash results to more impermeable concrete mixtures.

The effect of low-calcium fly ash on the pore size distribution at the ages of 28 days and 1 year for pastes with w/cm = 0.50 is shown in Fig. 2.18 (Manmohan and Mehta 1981). The partial replacement of cement with 30% fly ash results in a higher porosity and a greater volume of macropores measured at the age of 28-days. The total volume of the pores measured at the age of 1 year is reduced in both pastes, but the difference is most significant in the fly ash paste. In this case there is a very significant reduction in the capillary-sized pores between 28 days and 1 year. It is also noticeable that there is a significant shift from the macropores to mesopores for this mixture resulting to a more refined pore structure of the fly ash paste as compared with that of the plain cement paste (100% Portland cement (PC) at the age of 1 year. The improvements in pore structure with time emphasize the importance of curing, especially with slowly reacting pozzolans, if the potential benefits associated with their use are to be realized.

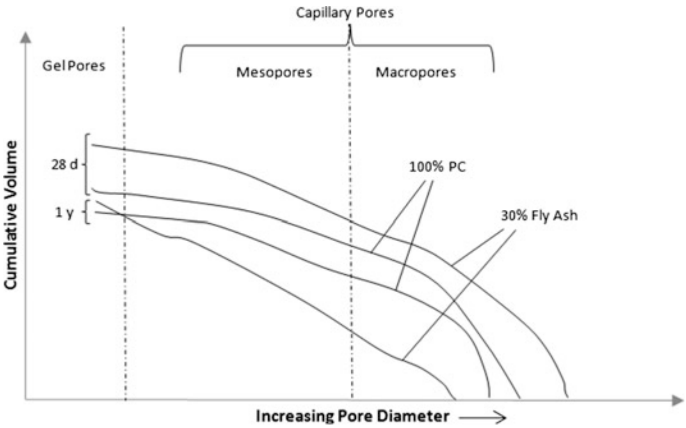

Fig. 2.18 Effect of fly ash on pore size distribution at 28 days and 1 year (data taken from Manmohan and Mehta 1981)

High-CaO lignite fly ashes exhibit both pozzolanic and hydraulic behaviour (Papayianni 1996). When mixed with water some high-calcium fly ashes will harden due to the hydration of crystalline calcium silicate, the reaction between free lime and some of the glass, and the formation of ettringite. According to Taylor (1997) the hydration products in blends of Portland cement and high CaO are essentially the same as those that form in Portland cement mixes with the addition of strätlingite and C_2AH_8 (and increased quantities of calcium aluminate hydrates).

The porosity of mixtures produced with high calcium fly ash (HCFA) at different ages is plotted in Fig. 2.19 (Sideris 1996). HCFA replaced ordinary Portland cement (OPC) at different levels up to 40%. All cement pastes produced were with a water/cement ratio of 0.50. Porosity measurements were taken up to the age of 730 days (two years). The porosity of cement pastes at the age of 5475 days (15 years) was calculated using the cement hydration equation model (Sideris and Sideris 1997, 2003). Total porosity of fly ash cement pastes was slightly increased

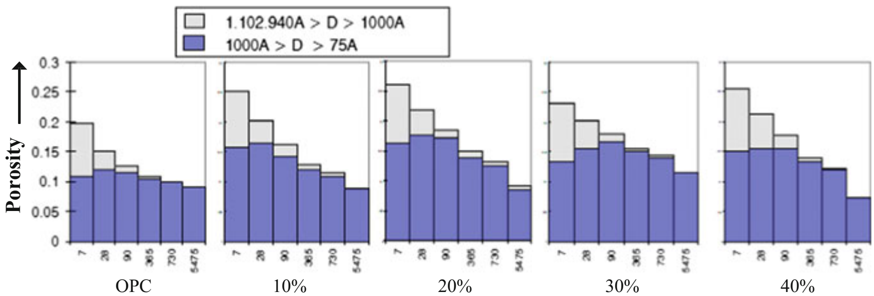

Fig. 2.19 Total (1.102.940 Å < D < 75 Å) and water permeable (1.102.940 Å < D < 1000 Å) porosity of cement pastes produced with high calcium fly ash (data taken from Sideris 1996)

at all ages as compared with OPC paste. However, the water permeable porosity was decreased or remained the same with the one measured on OPC pastes at ages greater than 90 days for replacement levels of 20–40%.

This pore refinement taking place at later ages is responsible for the impermeability observed in fly ash mixtures. Davis (1954) was among the first researchers who studied the permeability of concrete used for pipes and the effects of replacing 30 or 50% of the cement with Class F fly ash from two different sources. Fly ash concrete was found to be more permeable at the age of 28 days, especially at higher levels of replacement. However, the trend was reversed at the age of 180. At this age fly ash concrete was found to be significantly less permeable.

2.10.1 Carbonation

Kasai et al. (1983) studied the carbonation of mortar specimens produced with different types of cement and fly ash after 7 days of moist curing. The researchers observed that (i) carbonation was found to progress rapidly up to the age of 3 months and after that it slowed down; and (ii) the greater the coefficient of permeability of the specimen, the greater was its susceptibility against carbonation. Specimens prepared with fly ash cement exhibited greater carbonation depth than ordinary Portland cement specimens.

Nagataki and Ohga (1992) found that addition of fly ash increased the carbonation depth of mortars. However, longer curing periods reduced the rate of carbonation, and mortars with greater fly ash contents were found to be more sensitive to extension of the curing period. These results are consistent with the slower hydration and development of a discontinuous pore system in fly ash cement pastes.

Sideris et al. (2006) produced 9 different cement mortars using high calcium lignite fly ashes—HCFA—in replacement levels up to 60%. Different w/cm ratios were used in each case in order to keep the mixtures' fluidity constant. All specimens were water cured for 28 days. After this age they were exposed to indoor conditions. Carbonation measurements were taken for a time period of up to 18 months. The researchers reported that carbonation depths of all fly ash mixtures were greater than the one of the plain cement mixture. This finding was also reported by Papadakis et al. (1992). On the other hand, the carbonation rate, i.e., the increase in carbonation depth at later ages as compared with the one at the initial measurement (6 months), was greater with the plain cement mixture. Carbonation rate generally reduced, as the fly ash content increased. The researchers attributed this finding to the pore refinement phenomenon.

Sideris and Savva (2001) produced five different concrete mixtures using two natural pozzolans and two lignite fly ashes. All SCMs replaced Portland cement at a constant level of 20%. Concretes were produced with a w/cm ratio of 0.65 and the content of cementitious materials was 350 kg/m^3. Concrete specimens were fog cured for 28 days. After this age specimens were exposed in two different environments: (a) specimens of the first series were exposed to a coastal environment, 150 m away from the beach and left unprotected to the rain, and (b) specimens of the second series were exposed in indoor conditions. Carbonation measurements were performed at different ages up to 4 years.

Carbonation depth of blended cement mixtures was in both curing environments greater than the one of normal Portland cement mixture. Among all blended cement mixtures tested, specimens with pre-treated high calcium lignite fly ash performed the lowest carbonation rate, mainly due to the high CaO content of the ash.

Papadakis (2000a, b) examined the carbonation resistance of different mortars produced with low calcium fly ash (FL) and high calcium lignite fly ash (FH). Both ashes were used to replace cement or aggregates at percentages of up to 30%. All specimens were kept for 28 days in a laboratory air environment. They were then placed in a carbonation chamber with a controlled 3% concentration of CO_2, at a temperature of 25 °C, and relative humidity of 61% for 100 days. He reported that the carbonation depth decreased as aggregate replacement by fly ash increased (positive replacement on the wright of horizontal axis), and increased as cement replacement by fly ash increased (negative replacement on the left of horizontal axis). The lowest carbonation depth was observed for high-Ca fly ash, then for low-Ca fly ash produced concretes (Figs. 2.20 and 2.21).

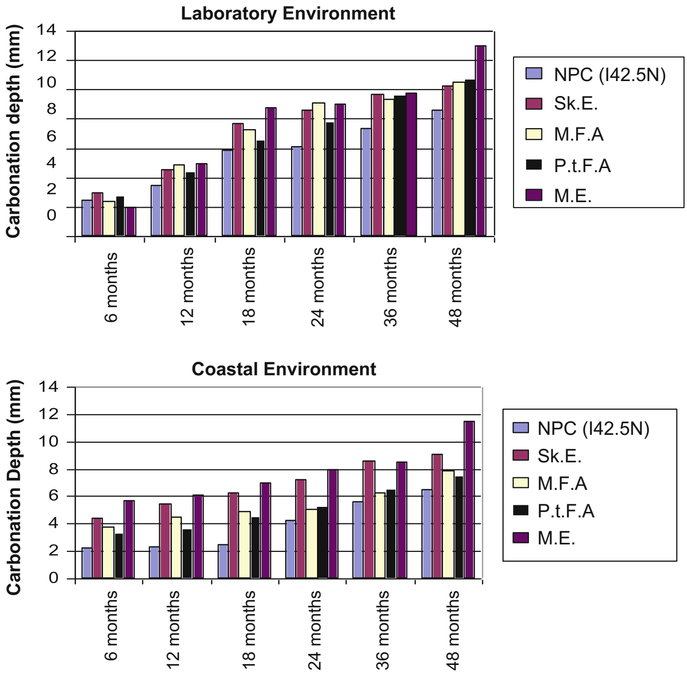

Fig. 2.20 Carbonation depth of concrete mixtures produced with ordinary Portland cement, natural pozzolans (SkE and ME) and lignite fly ashes (PtFA and MFA) (data taken from Sideris and Savva 2001)

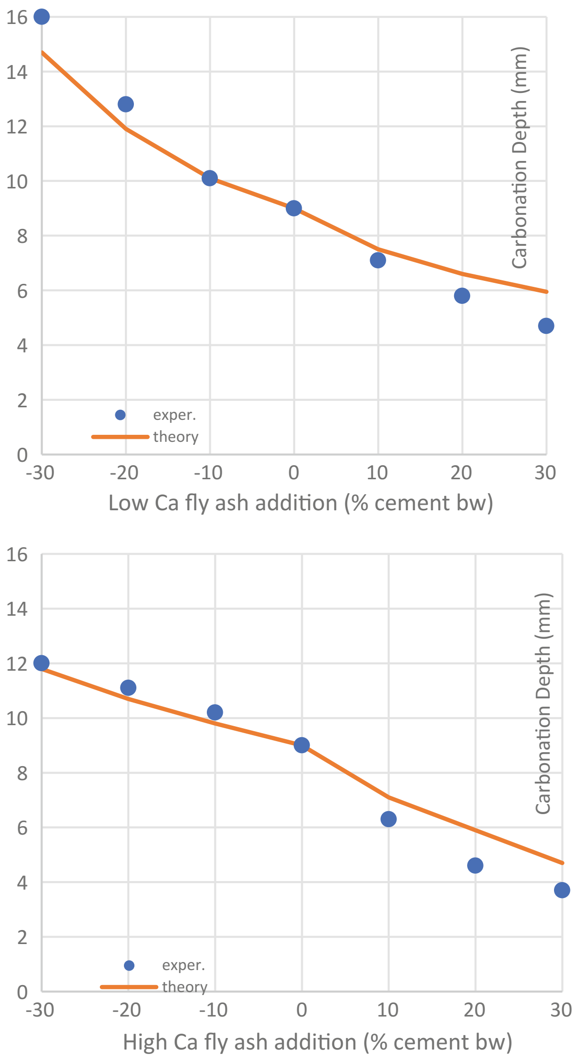

Fig. 2.21 Experimental results and model predictions of carbonation depth of mortars incorporating low-calcium fly ash and high-calcium fly ash as cement (left hand) or aggregate (right hand) replacement (data taken from Papadakis 2000a, b)

The influence of fly ash on carbonation depth of concrete mixtures depends on many parameters such as:

- the chemical and mineralogical composition of the ash, the fineness of the ash.
- the water to cementitious materials ratio (c/cm),
- the level of replacement and the type of replacement (replacing cement or aggregates),
- the type of ordinary Portland cement used (chemical composition and fineness), and the curing period of the specimens.

One must be very careful when comparing some of the conflicting data available in the literature due to the parameters mentioned above.

2.10.2 Resistance to Chloride Ingress

There are many research results available in the literature in the majority of which researchers report that fly ash improves the resistance of concrete to chloride ion penetration, however the extent of the improvement depends on the following factors:

- the chemical and mineralogical composition,
- the replacement level and the fineness of the ash,
- the w/c, and to a lesser extent, the composition and fineness of the Portland cement used,
- the maturity of the concrete,
- the exposure conditions (mainly temperature and carbonation of the concrete), and,
- the extension of the initial curing period of the mixtures.

Papadakis (2000a, b) examined the resistance to chloride ingress of different mortars produced with low calcium fly ash (FL) and high calcium lignite fly ash (FH) by using the Rapid Chloride Permeability test (Fig. 2.22). Both ashes were used to replace cement or aggregates at percentages of up to 30%. The electrical charge passed through the control specimen may be higher than 4000 °C. This quite high value was due to high cement paste volume and the absence of coarse aggregate. All specimens incorporating fly ashes, whether it substituted aggregate or cement, exhibited lower electrical charge.

Most researches available in the literature focus on the chloride permeability of fly ash mixtures measured according to the standards at the age of 28 days. However, resistance of concrete to chloride penetration increases as the concrete matures. As mentioned above both total porosity and permeability of concrete containing fly ash is significantly reduced at later ages.

Thomas and Bamforth (1999) measured the chloride diffusion coefficient of different concrete blocks exposed to the south-eastern coast of the United Kingdom. Concrete blocks were produced with three different mixtures containing 100% ordinary Portland cement, 30% fly ash and 70% slag. All mixtures had the same compressive strength at the age of 28 days and were produced with w/cm ratio of 0.66, 0.54 and 0.44 respectively.

Results from this study indicated that at early ages (e.g., 28 days), the diffusivity of concrete containing 30% fly ash may be expected to have a similar chloride ion diffusivity as an equivalent grade Portland cement concrete. However, after approximately 2 years the diffusivity of the fly ash concrete may be one order of magnitude lower than the Portland cement and decrease further at later ages. This

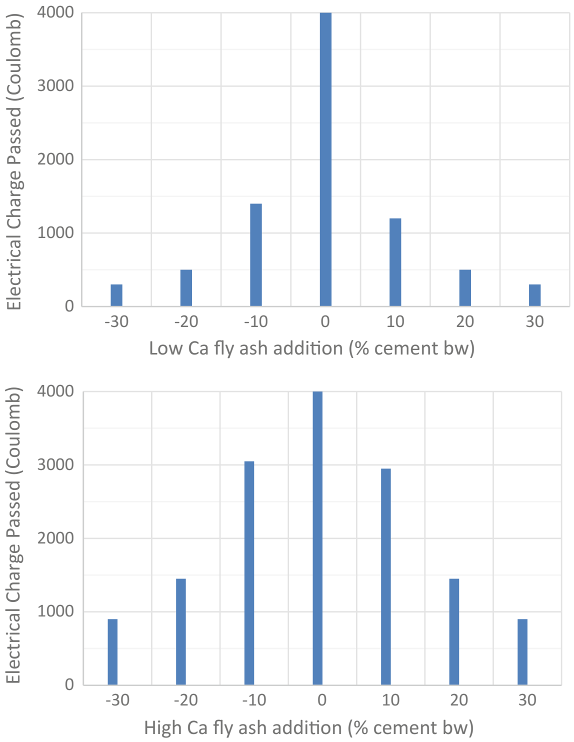

Fig. 2.22 Rapid chloride permeability of mortars incorporating low-calcium fly ash and high-calcium fly ash as cement (left hand) or aggregate (right hand) replacement (data taken from Papadakis 2000a, b)

reduction in the chloride diffusion coefficient of fly ash concrete mixtures has a significant impact on the long-term performance of concrete in chloride environments and on the interpretation of data from tests based on estimating the chloride diffusion coefficient (D28 value). This long term reduction in chloride diffusion coefficient is well known as the *aging factor*. The chloride diffusion coefficient at a particular time t during the service life of a structure is calculated using the following equation:

$$D_{app(t)} = D_{app(to)} \left(\frac{to}{t}\right)^a$$

where

Dapp (to) is the apparent diffusion coefficient measured at a reference time of to (usually at the age of 28 days)

a is the aging-factor giving the decrease over time of the apparent diffusion coefficient.

According to fib Bulletin 34 (2006) the aging factor *a* has a value of 0.30 for ordinary Portland cement and a value of 0.60 for fly ash cements with a fly ash replacement higher than 20%.

2.10.3 Sulfate Resistance

The principal method available to limit sulfate attack is the use of a sulphate resistant cement (Type II or Type V Portland cements instead of Type I Portland cement according to ASTM (2015) or sulfate resistant (SR) cements as described in EN197-1 [2013]) and by ensuring that the concrete has a low w/cm. Among the SR cements described in EN197-1, sulfate resistant pozzolanic cements CEM IV/A-SR and CEM IV/B-SR should contain combinations of natural pozzolanas and siliceous fly ash only up to a content of 55% per weight of cement. In this case the C_3A content of the cement should be lower than 9%, almost double the upper limit value of sulfate resistant Portland cement CEM I-SR5. Another alternative is the use of additives – such as natural pozzolanas, fly ashes or silica fume. Pozzolanic materials have an important role in the long-term durability of mixtures exposed in sulfate environments because they contribute chemically and physically to their properties. Their effect is thought to be explained by two primary mechanisms (Tikalsky et al. 1990): The "dilution effect" (decrease of the C_3A content of the binder when they replace a portion of Portland cement) and the "pozzolanic effect" (formation of secondary CSH). The latter results in a less permeable mortar, from which the excess calcium hydroxide has been consumed and rendered unavailable for the expansive formation of ettringite and gypsum compound (Mehta 1981; Al-AMoudi 1999).

Several attempts have been made in order to predict the sulfate resistance of a fly ash based on its chemical composition. Among them the first is that of Dunstan (1980). He introduced the "Resistance value" which was:

$$R = \frac{CaO - 5}{Fe_2O_3}$$

According to Dunstan, a fly ash improves the sulfate resistance of the mixture if R <1.5, whereas this decreases if the R-value of the ash is higher than 3. In a later research Dunstan (1987) reported that the sulfate resistance of mortars tested according to ASTM C-1012 will be improved, if fly ash with R ≤ 3.5 is used.

In other research (Tikalsky 1990) the ratio CaO/SiO_2 of the fly ash was introduced as an indicator of their contribution to the sulfate resistance of mixtures. According to the researchers, fly ash with CaO/SiO_2 ratio less than 0.25, contained no detectable C_3A and provided a level of resistance to sulfate attack equal or greater than that of cement Type II alone. When fly ash had a CaO/SiO_2 ratio greater than 0.60, it reduced the sulfate resistance of the mixtures. Erdogan et al. (1992) reported that the (Free CaO)/Fe_2O_3 and (C_3A + Free alumina)/(Free CaO) ratios of the cement-high lime fly ash mixtures can be used to determine their sulfate susceptibility. According to the authors, there is a clear relationship between these ratios and the sulfate resistance of the mixtures: sulfate resistance increases when the (Free CaO)/Fe_2O_3 ratio decreases and the (C_3A + Free alumina)/(Free CaO) ratio increases.

Mehta (1986a, b) observed that if a fly ash is high in reactive aluminate phases it will not improve the sulfate resistance of concrete. He found that sulfate resistance depends on the type of aluminate phases at the time of sulfate exposure. Upon immersion in sulfate solution, pastes containing monosulfoaluminate or calcium aluminate hydrate suffered from strength loss due to ettringite formation. In contrast blended cement pastes containing fly ash that promoted the formation of ettringite prior to immersion into sulfate solution showed superior resistance. The free SiO_2, the free CaO and the fineness of the material are also of great importance (Mehta 1981; Stamatakis et al. 1997).

Fay and Pierce (1989) performed a study on air-entrained fly ash concrete using three fly ashes from the United States, representing a range of CaO contents of 11–28.8% and used 10–100% fly ash by weight of the total cementitious material. The specimens were cured for 14 days in a 100% humidity room and for another 14 days in a 50% humidity room before they were immersed in 10% Na_2SO_4 solution or subjected to cyclic soaking and drying phases in 2.1% Na_2SO_4 solution to generate data by accelerated test. They concluded that both low-calcium Class C and Class F fly ashes can be effective cement replacements in controlling sulfate expansion, however Class F fly ash at replacement level of 30% significantly improved the sulfate durability for the cementitious levels and appeared to be optimum for both test conditions employed in their investigation, while for low-calcium Class C fly ash replacement levels were suggested to be greater than 30% and for high-calcium Class C fly ashes the corresponding suggested levels were greater than 75% to achieve the most improved sulfate durability.

Sideris et al. (2006) investigated the sulfate resistance of 8 different cement mortars prepared using two high calcium lignite fly ashes—MFA and PFA—in replacement levels up to 60%. Different w/cm ratios were used in each case in order to keep the mixture's fluidity constant. All cements used in this research were produced in the laboratory by mixing clinker, pozzolanic material and gypsum ($CaSO_4 \cdot 2H_2O$). The SO_3 content of the pozzolanic material was taken into consideration and the added gypsum was properly adjusted in order to keep the total SO_3 content of the binder (clinker + pozzolan) equal to 3.5%. This was not achieved for the mixtures with a high PFA content. The high SO_3 of PFA increased the total available amount of SO_3 of the mix (clinker + gypsum), although no gypsum was added. The sulfate resistance of binders was evaluated using expansion measurements of mortar prisms immersed in a 5% Na_2SO_4 solution, according to ASTM C1012-95 (2015), up to the age of two years.

They concluded that lignite fly ashes, with high CaO and SO_3 content may have a positive effect on the sulfate resistance of blended cements. Specimens containing PFA fly ash blended cements gave the smallest expansion among all cement mixtures tested in this research and developed high compressive strength from early ages. These specimens also gave the least reduction in compressive and flexural strengths due to sulfate attack. On the other hand specimens containing MFA fly ash blended cements gave the worst performance since they totally deteriorated very fast.

Table 2.9 Compressive and flexural strength loss (%), final expansion (%), deterioration age and first crack observed age (months) for all mixtures (data taken from Sideris et al. 2006)

Mixture	Compressive strength loss (%)	Flexural strength loss (%)	One year expansion (%)	Final expansion (%)	Deterioration age (months)	First crack (months)
CEM I 42.5N	30	67.5	1.10	1.10	6–8	6
10% FA	(–)	(–)	0.544	0.544	3–4	No cracks
20% MFA	(–)	(–)	0.428	0.428	3–4	2
30% MFA	30	(–)	0.408	0.408	4–6	No cracks
30% PFA	19	17	0.033	0.049	12–16	No cracks
40% PFA	15.3	14.7	0.033	0.055	16–20	16
50% PFA	−0.8[a]	−153[a]	0.016	0.022	Not deteriorated	No cracks
60% PFA	−8[a]	−179[a]	0.012	0.016	Not deteriorated	No cracks

–Totally deteriorated, not measured;
[a]Strength increased

The R-value for the two ashes used were RMFA = 1.86 and RPFA = 1.21. Despite the fact that in both cases the R-value is much less than 3.5, their contribution to the sulfate resistance of the mixtures was totally different: MFA had a deleterious effect, whereas PFA had a beneficial one. The two examined lignite fly ashes had similar chemical composition but they had totally different performance regarding the sulfate resistance of the mixtures, indicating that it is the mineralogical composition that really counts and makes the difference (Table 2.9).

2.10.4 Freezing and Thawing Resistance

Addition of fly ash results to changes in pore size distributions due to pozzolanic reactions (Schiepl and Hardtle 1994). The phenomenon of pore refinement as a result of pozzolanic reactions leads to the breaking of continuity of the capillary pore structure. As reported by Malhotra et al. (1982) the pozzolanic reactions alter the pore structure of the cement paste and thus densify the transition zone between the paste and aggregates.

There are many researches in the literature dealing with freeze and thawing resistance of fly ash concretes (Perenchio and Klieger 1976; Majko and Pistilli 1984; Yuan and Cook 1983; Virtanen 1983; Carette and Malhotra 1984; Joshi 1987; Malhotra et al. 1990; Schmidt 1992; Joshi et al. 1993; Thomas 1999; Naik et al. 2003; Knutsson 2010). The majority of them conclude that air content has the greatest influence on the freeze–thaw resistance of concrete and that addition of fly ash had no influence on the freeze–thaw resistance of concrete if the air content of the mixtures is kept constant. However, if the fly ash contains some residual unburnt carbon, higher dosages of air entrainers may be used to achieve target air content and sometimes unstable air may occur.

2.10.5 Alkali Aggregate Reactions

Replacing cement with SCMs generally reduce expansion due to AAR (Thomas 2011). This has in general been thought to be caused by a reduction in pH (i.e. hydroxyl concentration) of pore water and a lower content of calcium hydroxide. In the author's opinion, the reduction in pH will be the case as long as the alkalis are busy in dissolving SCM in a catalytic way, but the implication is that this may cause only a delay of AAR until the SCM has reacted totally.

According to Thomas (2013) the level of cement replacement required to control AAR expansion increases as (1) SiO_2 content of SCM decreases, (2) CaO of SCM increases, (3) alkali content of SCM increases, (4) alkali availability in the concrete increases, and (5) reactivity of the aggregate increases. Shehata and Thomas (2000) showed that low calcium fly ashes (ASTM Class F) are much more effective in reducing AAR expansion (typical cement replacement level >20%) than high calcium fly ashes (ASTM class C). Shehata and Thomas (2002) demonstrated that the required level of low calcium fly ash could be reduced to 10% when combined with 5% SF as a ternary blend.

Some have suggested that the presence of alumina in SCMs contributes to prevent the release of alkali back to the pore solution by binding in the hydration products. However, Chappex and Scrivener (2012a) showed that this effect is extremely small, and instead it was found that alumina is an inhibitor of silica dissolution Chappex and Scrivener 2012b, 2013 as in their system with metakaoline as SCM.

References

Abdun Nur EA (1961) Fly Ash in concrete evaluation. Highways Res Bull 281

ACI committee 226 (1987) 3R-87: Fly ash in concrete. ACI Mater J 11:381–409

Al-Amoudi OSB (1999) Mechanisms of sulfate attack in plain and blended cements: a review. In: Proceedings of the conference extending performance of concrete structures, international congress "creating with concrete", Dundee, pp 247–260

Alonso JL, Wesche K (1992) Characterization of Fly Ash. Fly ash in concrete, properties and performance, RILEM Report, E & FN Spon, pp 3–23(1992)

ASTM C 618 (2015) Standard specification for coal fly ash and raw or calcined natural pozzolan for use as a mineral admixture in concrete. Annual Book of ASTM Standards, Philadelphia

ASTM C1012-95 (1995) Length Change of hydraulic-cement mortars exposed to a sulfate solution. American Society for Testing and Materials, vol 04.01, Philadelphia, USA

ASTM C150-95 (2015) Standard specification for Portland cement. American Society for Testing and Materials, vol 04.01, Philadelphia, USA
Braun H, Gebauer J (1983) Moeglichkeiten und grenzen der verwendung von flugaschen im zement. Zement-Kalkgips (ZKG) 36(5):254–258
Brown JH (1982) The strength and workability of concrete with PFA substitution. In: Proceedings International Symposium on the Use of PFA in Concrete, University of Leeds, England, pp 151–161
Camoes A, Agiar B, Jalali S (2003) Durability of low cost high performance fly ash concrete. In: The 2003 International Ash Utilisation Symposium, Center for Applied Energy Research, Kentucky, USA
Carette GG, Malhotra VM (1984) Characterization of Canadian fly ashes and their performance in concrete. Division report MRP/MSL 84–137, CANMET, Energy, Mines and Resources, Canada
Central Electricity Generating Board (CEGB) (1967) PFA data book. London
Chappex T, Scrivener KL (2012a) Alkali fixation of C-S–H in blended cement pastes and its relation to alkali silica reaction. Cem Conc Res 42:1049–1054
Chappex T, Scrivener KL (2012b) The influence of aluminum on the dissolution of amorphous silica and its relation to alkali silica reaction. Cem Conc Res 42:1645–1649
Chappex T, Scrivener KL (2013) The effect of aluminum in solution on the dissolution of amorphous silica and its relation to cementitious systems. J Am Ceram Soc 96:592–597
Chindaprasirt P, Chotithanorm C, Cao HT, Sirivivatnanon V (2007) Influence of fly ash fineness on the chloride penetration of concrete. Construct Build Mater 21(2):356–361
Costa U, Massazza F (1983) Some properties of pozzolanic cements containing fly ashes. In: Proceedings of the first CANMET/ACI international conference on the use of fly ash, silica fume, slag and other mineral by-products in concrete, ACI SP-79, pp 235–254
Davies RE (1954) Pozzolanic materials—with special reference to their use in concrete pipe. Technical memo, American Concrete Pipe Association
Davis RE, Carlson RW, Kelly JW, Davis HE (1937) Properties of cements and concretes containing fly ash. J Am Concr Inst 33:577–612
Demirboğa R, Türkmen I, Karakoc MB (2007) Thermo-mechanical properties of concrete containing high-volume mineral admixtures. Build Environ 42(1):349–354
Diamond S (1985) Selection and use of fly ash for high way concrete. Joint Highway Research Project, Purdue University, Indiana
Dunstan ER Jr (1980) A possible method for identifying fly ashes that will improve sulfate resistance. Cem Concr Aggregates 2(1):20–30
Dunstan ER (1987) Sulfate resistance of fly ash concretes: the R-value. In: Proceedings of the katharine and bryant mather international conference on concrete durability, ACI SP-100, pp 2027–2040
Efes Y (1980) Untersuchungen ueber einfluesse auf die spezifische oberflaeche nach blaine von steinkohlenflugaschen und ueber die auswirkungen des blaine-wertes auf andere eigenschaften. Tizfachberichte 104(1):20–29
Elsageer M (2011) Early age strength development of fly ash mixes as affected by temperature (Ph. D. thesis). The University of Liverpool
EN 206-13 (2013) European Committee for Standardization, European Standard EN 206: Concrete —specification, performance, production and conformity. CEN, Brussels
Erdogan TY, Tokyay M, Ramyar K (1992) Investigations on the sulfate resistance of high-lime fly ash incorporating PC-FA mortras. In: Proceedings of the 4th CANMET/ACI international conference on fly ash, silica fume, slag and natural pozzolans in concrete, ACI SP-132, Istanbul, pp 271–280
Erdoğdu K, Türker P (1998) Effects of fly ash particle size on strength of Portland cement fly ash mortars. Cem Concr Res 28(9):1217–1222
EUROGYPSUM-ECOBA-VGB (2005) FGD Gypsum—Quality criteria and analysis methods

Fay KFV, Pierce JS (1989) Sulfate resistance of concretes with various fly ashes. ASTM standardization news, pp 32–37

Fib Bulletin 34 (2006) Model code for service life design, fib (ISBN 2-88394- 074-6)

Gebler SH, Klieger P (1986) Effect of fly ash on physical properties of concrete. In: Proceedings of the 2nd international conference on fly ash, silica fume, slag, and natural pozzolans in concrete, ACI SP-91, vol 1, pp 1–50

Gomes S, François M, Abdelmoula M, Refait Ph, Pellissier C, Evrard O (1999) Characterization of magnetite in silico-aluminous fly ash by SEM, TEM, XRD, magnetic susceptibility, and Mössbauer spectroscopy. Cem Concr Res 29(11):1705–1711

Haque MN, Langan BW, Ward MA (1988) High fly ash concretes. ACI Mater J 8(1):54–60

Hatzitheodorou A (2007) In-situ strength development of concretes with supplementary cementitious materials (Ph.D. thesis). The University of Liverpool

Hellenic Technical Specification (2007) Greek gly ashes. J Gov Hellenic Democracy Bull 2(551) (in Greek)

Helmuth R (1987) Fly ash in cement and concrete, PCA, Skokie, Ill., p 203

Idorn GM, Henriksen KR (1984) State of the art for fly ash uses in concrete. Cem Concr Res 14 (4):463–470

Jaturapitakkul C, Kiattikomol K, Sata V, Leekeeratikul T (2004) Use of ground coarse fly ash as a replacement of condensed silica fume in producing high-strength concrete. Cem Concr Res 34 (4):549–555

Jiang LH, Malhotra VM (2000) Reduction in water demand of non-air-entrained concrete incorporating large volumes of fly ash. Cem Concr Res 30(11):1785–1789

Joshi RC (1979) Sources of pozzolanic activity in fly ashes—a critical review. In: Proceedings of the 5th international fly ash utilization symposium, Atlanta, GA, USA, pp 610–623

Joshi RC (1987) Effect of a sub-bituminous fly ash and its properties on sulfate resistance of sand cement mortars. J Durab Build Mater 4:271–286

Joshi RC, Lohtia RP (1993) Effects of premature freezing temperatures on compressive strength, elasticity and microstructure of high volume fly ash concrete. In: Proceedings of third canadian symposium on cement and concrete, Ottawa, Canada

Joshi RC, Lohtia RP, Salam MA (1993) High strength concrete with high volumes of Canadian sub-bituminous coal ash. In: Proceedings of the third international symposium on utilization of high strength concrete, Lillachammer, Norway

Kasai Y, Matsui I, Fukushima U, Kamohara H (1983) Air permeability of blended cement mortars. In: Proceedings of the 1st international conference on the use of fly ash, silica fume, slag and other mineral by-products in concrete. ACI SP 29, pp 435–451

Khan MI (2010) Rheological characteristics of HPC containing composite cementitious materials. Concrete Technology—Journal of the Concrete Plant International, No 02/10, Germany, pp 78–84

Klieger P, Perenchio WF (1972) Laboratory studies of blended cement: Portland- pozzolan cements. Research and Development Bulletin RD013, Portland cement Association, USA

Knutsson A (2010) Freeze/Thaw durability of concrete with fly ash. Master of Science Thesis in the Master's Programme Structural engineering and Building Performance Design, Department of Civil and Environmental Engineering, Division of Building Technology, Building Materials, Chalmers University of Technology, Göteborg, Sweden, Master's Thesis 2010:154

Korac V, Ukraincik V (1983) Studies into the use of fly ash in concrete for water dam structures. ACI Special Publication SP 79:173–185

Lane RO, Best JF (1982) Properties and use of fly ash in Portland cement concrete. Concr Int 4 (7):81–92

Majko RM, Pistilli MF (1984) Optimizing the amount of Class C fly ash in concrete mixtures. Cem Concr Aggregates CCAGDP 6(2):105–119

Malhotra VM, Carette GG, Bremmer TW (1982) Durability of concrete containing granulated blast furnace slag or fly ash or both in Marine environment. CANMET, EMR, Canada Report 80-18E

Malhotra VM, Caratte GG, Bilodeau A, Sivasundram V (1990) Some aspects of durability of high volume ASTM class F (Low-calcium) fly ash concrete. Mineral sciences laboratories [Division report MSL-90–20 (OP & J)]

Manmohan D, Mehta PK (1981) Influence of pozzolanic, slag, and chemical admixtures on pore size distribution and permeability of hardened cement pastes. Cem Concr Aggregates 3(1):63–67

McCarthy GJ, Johansen DM, Steinwand SJ (1988) X-ray diffraction analysis of fly ash. In: Barrett CS et al (eds) Advances in X-Ray analysis, vol 31. Plenum Press, New York

McCarthy GJ, Berry EE, Majko RM (1998) Fly ash and coal conversion by-products: characterization, utilization, and disposal IV. In: Materials research society symposium proceedings. (ISBN 978-0931837814)

Mehta PK (1981) Studies on blended Portland cements containing Santorin earth. Cem Concr Res 11(3):507–518

Mehta PK (1986a) Effect of fly ash composition on sulfate resistance of cements. ACI Mat J 83 (6):994–1000

Mehta PK (1986b) Concrete: structure, properties and materials. Prentice Hall, Englewood Cliffs

Mehta PK (1988) Standard specifications for mineral admixtures—an overview. ACI SP 91:637–658

Mehta PK (1994) In: Khayat IH, Aitcin PC (eds) Symposium on durability of concrete, Nice, France pp 99–118

Monzo J, Paya J, Peris-Mora E, Borrachero MV (1995) Mechanical treatment of fly ashes: strength development and workability of mortars containing ground fly ashes. In: Proceedings of 5th CANMET/ACI international conference on the use of fly ash, silica fume, slag and natural pozzolans in concrete, pp 339–354

Nagataki S, Ohga H (1992) Combined effect of carbonation and chloride on corrosion of reinforcement in fly ash concrete. In: Proceedings 4th international conference on the use of fly ash, silica fume, slag, and natural pozzolans in concrete, Istanbul, Turkey, pp 227–244

Naik TR, Ramme BR, Kraus RN, Siddique R (2003) Long-term performance of high-volume fly ash concrete pavements. ACI Mater J 100(2):150–155

Neville AM (1995) Properties of concrete, 4th edn. Pearson, Harlow, UK

Ng S, Justnes H (2016) Influence of plasticizers on the rheology and early heat of hydration of blended cements with high content of fly ash. Cem Concr Comp 65:41–54

Owens PL (1979) Fly ash and its usage in concrete. Concr Soc J 13(7):21–26

Papadakis VG (1999) Effect of fly ash on Portland cement systems. Part I: Low calcium fly ash. Cem Conc Res 29:1727–1739

Papadakis VG (2000a) Effect of supplementary cementing materials on concrete resistance against carbonation and chloride ingress. Cem Conc Res 30(1):291–299

Papadakis VG (2000b) Effect of fly ash on Portland cement systems. Part II: High calcium fly ash. Cem Conc Res 30:1647–1654

Papadakis VG, Tsimas S (2002) Supplementary cementing materials in concrete: Part I: efficiency and design. Cem Concr Res 32(10):525–1532

Papadakis VG, Fardis MN, Vayenas CG (1992) Hydration and carbonation of pozzolanic cements. ACI Mat J 89(2):119–130

Papayianni J (1996) Standards for Using fly ashes in concrete production and use of greek fly ashes. In: Proceedings of the 12th hellenic congress on concrete, Lemesos, Cyprus, pp 146–155 (in Greek)

Papayianni I (2010a) Use of calcareous ash in civil engineering. In: Proceedings of the international conference eurocoalash 2010, pp 45–58

Papayianni I (2010b) Use of calcareous ash in civil engineering. In: Proceedings of Eurocoalash 2010, pp 58–72

Papayianni-Papadopoulou J (1981) Research for the possibility of using Ptolemaida's fly ash for concrete production. Ph.D. Dissertation, Aristotle University of Thessaloniki, Thessaloniki, Greece (in Greek)

Perenchio WF, Klieger P (1976) Further laboratory studies of Portland-pozzolan cements. Portland Cement Research and Development Bulletin RD041.01T

Poole JL, Rinding K, Juenger M, Folliard K, Schindler A (2010) Effect of supplementary cementitious materials on apparent activation energy. J ASTM Int 7(9):1–16

Ramakrishan V, Coyle WV, Brown J, Tluskus A, Benkataramanyam P (1981) Performance characteristics of concrete containing fly ash. In: Diamond S (ed) Proceedings symposium on fly ash incorporation in hydrated cement systems, Materials Research Society, Boston, pp 233–243

Ravina D (1980) Optimized determination of PFA fineness with reference to pozzolanic activity. Cem Concr Res 10(4):573–580

Rodway LE, Fedriko WM (1989) Superplasticized high volume fly ash structural concrete. ACI SP 114(1):98–112

Roy DM (1987) Hydration of blended cements containing slag, fly ash, or silica fume. In: Proceedings of meeting institute of concrete technology, Coventry, UK, pp 29–39

Schiepl P, Hardtle R (1994) Relationship between durability and fore structure properties of concretes containing fly ash. In: Khayat IH, Aitcin PC (eds) P.K. Mehta symposium on durability of concrete, Nice, France, pp 99–118

Schmidt M (1992) Cement with inter-ground additives—capabilities and environmental relief. Part 2. Zement-Kalk Gips

Shehata MH, Thomas MDA (2000) The effect of fly ash composition on the expansion of concrete due to alkali silica reaction. Cem Conc Res 1063–1072

Shehata MH, Thomas MDA (2002) Use of ternary blends containing silica fume and fly ash to suppress expansion due to alkali-silica reaction in concrete. Cem Conc Res 341–349

Siddique R (2003) Effect of fine aggregate replacement with class F fly ash on the mechanical properties of concrete. Cem Concr Res 33(4):539–547

Siddique R, Khan MI (2011) Supplementary cementing materials. Springer (ISBN 978-3-642-17865-8)

Sideris KK (1996) Influence of natural pozzolanas and fly ash on the compressive strength and porosity of cement mortars and concretes. Ph.D. dissertation, Xanthi (in Greek)

Sideris KK, Savva A (2001) Resistance of fly ash and natural pozzolans blended cement mortars and concrete to carbonation, sulfate attack and chloride ion penetration. In: Proceedings of the seventh CANMET/ACI international conference on fly ash, silica fume, slag and natural pozzolans in concrete, Madras, India, CANMET/ACI SP 119 Volume II, pp 275–293

Sideris K, Sideris KK (1997) The cement hydration equation and its application to several hydration criteria according to the literature. In: Justnes H (ed) Proceedings of the 10th international congress on the chemistry of cement, Gothenburg, Sweden, 2ii061

Sideris K, Sideris KK (2003) Ten years cement hydration equation and its application to chemistry and physics of cement paste, mortar and concrete, Xanthi, p 320 (ISBN 960-343-722-0)

Sideris KK, Savva AE, Baltzopoulou KD, Economou CM, Sideris K (1997) Influence of silica and limestone aggregates on the final compressive strength of blended cement concretes prepared with the use of three different pozzolanas. In: Justnes H (ed) Proceedings of the 10th international congress on the chemistry of cement, Göthenburg, Sweden

Sideris KK, Savva A, Papayianni J (2006) Sulfate attack and carbonation of plain and blended cements. Cem Concr Comp 28(1):47–56

Sivasundram V, Carette GG, Malhotra VM (1990) Selected properties of high volume fly ash concretes. ACI Concrete International, pp 47–50

Soutsos M, Hatzitheodorou A, Kwasny J, Kanavaris F (2016) Effect of in situ temperature on the early age strength development of concrete with supplementary cementitious materials. Constr Build Mat 103:105–116

Stamatakis M, Fragulis D, Papageorgiou A (1997) Quality of Greek fly ash and its influence on blended cement production. In: Proceedings of the conference use of fly ash on construction Greece, pp 213–228, 3–4 October 1997 (in Greek)

Tattersall GH, Banfill PFG (1983) The rheology of fresh concrete. Pitman, London

Taylor HFW (1997) Cement chemistry, 2nd edn. Thomas Telford, London

Thomas MDA (1999) Laboratory and field studies of salt scaling in fly ash concrete. In: Setzer MJ, Auberg R (eds) Proceedings of the RILEM international workshop on frost resistance of concrete with and without deicing chemicals, Essen, Germany, Sept 1997

Thomas MDA (2011) The effect of supplementary cementing materials on alkali silica reaction: a review. Cem Concr Res 41:1224–1231

Thomas M (2013) Supplementary cementing materials in concrete. CRC Press, Taylor & Francis Group, pp 190 (ISBN 978-1-4665-7298-0)

Thomas MDA, Bamforth PB (1999) Modelling chloride diffusion in concrete: effect of fly ash and slag. Cem Concr Res 29(2):487–495

Tikalsky PJ, Carrasquillo RL, Snow PG (1990) Sulfate resistance of concrete containing fly ash. In: Proceedings of the G. M. Idorn international symposium on durability of concrete, ACI SP-131, pp 255–265

Virtanen J (1983) Freeze–thaw resistance of concrete containing blast furnace slag, fly ash or condensed silica fume. In: Proceedings of the 1st international conference on the use of flyash, silica fume, slag and other mineral by-products, ACI SP-79, pp 923–942

Wesche K (1991) Fly Ash in Concrete: Properties and Performance. E & FN Spon, London

Whiting D (1989) Strength and durability of residential concretes containing fly ash, Research and Development Bulletin RD099, Portland Cement Association, http://www.cement.org/pdf_files/RD099.pdf, pp 42

World Coal Institute (2003) UK's energy future?, Ecoal, The News Letter of the World Coal Institute, vol 45, 3, (2003)

www.ecoba.com/ecobaccpprod.html (2007) Production and utilization of CCP's in Europe [EU 15]

Yuan RL, Cook JE (1983) Study of class C fly ash in concrete. In: Proceeding of the 1st international conference on the use of fly ash, silica fume, slag, and other mineral byproducts in concrete, ACI SP-79 307–319

Yuan RZ, Jin SX, Qian JC (1982) Effects of fly ash on rheology of fresh cement paste. In: Proceedings materials and research society symposium, pp 182–191

Chindaprasirt, P., Chotithanorm, C., Cao, H.T., Sirivivatnanon, V.: Influence of fly ash fineness on the chloride penetration of concrete. Construct. Build. Mater. 21(2), 356–361 (2007).

http://www.springer.com/978-3-319-70605-4

Properties of Fresh and Hardened Concrete Containing
Supplementary Cementitious Materials
State-of-the-Art Report of the RILEM Technical
Committee 238-SCM, Working Group 4
De Belie, N.; Soutsos, M. .; Gruyaert, E. (Eds.)
2018, XXVIII, 315 p. 142 illus., Hardcover
ISBN: 978-3-319-70605-4