

# Chapter 1

## Fly Ash

### 1.1 Introduction

The *fly ash*, also known as pulverised fuel ash, is produced from burning pulverized coal in electric power 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, 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, approximately 85–99% 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 produced from thermal power plants is a variable material because of several factors. These factors are (1) type and mineralogical composition of the coal; (2) degree of coal pulverization; (3) type of furnace and oxidation conditions; and (4) 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-h-period.

Fly ash particles size is primarily depends upon the type of dust collection equipment. It is generally finer than Portland cement. Diameter of fly ash particles ranges from less than 1–150  $\mu\text{m}$ . 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 ( $\text{SiO}_2$ ) (both amorphous and crystalline), aluminium oxide ( $\text{Al}_2\text{O}_3$ ) and calcium oxide ( $\text{CaO}$ ), both being endemic ingredients in many coal bearing rock strata.

### ***1.1.1 Handling of Fly Ash***

Generally, collected fly ash is typically conveyed pneumatically from the electro static precipitators ESP or filter fabric hoppers to storage silos where it is kept dry pending utilization or further processing, or to a system where the dry ash is mixed with water and conveyed (sluiced) to an on-site storage pond. The collected dry ash is normally stored and handled using equipment in a similar way the Portland cement is handled:

- Fly ash is stored in silos, domes and other bulk storage facilities
- It can be transferred using air slides, bucket conveyors and screw conveyors, or it can be pneumatically conveyed through pipelines under positive or negative pressure conditions
- It is transported to markets in bulk tanker trucks, rail cars and barges/ships
- It can be packaged in super sacks or smaller bags for specialty applications

Dry collected fly ash can also be moistened with water and wetting agents, whenever needed/applicable, using specialized equipment and hauled in covered dump trucks for special applications such as structural fills. Water conditioned fly ash can be stockpiled at jobsites. Exposed stockpiled material should be kept moist or covered with tarpaulins, plastic, or equivalent materials to prevent dust emission.

### ***1.1.2 Environmental Benefits of Using Fly Ash***

Utilization of fly ash in cement and concrete has significant environmental benefits such as

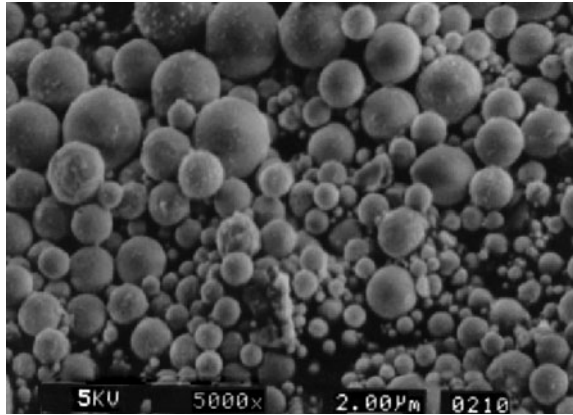
- Increasing the life of concrete roads and structures by improving concrete durability,
- Reduction in energy use and greenhouse gas and other adverse air emissions when fly ash is used to replace or displace manufactured cement.
- Reduction in amount of coal combustion products that must be disposed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

## **1.2 Properties of Fly Ash**

### ***1.2.1 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

**Fig. 1.1** Fly ash particles at  $\times 5,000$  magnification



ranges between 10 and 100  $\mu\text{m}$  (Fig. 1.1). These small glass spheres improve the fluidity and workability of fresh concrete. Fineness is one of the important property 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 color is attributed to elevated unburned carbon (LOI) content. Fly ash color is usually very consistent for each power plant and coal source.

### ***1.2.2 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 5  $\mu\text{m}$  (#325) sieve. ASTM C618 [5] limits the maximum amount of fly ash retained on the 45  $\mu\text{m}$  (#325) mesh sieve on wet sieving as 34%. Generally, a large fraction of ash particle is smaller than 3  $\mu\text{m}$  in size. In bituminous ashes, the particle sizes range from less than 1 to over 100  $\mu\text{m}$ . Joshi [53] reported that average size lies between 7 and 12  $\mu\text{m}$ . A coarser gradation can result in a less reactive ash and could contain higher carbon content.

### ***1.2.3 Specific Gravity***

The specific gravity of fly ash is related to shape, color and chemical composition of fly ash particle. In general, specific gravity of fly ash may vary from 1.3 to 4.8 [53].

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.

### ***1.2.4 Pozzolanic Activity***

The property of fly ashes, possessing little or no cementing value to react with calcium oxide in the presence of water, and produce highly cementitious water insoluble products, is called pozzolanic reactivity. The meta-stable silicates present in self-cementitious fly ash react with calcium ions in the presence of moisture to form water insoluble calcium-alumino-silicate hydrates.

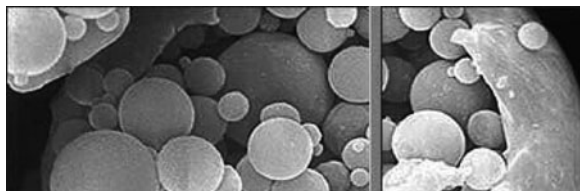
The pozzolanic activity of a fly ash depends upon its (1) fineness; (2) calcium content; (3) structure; (4) specific surface; (5) particle size distribution; and (6) and LOI content [54]. Several investigators have reported that when fly ash is pulverized to increase fineness, its pozzolanic activity increases significantly. However, the effect of increase in specific surface area beyond 6,000 cm<sup>2</sup>/g is reported to be insignificant.

### ***1.2.5 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) [30, 53, 56, 80]. 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. Colors range from white to dark gray (Fig. 1.2).

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

**Fig. 1.2** Cenospheres from fly ash



better defined than those of high-calcium oxide fly ashes which may have surface coatings of material rich in calcium.

### 1.2.6 Moisture

Any amount of moisture in Class C fly ash will 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. Therefore, it is important that such ashes have to be kept dry before being mixed with cement.

Physical properties of fly ashes reported by Electric Power Research Institute [35] are given in Table 1.1.

### 1.2.7 Chemical Composition

Chemical composition of fly ashes include silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ), and oxides of calcium ( $\text{CaO}$ ), iron ( $\text{Fe}_2\text{O}_3$ ), magnesium ( $\text{MgO}$ ), titanium ( $\text{TiO}_2$ ), sulfur ( $\text{SO}_3$ ), sodium ( $\text{Na}_2\text{O}$ ), and potassium ( $\text{K}_2\text{O}$ ), and unburned carbon (LOI). Amongst these  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  together make up about 45–80% of the total ash. The sub-bituminous and lignite coal ashes have relatively higher proportion of  $\text{CaO}$  and  $\text{MgO}$  and lesser proportions of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  as compared to the bituminous coal ashes. Table 1.2 presents the chemical analysis of different fly ashes [2].

### 1.2.8 Mineralogical Characteristics

X-ray diffraction study of the crystalline and glassy phases of a fly ash is known as mineralogical analysis. Mineralogical characterization determines the crystalline phases that contain the major constituents of fly ash. Generally, fly ashes have 15–45% crystalline matter. The high-calcium ashes (Class C) contain larger

**Table 1.1** Physical properties of fly ashes [35]

Parameter	Range
Retained on #325 sieve (%)	3.55–36.90
Blaine fineness ( $\text{cm}^2/\text{g}$ )	1579–5550
Specific gravity	2.14–2.69
Moisture content (%)	0.0–0.38

**Table 1.2** Composition of Class F and Class C fly ashes [2]

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
Potassium oxide (%)	0.7–2.9	0.4–1.9
Loss on ignition (%)	0.4–7.2	0.3–1.9

amounts of crystalline matter ranging between 25 and 45%. Table 1.3 presents crystalline phases in fly ashes identified by XRD analysis [76].

Although high-calcium Class C ashes may have less glassy or amorphous material, they do contain certain crystalline phases such as anhydrite ( $\text{CaSO}_4$ ), tricalcium aluminate ( $3\text{CaOAl}_2\text{O}_3$ ), calcium sulpho-aluminate ( $\text{CaSAI}_2\text{O}_3$ ) and very small amount of free lime ( $\text{CaO}$ ) that participate in producing cementitious compounds. Also, glassy phase in Class C ashes is usually more reactive. The glassy particles in Class C fly ashes contain large amount of calcium which possibly makes the surface of such particles highly strained, and probably, it is because of highly reactive nature of Class-C fly ashes.

Anhydrite ( $\text{CaSO}_4$ ) is formed from the reaction of  $\text{CaO}$ ,  $\text{SO}_2$  and  $\text{O}_2$  in the furnace or flue. Quantity of anhydrite increases with the increase in  $\text{SO}_3$  and  $\text{CaO}$  contents. It plays a significant role in fly ash hydration behavior because it

**Table 1.3** Crystalline phases in fly ashes from North America (McCarthy et al. 1988)

Class of fly ash and code	Name	Nominal composition
Low-calcium/Class F		
Hm	Hematite	$\text{Fe}_2\text{O}_3$
Mu	Mullite	$\text{Al}_6\text{Si}_2\text{O}_{13}$
Qz	Quartz	$\text{SiO}_2$
Sp	Ferrite spinel	$(\text{Mg.Fe})(\text{Fe,Al})_2\text{O}_4$
High-calcium/Class C		
Ah	Anhydrite	$\text{CaSO}_4$
AS	Alkali sulfate	$(\text{Na,K})_2\text{SO}_4$
$\text{C}_2\text{S}$	Dicalcium silicate	$\text{Ca}_2\text{SiO}_4$
$\text{C}_3\text{A}$	Tricalcium aluminate	$\text{Ca}_3\text{Al}_2\text{O}_6$
Hm	Hematite	$\text{Fe}_2\text{O}_3$
Lm	Lime	$\text{CaO}$
Ml	Melilite	$\text{Ca}_2(\text{Mg,Al})(\text{Al,Si})_2\text{O}_7$
Mu	Mullite	$\text{Al}_6\text{Si}_2\text{O}_{13}$
Mw	Merwinite	$\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$
Pc	Periclase	$\text{MgO}$
Qz	Quartz	$\text{SiO}_2$
So	Sodalite structure	$\text{Ca}_2(\text{Ca,Na})_6(\text{Al,Si})_{12}\text{O}_{24}(\text{SO}_4)_{1-2}$

**Table 1.4** Concentration range of minerals in fly ashes [3]

Minerals	Concentration (%)
Mullite	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

participates along with tricalcium aluminate and other soluble aluminates to produce ettringite and calcium sulphoaluminate hydrate.

Tricalcium aluminate ( $3\text{CaOAl}_2\text{O}_3$ ) 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,  $\text{Mg}(\text{OH})_2$ . 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 glassy phases of  $\text{Fe}_2\text{O}_3$ .

The concentrations of important minerals found in fly ashes bituminous coal, as reported by Alonso and Wesche [3] are given in Table 1.4.

### 1.3 Classification of Fly Ash

ASTM C618 [5] categorizes natural pozzolans and fly ashes into the following three categories.

*Class F* Class F fly ashes are low in CaO. They are normally produced from burning anthracite or bituminous coal falls in this category. This class of fly ash exhibits pozzolanic property but rarely, if any, self hardening property. They are predominantly (>70%) noncrystalline silica which is the determining factor for pozzolanic activity. Their crystalline minerals are generally composed of quartz, hematite, mullite, magnetite [106].

*Class C* 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 contained more than 15% CaO. But some Class C fly ashes may contain as little as 10% CaO). Class C fly ashes contain predominantly calcium aluminosilicate glass which is highly reactive. Crystalline phases in Class C ash includes quartz, lime, mullite, gehlenite, anhydrite, and cement materials such as  $\text{C}_3\text{A}$ ,  $\text{C}_2\text{S}$  and  $\text{C}_4\text{A}_3\text{S}$ .

**Table 1.5** Requirements for fly ash and natural pozzolans for use as mineral admixtures in Portland cement concrete (ASTM C618 [5])

Requirements	Fly ash classification		
	N	F	C
Chemical requirements $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ , min (%)	70.0	70.0	50.0
$\text{SO}_3$ , max (%)	4.0	5.0	5.0
Moisture content, max (%)	3.0	3.0	3.0
Loss on ignition, max (%)	10.0	6.0	6.0
Physical requirements Amount retained when wet sieved on 45- $\mu\text{m}$ sieve, max (%)	34	34	34
Pozzolanic activity index, with Portland cement at 28 days, min (%) of control	75	75	75
Pozzolanic activity index with lime at 7 days, min (MPa)	5.5	5.5	–
Water requirement, max (%) of control	115	105	105
Autoclave expansion or contraction, max (%)	0.8	0.8	0.8
Specific gravity, max variation from average	5	5	5
Percentage retained on 45- $\mu\text{m}$ sieve, max variation, percentage points from average	5	5	5

*Class N* Raw or calcined natural pozzolans such as some diatomaceous earths, opaline chert and shale, stuffs, volcanic ashes and pumice are included in this category. Calcined kaolin clay and laterite shale also fall in this category of pozzolans.

Table 1.5, presents chemical and physical requirements for fly ash and natural pozzolans for use as a mineral admixture in Portland cement concrete.

## 1.4 Reaction Mechanism

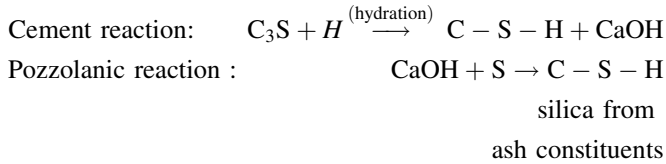
Setting or hardening of OPC concretes occurs due to the hydration reaction between water and cementitious compounds in cement which give rise to several types of hydrates of calcium silicate (CSH), calcium aluminate (CAH) besides calcium hydroxide (CH). These hydrates are generally called as “Tobermorite gel”. The adhesive and cohesive properties of the gel bind the aggregate particles. Calcium hydroxide is a by-product of cement hydration.

When fly ash is incorporated in concrete, the calcium hydroxide liberated during hydration of OPC reacts slowly with the amorphous aluminosilicates, the pozzolanic compounds, present in the fly ash. The products of these reactions, termed as pozzolanic reaction products, are time dependent but are basically of the same type and characteristics as the products of the cement hydration.



Thus additional cementitious products become available which impart additional strength to concrete.

The following equations illustrate the pozzolanic reaction of fly ash with lime to produce additional calcium silicate hydrate (C-S-H) binder:



## 1.5 Uses of Fly Ash

Coal fly ash as an engineering material can be used in following ways

- Portland cement
- Stabilized base course
- Flowable fill
- Structural fills/embankments
- Soil improvement
- Asphalt pavements
- Grouts for pavement subsealing

### 1.5.1 Uses of Fly Ash in Cement Concrete

Utilization of fly ash in cement or concrete can be categorized based on the volume of its usage.

#### 1.5.1.1 Medium Volume Uses

This includes the use of fly ash

- as raw material in cement production
- as an admixture in blended cements
- as partial replacement of cement or as a mineral admixture in concrete
- in addition coal ash including fly ash may be used as partial replacement of fine aggregate in concrete
- for production of light weight aggregates for concrete and many other applications

### **1.5.1.2 High Volume Uses**

High volume utilization of fly ash includes

- as structural fills in embankments, dams, dikes and levees, and
- as sub-base and base courses in road way construction

### **1.5.1.3 Low Volume Uses**

This includes the coal ash utilization

- in high value added applications such as metal extractions. High value metal recovery of Aluminum (Al), Gold (Au), Silver (Ag), Vanadium (Va) and Strontium (Sr) fall in this category.
- Fly ash has potential uses for producing light weight refractory material and exotic high temperature resistant tiles.
- Cenospheres or floaters in fly ash are used as special refractory material and also as additives in forging to produce high strength alloys.

### **1.5.1.4 Miscellaneous Uses**

Based upon its physical properties, coal ash is used

- as land fill for land reclamations for residential, commercial and recreational development projects.
- as filler in asphalt, plastics, paints and rubber products.
- in water treatment and as absorbent for oil and chemical spills.

## **1.6 Objectives of Using Fly Ash in Cement/Concrete**

The objective of using fly ash in concrete is to achieve one or more of the following benefits:

- Reducing the cement content to reduce costs
- Improving workability
- Obtaining reduced heat of hydration, especially in mass concreting
- Attaining required levels of strength in concrete at ages beyond 56 days

## **1.7 Benefits of Using Fly Ash in Cement/Concrete**

Inclusion of fly in cement or concrete has several benefits. Benefits to concrete vary depending on the type of fly ash, proportion used, other mix ingredients,

mixing procedure, field conditions and placement. Some of the benefits of fly ash in concrete are:

### ***1.7.1 Reduced Bleeding and Segregation***

Bleeding and segregation are considerably reduced with the use of fly ash as a mineral admixture in concrete and thus improving the pumpability of concrete. This is due to (1) the lubricating effect of the glassy spherical fly ash particles; and (2) increased ratio of solids to liquid make the concrete less prone to segregation and increase concrete pumpability.

### ***1.7.2 Improved Workability***

The spherical shape and glassy surface of fly ash particles permit greater workability for equal w/c ratio. In other words, w/c ratio may be reduced for equal workability.

### ***1.7.3 Reduced Heat of Hydration***

Hydration of cement paste is accompanied by liberation of heat that raises the temperature of concrete. Because of the slower pozzolanic reactions, partial replacement of cement by fly ash results in release of heat over a longer period of time, and the concrete temperature remains lower slowly. This is of immense importance in mass concrete where cooling, following a large temperature rise, can lead to cracking. Low-calcium Class F fly ashes generally tend to reduce the rate of temperature rise more as compared to high-calcium Class C fly ashes

### ***1.7.4 Higher Ultimate Strength***

The additional binder produced by the fly ash reaction with available lime allows fly ash concrete to continue to gain strength over time. Mixtures designed to produce equivalent strength at early ages (less than 90 days) will ultimately exceed the strength of straight cement concrete mixes.

### ***1.7.5 Reduced Permeability***

The decrease in water content combined with the production of additional cementitious compounds reduces the pore interconnectivity due to refinement of

pore structure of concrete resulting in reduced permeability. The reduced permeability results in improved long-term durability and resistance to various forms of deterioration.

### ***1.7.6 Increased Resistance to Sulfate Attack***

Fly ash in concrete increases the sulphate resistance and potentially corrosive salts that penetrate into concrete and cause steel corrosion with accompanying cracking and spalling of concrete. Fly ash induces three phenomena that improve sulfate resistance (1) consumes the free lime making it unavailable to react with sulfate; (2) reduced permeability prevents sulfate penetration into the concrete; and (3) replacement of cement reduces the amount of reactive aluminates available

### ***1.7.7 Improved Resistance to Corrosion***

Fly ash addition to concrete improves the long term corrosion resistance of concrete. The reaction of fly ash with  $\text{Ca(OH)}_2$  produces a denser concrete and thus inhibits the ingress of chloride ions takes place at a slower rate.

### ***1.7.8 Increased Resistance to Alkali-Silica Reactivity (ASR)***

Fly ash reacts with available alkali in the concrete, which makes them less available to react with certain silica minerals contained in the aggregates.

## **1.8 Effect of Fly Ash on the Fresh Properties of Cement 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, pumpability, compactability, and finishability. In fresh concrete, fly ash plays an important role in the fluidity of concrete.

### ***1.8.1 Workability***

Workability is defined as the ease with which a freshly mixed concrete can be properly compacted, transported, placed, and finished. Workability is one of the

governing factors of concrete mix design. Workability is determined by the rheological behavior of fresh concrete. Water content of concrete plays a dominant role in controlling workability. Workability depends on (1) water content; (2) aggregate shape and size; (3) cementitious content; and (4) age (level of hydration), and can be modified by adding mineral/chemical admixtures. 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.

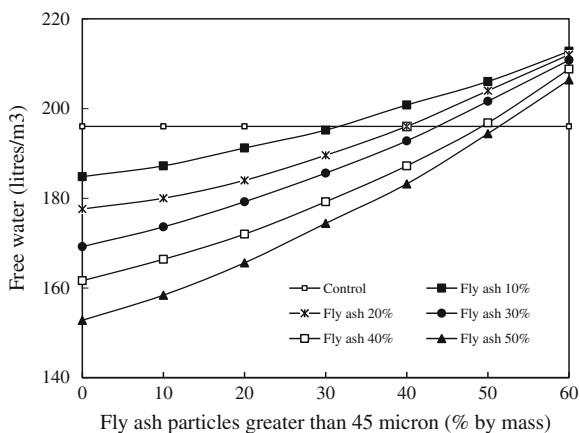
Lane and Best (1980) concluded that use of fly ash as partial replacement of cement usually reduces the water content for a given consistency. With proper proportioning of the concrete, cohesion and plasticity are adequate, and bleeding is reduced. Helmuth [45] has reported that if the water reduction 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 [15] 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. [130] showed that the water demand decreased when the quantity of fly ash was between 15 and 20%, and increased when fly ash content was more than 20%. This was attributed to increase in water demand to the introduction of additional specific surface and porous grains, and decrease to deflocculation by adsorption of fine grains of fly ash on cement clusters.

Owens [96] 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 unburned 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.

**Fig. 1.3** Influence of coarse particulate of fly ash on the water required for equal workability in concrete [96]



**Fig. 1.4** Influence of fly ash content on plastic viscosity and yield stress of concrete [61]

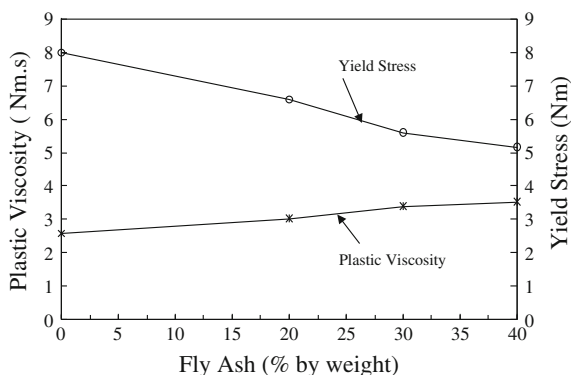


Figure 1.3 shows the effects of coarse fly ash particles on the water demand of concrete mixtures.

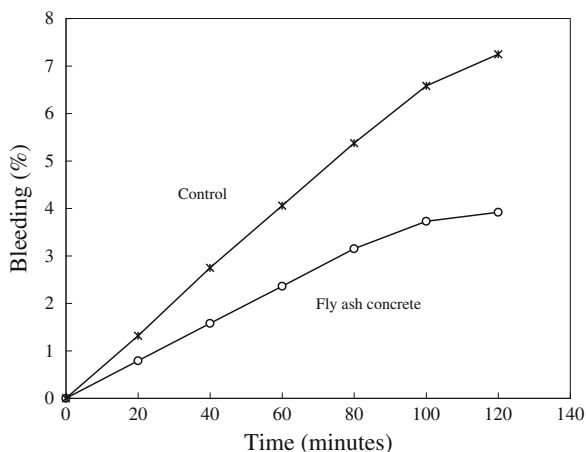
In order to develop a theoretical concept and understanding of the rheology of fresh fly ash concrete, Tattersall and Benfill [119] suggested mathematical expressions relating the yield value ( $\tau$ ) and the plastic viscosity ( $\mu$ ) varying with volumetric parameters of concrete, in terms of Bingham model. Yield stress and plastic viscosity varied with volumetric parameters of concrete, water-to-cement ratio, replacement levels of cement/aggregates 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 given water content when used as partial replacement of cement or fine aggregate. Khan [61] 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 as shown in Fig. 1.4

### 1.8.2 Bleeding and Segregation

Incorporation of fly ash in mortar or concrete significantly reduces the bleeding and segregation. This is due to the lubricative effect of the glassy spherical fly ash particles and the increased ratio of solids to liquid make the concrete less prone to segregation and increase concrete pumpability. Figure 1.5 shows the bleeding rate of fly ash concrete compared to that of control concrete.

Joshi and Lohtia [57] 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 sub-sided more slowly and gradually than the control mixes which exhibited abrupt fall or subsidence.

**Fig. 1.5** Relative bleeding of control and fly ash concretes [23]



### 1.8.3 Air Entrainment

Fly ash addition affects both air-content and loss of air-content with time in fresh concrete depending upon type of fly ash concrete. For entraining a specified amount of air content, usually around 4–6% more air-entraining agent (AEA) is required in fly ash concrete than for a similar concrete containing no fly ash concrete. This is (1) because of the greater surface area of fly ash in concrete. Fly ash is generally finer than cement and volume of fly ash added is normally more than the volume of cement replaced. Because of this, surface area of the binder within the concrete mix is increased. Thus greater volume of air entraining agent is needed to provide the same concentrations of the air voids in the mortar or concrete containing fly ash; and (2) secondly, the main reason leading to the increased demand of AEA is related to the carbon content, expressed in terms of loss on ignition (LOI) of fly ash. The carbon absorbs a portion of the air-entraining agent, which limits its availability for producing the needed air bubbles. The amount of absorption varies with the amount of carbon content.

Gebler and Klieger [40] investigated the requirements of AEA for Class C and Class F fly ashes. They reported that (1) concretes made with Class C fly ash generally require less AEA than those made with Class F fly ashes; (2) for 6% air content in concrete, the AEA varied from 126 to 173% for fly ashes having more than 10% CaO, whereas it was in the range of 177 to 553% for fly ashes containing less than 10% CaO; and (3) increase in both total alkalis and  $\text{SO}_3$  contents in fly ash affect the air entrainment favorably. A concrete containing a Class F fly ash that has relative high CaO content and less organic matter or carbon tends to be less vulnerable to loss of air.

Joshi et al. [58] reported that for some Class F fly ashes replacing about 50% cement, the average requirement of AEA was found to be more than double of the equivalent plain concrete. A wide range of AEA demand was reported by Carrette

and Malhotra [19] from the study of concretes made with Canadian fly ashes to entrain about 6% air content.

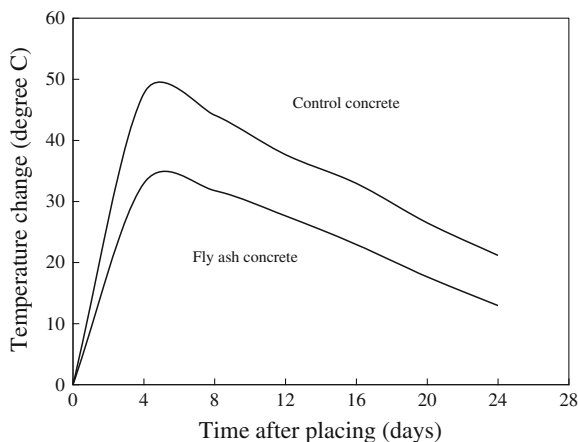
Burns et al. [16] made attempts to neutralize the absorption characteristics of activated carbon in fly ash by using chlorine gas, calcium hypochlorite and some other surface active agents to resolve the problem of increased AEA demand. However, these studies need to be substantiated for practical use. The deactivating agents used for carbon in fly ash should not interfere with air entrainment and concrete durability on their own. Economy is another important factor to be considered in developing suitable remedial additives for solving the problem of AEA demand in concrete.

### 1.8.4 Temperature Rise

Hydration of cement paste is accompanied by liberation of heat that raises the temperature of concrete. Because of the slower pozzolanic reactions, partial replacement of cement by fly ash results in release of heat over a longer period of time and the concrete temperature remains lower slowly. This is of immense importance in mass concrete where cooling, following a large temperature rise, can lead to cracking. Low-calcium Class F fly ashes generally tend to reduce the rate of temperature rise more as compared to high-calcium Class C fly ashes.

Compton and Macinnis [24] reported temperature–time curves (Fig. 1.6) for control and fly ash concretes. In fly ash concrete, cement was replaced with 30% fly ash. This particular phenomenon is very useful in mass concreting, where cooling, following a significant temperature rise due to the generation of the heat of hydration occurs, stresses can develop and cause cracking. Temperature rise, in fact, depends upon more factors than the rate of heat generation associated with

**Fig. 1.6** Temperature rise curve for fly ash and plain concrete test sections [24]





hydration and pozzolanic reactions, including the rate of heat loss and the thermal properties of the concrete and the surrounding medium.

Fly ash retards the hydration of  $C_3S$  in the early stages but accelerates it at later stages [51, 94]. Jawed and Skalny [51] found that two chemically similar Class F fly ashes with different surface areas (314 and 205  $m^2/kg$ ) had similar retarding effects on  $C_3S$  hydration, but the effect changed dramatically in 0.5 M NaOH solutions. They attributed the retardation to two factors (1) chemisorptions of calcium ions on the fly ash particles, resulting in a reduction in its concentration in the liquid phase and a delay in  $Ca(OH)_2$  nucleation and (2) poisoning of the nucleation and growth of  $Ca(OH)_2$  and C–S–H by soluble silicates and aluminates.

Takemoto and Uchikawa [118] concluded that hydration of  $C_3A$  in the presence of calcium hydroxide, gypsum, and fly ash was accelerated in the presence of pozzolan due to the adsorption of calcium ions from the solution and generation of sites for ettringite or other hydrates to precipitate.

Bamforth [12] investigated the temperature rise in large size foundation made with concrete containing fly ash and slag. Three types of concretes were used (1) control concrete with a Portland cement content of 400  $kg/m^3$ ; (2) mix with 75% of the Portland cement replaced by ground granulated blast furnace slag (GGBS); and (3) mix with 30% of the Portland cement replaced by a bituminous fly ash. It was observed that with an increase in the quantity of cement replaced by fly ash and slag, the rate of heat release was slowed down and as a result the maximum temperature reached at any point in the concrete mass was lower than the control concrete.

Sivasundram et al. [114] and Langley et al. [68] reported favorable effect of fly ash incorporation in concrete on temperature rise of not only massive concrete dams, but also in concrete mat foundations and massive columns in lower storey of the tall buildings. Low-calcium Class F fly ashes generally tend to reduce the rate of temperature rise more as compared to high-calcium Class C fly ashes [26]. Some high-calcium Class C fly ashes with self cementitious properties may react very rapidly with water, thus releasing excessive heat just like normal Portland cement hydration.

ACI Committee 211.1.81 [1] estimated that on the basis of equivalent mass, fly ash contributes to early age heat liberation in the range of 15 to 30% compared to normal Portland cement. Low-calcium bituminous fly ash was successfully used to control the rise of temperature at early age in the construction of concrete structures, particularly dams. In general, incorporation of fly ash as replacement of normal Portland cement exhibits less temperature rise than concrete without fly ash. Where early age strength is not the main design consideration, large quantities of cement replaced by fly ash are anticipated to reduce the rate and also amount of heat hydration significantly.

Atis [6] studied the heat evolution of high-volume fly ash (HVFA) concrete. Heat evolution of concrete was studied by measuring the temperature increase in concrete under adiabatic curing condition. They concluded that (1) characteristic of heat evolution of fly ash concrete was found to be strongly dependent on the replacement level of fly ash and dosage of superplasticizer; (2) use of fly ash as

cement replacement resulted in reduction in maximum temperature rise. Increasing the replacement level of fly ash caused lower temperature rise in concrete; (3) superplasticizer caused a delay in peak temperature rise time. This is taken as an indicator that high-dosage superplasticizer used in concrete caused retardation in hydration of cement. Concretes having similar ingredients showed similar peak temperature rise whether they are superplasticized or not.

### ***1.8.5 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 generally show some degree of retarding effect on cement setting. High-calcium fly ashes, generally low in carbon and high in reactive and/or cementitious components sometimes exhibit opposite behavior of reduced setting time. Not all Class C fly ashes cause rapid setting.

Ramakrishnan et al. [102] reported an increase in setting time with the use of high-calcium fly ash in concrete. Lane and Best [66] 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 [19] 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. Chemical properties of fly ashes are given in Table 1.6. Fresh concrete properties are given in Table 1.7.

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 to maintain workability.

Sivasundram et al. [115] 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. [58] 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 non-fly ash concrete.

**Table 1.6** Properties of some Canadian fly ashes [19]

Fly ash source	Type of coal	Major chemical compounds (% by weight)					
		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	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

**Table 1.7** Properties of concrete incorporating Canadian fly ashes [19]

Mix no.	Cement (kg/m <sup>3</sup> )	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	105	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

The final setting time varied from 10 to 13 h as against 7 h for control mixes without fly ash.

## 1.9 Effect of Fly Ash on Properties of Cement Concrete in Hardened State

### 1.9.1 Compressive Strength

The pozzolanic reaction has several characteristics that affect the strength. Mehta [79] has identified 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

Rate of strength development depends upon following factors:

- fly ash characteristics such as its chemical and mineralogical composition fineness, pozzolanic reactivity
- type of cement
- replacement level of cement with fly ash
- mixture proportions
- ambient temperature
- curing environment

The low-calcium fly ashes do not exhibit significant pozzolanic activity to affect strength until about 2 weeks after hydration, but highly pozzolanic fly ashes start their contribution to strength development almost from the onset of Portland cement hydration. Some high-calcium fly ashes, with calcium oxide content more than 15%, may start contributing to compressive strength development as early as 3 days after mixing because of their self hardening and pozzolanic properties.

Because of its fineness as well pozzolanic reactivity, fly ash in cement concrete significantly improves the quality of cement paste and the micro-structure of the transition zone between the binder matrix and the aggregate. 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 Class C fly ashes are used, the strength development with time is likely to be different from the one using Class F fly ash. The self-hardening reactions in the Class C 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. The pozzolanic activity of such cementitious fly ashes further enhances strength at later ages.

Lane and Best [66] 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. When replacement is on two or three-to-one basis and the fine aggregate content are reduced accordingly, 3-day strength is slightly reduced compared to the control, 28-day strength is comparable, and later-age strength is higher.

Cook [25] conducted investigations using a high-calcium fly ash with CaO content of 30.3% at 25% replacement level to develop concrete mixes with 28-day strength in the range of 55–75 MPa. He reported that as cement factor was increased, sand content and the water-to-cementitious material ratio was reduced. To maintain slump around 100 mm, water reducing admixture was

**Table 1.8** Compressive Strength of hardened concrete [19]

Mixture 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

**Table 1.9** Compressive of high-calcium fly ash concrete [101]

Cement (kg/m <sup>3</sup> )	Fly ash (kg/m <sup>3</sup> )	Compressive strength (kg/m <sup>2</sup> )		
		Percentage of control		Percentage gained from 28 to 56 days
		28 days	56 days	
91	50	318	354	15.2
	59	352	393	16.0
	68	401	435	13.6
	77	471	494	10.5
136	50	210	228	10.2
	59	231	256	11.8
	68	245	269	11.1
182	77	253	274	10.3
	50	149	155	8.2
	59	153	167	12.4
	68	163	177	12.0
	77	187	190	6.2

used in all the mixes. The 180-day strength of the mixes ranged between 68 and 86 MPa.

Carette and Malhotra [19] 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 1.8. It can be seen from this table that compressive strength continued to increase with age, indicating pozzolanic action of fly ashes.

Raba et al. [101] determined the compressive strength of concrete made with bituminous fly ash (CaO 20%). In the mixes, fine aggregate was replaced with fly ash by volume, and mass of cement and coarse aggregate was kept constant for each series (Table 1.9).

Swamy and Mahmud [117] reported that concrete containing 50% low-calcium bituminous fly ash as partial replacement of cement developed 20–30 MPa compressive strength at 3 days, 60 MPa at the age of 28 days.

Joshi et al. [58] tested a large number of fly concrete mixes made by using three different Alberta fly ashes containing about 10% calcium oxide. The replacement level varied between 40 and 60% by weight of cement. The mixes were superplasticized and air-entrained to obtain 100 to 120 mm slump and  $6 \pm 1\%$  air content. The cementitious material content varied from 380 to 466 kg/m<sup>3</sup>, water-to-cementitious material ratio from 0.27 to 0.37, coarse aggregate ranged from 1,012 to 1,194 kg/m<sup>3</sup>, and fine aggregate or sand varied from 712 to 643 kg/m<sup>3</sup>. They reported that (1) at 7 days, the fly ash concretes obtained strength between 27.9 and 41.0 MPa compared to 44.1 MPa of control concrete. However at the age of 28 days, the fly ash concretes developed strength varying from 37.6 to 50.7 MPa against 58.7 MPa for control concrete. At 120 days, strength of fly ash concrete ranged from 54.8 to 74.6 MPa whereas it was 74.6 MPa of control concrete.

Mehta [82] have 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 equaled that of control concrete.

Haque et al. [44] 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 [63] found that concrete made with Type-I fly ash cement had lower strength than the control at all ages through 3 years. Lower casting and initial-curing temperatures resulted in higher strengths at later ages for both types of concretes. Korac and Ukraincik [65] found that the early-age strengths of 50% fly ash concrete were lower than the controls; after 90 days strengths were comparable.

Erdoğan and Türker [37] studied the effect of particle size of high and low-calcium fly ash on the compressive strength of mortar. Major chemical compounds in high-calcium ash were Al<sub>2</sub>O<sub>3</sub> (19.43%), SiO<sub>2</sub> (46.45%), CaO (12.69%) and Fe<sub>2</sub>O<sub>3</sub> (9.32%), whereas low-calcium fly ash had Al<sub>2</sub>O<sub>3</sub> (27.72%), SiO<sub>2</sub> (57.30%), CaO (2.24%) and Fe<sub>2</sub>O<sub>3</sub> (5.72%). Fly ashes were sieved from the 125, 90, 63, and 45- $\mu$ m sieve by a sieve-shaker. Six different size groups, including the all-in ash, were obtained for both the ashes and the materials retained on each sieve. They were; material retained on 125  $\mu$ m sieve, material having 125–90, 90–63, and 63–45, and material passing 45- $\mu$ m 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 1.10. It is evident from these results that (1) high-calcium ash incorporated mortars exhibited higher strength than mortars with low-calcium ash at all ages; (2) for both of the ashes, the finer the size of a fraction, higher was the compressive strength.

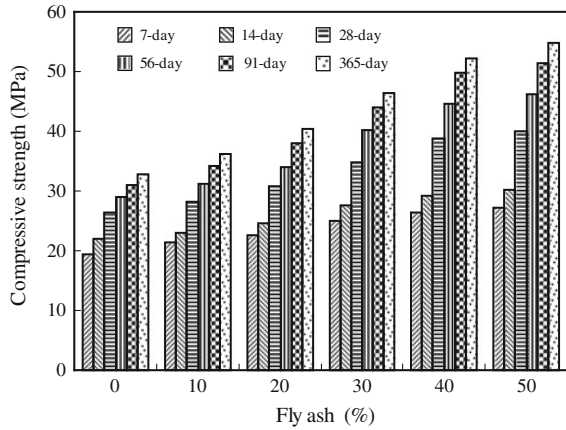
**Table 1.10** Compressive strength results of the mortars [37]

		Compressive strength (N/mm <sup>2</sup> )			
		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 $\mu\text{m}$	19.2	26.6	31.2	33.2
	125–90 $\mu\text{m}$	22.6	27.6	35.0	38.4
	90–63 $\mu\text{m}$	24.8	31.3	35.4	42.6
	63–45 $\mu\text{m}$	26.6	35.1	41.4	47.5
	Under 45 $\mu\text{m}$	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 $\mu\text{m}$	17.9	24.4	26.7	29.9
	125–90 $\mu\text{m}$	21.6	29.2	32.0	37.1
	90–63 $\mu\text{m}$	22.6	29.6	34.9	40.6
	63–45 $\mu\text{m}$	23.8	33.5	37.4	46.8
	Under 45 $\mu\text{m}$	26.6	37.3	43.4	57.2
100% PC 32.5		38.0	44.4	51.6	58.2

Saraswathy et al. [107] investigated the influence of activated fly ash on the compressive strength of concrete. Various activation techniques, such as physical, thermal and chemical were adopted. Concrete specimens were prepared with 10, 20, 30 and 40% of activated fly ash replacement levels with cement. Compressive strength was determined at 7, 14, 28 and 90 days. They concluded that (1) activation of fly ash improved the strength of concrete. However, the compressive strength of fly ash concrete was less than that of ordinary portland cement (OPC) even after 90 days of curing; and (2) among the activation systems, chemically activated coal fly ash (CFA) improved the compressive strength to a certain extent, only with 10 and 20% replacements. Since the CFA surface layer is etched by a strong alkali to facilitate more cement particles to join together and also the addition of CaO which is further promoting the growth of CSH gel and Ca(OH)<sub>2</sub> which is more advantageous to enhance the strength development.

Siddique [112] 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 levels of percentages (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. 1.7. Based on the results, it was concluded that (1) compressive strength of fine aggregate (sand) replaced fly ash concrete specimens was higher than the plain concrete (control mix) specimens at all the ages. The strength differential 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; (3) The maximum compressive strength occurs with 50% fly ash content at all ages. It was 40.0 MPa at 28-day, 51.4 MPa at 91-day, and 54.8 MPa at 365-day; and (4) results of this investigation suggests that Class-F fly ash could be very conveniently used in structural concrete.

**Fig. 1.7** Compressive strength versus fly ash percentage [112]



Demirboğa et al. [28] 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 3, 7, 28 and 120 days. Based on the investigation, they reported that (1) fly ash FA reduced compressive strength of concrete at all levels of replacement at 3, 7, 28 and 120 days; (2) reductions were very high at early ages, but with the increase in curing period, the reduction percent decreased. Reductions at 3-day curing period were 69, 84 and 91% for 50, 60 and 70% fly ash replacement of Portland cement, respectively. At 28-days curing period, these values reduced to 52, 68 and 78% for 50, 60 and 70% fly ash replacement of Portland cement, respectively. At 120-days curing periods, reductions were 36, 43 and 50% for 50, 60 and 70% fly ash replacement of Portland cement, respectively; and (3) cement paste containing fly ash showed a steady reduction in strength at 3, 7, 28 and 120 days as a function of replacement percentage. This can be directly related to the properties of fly ash that decrease the heat of hydration of cement and required long curing period. Results of numerous studies have indicated that fly ash slows the rate of hardening and reduces the early age compressive strength of concrete.

Chindaprasirt et al. [22] 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, normal 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 0.25 with the use of superplasticizer. The fly ash dosage of 30% by weight of binder was used for all fly ash concrete mixes. Compressive strength of concrete mixes was determined up to the age of 90 days (Table 1.11). It can be seen from this table that the strength of fly ash concrete were higher than those of the portland cement concrete in the same group. For the normal-strength concrete,



**Table 1.11** Compressive strength of concrete [22]

Mix	Compressive strength (MPa)		
	7 days	28 days	90 days
PC1	24.5	33.5	35.2
100FA1	24.5	41.0	47.0
45FA1	32.5	40.5	49.0
10FA1	31.0	46.5	51.5
PC2	33.0	48.5	53.0
100FA2	31.0	46.0	55.0
45FA2	32.5	44.0	57.5
10FA2	35.5	52.0	61.5
PC3	62.5	79.5	85.5
100FA3	51.5	84.0	88.5
45FA3	50.5	72.5	83.5
10FA3	59.5	71.0	82.5

the 28-day strength of the PC2 concrete was 48.5 MPa, whereas those of fly ash concretes were between 44.0 and 52.0 MPa. For the high strength concrete, the strength of the PC3 concrete was 79.5 MPa, whereas those of the fly ash concretes were between 71.0 and 84.0 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 contribute 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.

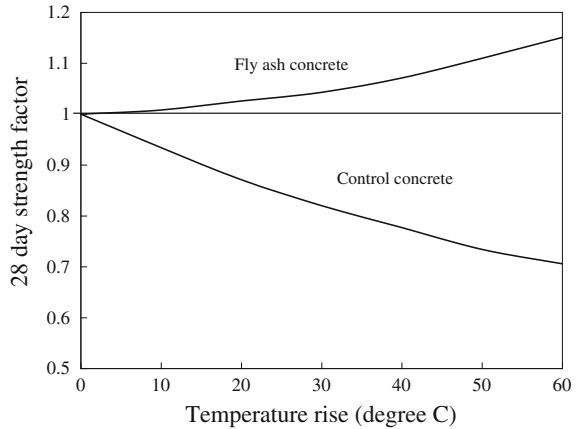
### *1.9.2 Effect of Curing Temperature at Early Age on Strength*

The rate of pozzolanic reaction of fly ash in cement concrete is significantly influenced by curing temperatures at early ages as is the case of cement hydration reactions. Pozzolanic reactions are highly temperature dependent. Higher the curing temperature, higher is the rate of the pozzolanic reactions. When concrete made with Portland cement is cured at temperatures in excess of 30°C, an increase is seen in strength at early ages but a marked decrease in strength is observed in mature concrete [92].

Ravina [103] observed that fly ash concrete subjected to high temperature at an early age of curing, exhibited increased rate of strength gain possibly due to the higher rate of pozzolanic reactions. It was suggested that when concrete was cured at elevated temperatures, large quantities of fly ash may be incorporated with a significant improvement in strength compared to the rather limited contribution under normal curing conditions up to 28 days.

William and Owens [125] reported that concrete containing fly ash behaved significantly different than concrete made with Portland cement (Fig. 1.8). In contrast

**Fig. 1.8** Effect of temperature rise during curing on the compressive strength development of concretes [125]



to the loss of strength that occurred with ordinary Portland cement concrete, fly ash concretes exhibited strength gains as a consequence of heating. The favorable effects of fly ash in concrete cured at moderately elevated temperatures can be advantageously used in the construction of mass concrete or concrete construction at elevated temperatures.

### ***1.9.3 Effects of Curing Conditions on Compressive Strength***

Ozer and Ozkul [95] reported the influence of initial water-curing on the strength development of ordinary Portland cement and pozzolanic cement concretes. They concluded that poor curing conditions adversely affect the strength of concrete made from pozzolanic cement than that of ordinary Portland cement. Atis [9] worked on strength properties of high-volume fly ash roller compacted and workable concrete, and the influence of curing condition. He reported that fly ash–cement concrete was more sensitive to dry curing conditions than conventional concrete.

Termkhajornkit et al. [121] studied the effect of water-curing condition on compressive strength of fly ash–cement paste. Replacement ratios of fly ash were 0, 25 and 50% of total powders. The water-to-binder ratio was 0.80 and 1.00 by volume. Mix proportion and curing condition details are given in Table 1.12. Compressive strength results of fly ash–cement paste are given in Table 1.13. They reported that (1) for the samples prepared with water curing condition, the compressive strength of 0% fly ash increased until 91 days but suddenly dropped at 182 days. The compressive strength of 25% fly ash and 50% fly ash continuously increased until 182 days. At 182 days, the compressive strength of 25% fly ash was higher than that of the cement paste. For the samples prepared under 7 days initial curing, the compressive strength of 0% fly ash was almost constant. The compressive strength of 50% fly ash increased until 28 days, and after that became

**Table 1.12** Mix proportion and curing condition [121]

Water/binder (W/B)	Fly ash (%)	Curing condition	Code
0.8	0	In water	0.8-0-W
0.8	25	In water	0.8-25-W
0.8	50	In water	0.8-50-W
1.0	0	In water	1.0-0-W
1.0	25	In water	1.0-25-W
1.0	50	In water	1.0-50-W
1.0	0	In water 7 days	1.0-0-W7
1.0	25	In water 7 days	1.0-25-W7
1.0	50	In water 7 days	1.0-50-W7
1.0	0	In water 3 days	1.0-0-W3
1.0	25	In water 3 days	1.0-25-W3
1.0	50	In water 3 days	1.0-50-W3

**Table 1.13** Compressive strength of fly ash–cement paste [121]

Mix/curing condition code	Compressive strength (MPa)				
	7 days	28 days	56 days	91 days	182 days
0.8-0-W	117.03	150.91	145.99	129.91	150.11
0.8-25-W	80.89	113.36	115.06	116.7	163.29
0.8-50-W	41.45	65.42	69.41	83.72	104.81
1.0-0-W	91.84	114.71	127.24	128.63	90.19
1.0-25-W	55.39	78.58	88.72	94.2	94.7
1.0-50-W	29.93	44.7	46.51	55.69	69.24
1.0-0-W7	91.84	95.89	94.97	96.68	97.94
1.0-25-W7	55.39	71.54	69.37	84.75	89.51
1.0-50-W7	29.93	42.84	48.45	48.29	46.77
1.0-0-W3	85.02	95.47	94.61	97.04	94.01
1.0-25-W3	65.17	71.82	87.68	77.18	98.51
1.0-50-W3	30.78	40.19	46.9	45.04	48.55

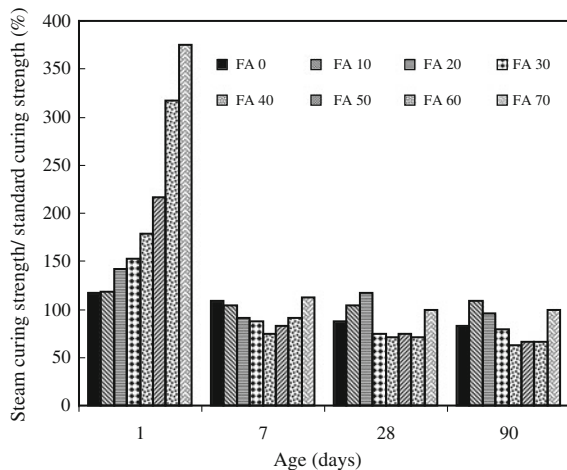
nearly constant. In contrast, the compressive strength of 25% fly ash constantly increased until 56 days. At this age, its compressive strength became close to that of cement paste; and (2) regarding the effect of curing condition on the compressive strength, for 0% fly ash, the compressive strength of samples cured in water was higher than others except at 182 days. In contrast, there was no significant difference among compressive strength of samples cured in water 7 and 3 days. As for 25% fly ash and 50% fly ash, the effect of water curing condition is small, especially for 25% fly ash.

Yazici et al. [126] investigated the effect of curing condition on the compressive strength of high-volume fly ash concrete mixtures. Cement was replaced with up to 70% fly ash, and concrete mixtures with 360 kg/m<sup>3</sup> cementitious content and a constant water/binder ratio of 0.40 were made. The curing conditions were standard curing in water and steam curing. Compressive strength of concrete

mixtures was determined up to the age of 90 days. Based on the test results, they concluded that (1) under standard curing conditions, the 1-day compressive strength decreased sharply with increasing fly ash content. However, at later ages (beyond 3 days), this difference diminished. The strength of 30% fly ash mixture was approximately equal to control mix strength at 3 days. At 7 days, 40% fly ash mixture exceeded the control mix strength, while the 50 and 60% fly ash mixtures reached the control mix strength at 28 and 56 days, respectively. Strength was approximately 10 MPa at 1-day and 20 MPa at 3 days with 50 and 60% fly ash content, which is quite satisfactory for most cast-in place structural elements; and (2) under steam curing, with increasing amount of fly ash content, compressive strength at early ages decreased. However, application of steam curing increased the 1-day compressive strength of 50% fly ash concrete to 20 MPa, which is adequate for formwork removal, and therefore, beneficial for fabrication of precast products. Application of steam curing did not improve the later-age compressive strength of high volume fly ash concrete as much as standard curing. For example, steam-cured high-volume fly ash concrete mixture containing 50% fly ash showed only 40 MPa strength at 90 days compared to 60 MPa for the standard-cured mixture at the same age. Figure 1.9 shows the effectiveness of steam-curing versus standard curing for different ages. It is evident from this figure that the high-volume fly ash systems containing 40% or more fly ash, steam-curing may be of interest only when 1-day strength is the sole consideration.

Swamy and Mahmud [117] examined the effect of curing regime on strength development of high volume fly ash concrete mixes (Table 1.14). They reported 50–100% increase in strength over the 28-day strength of fly ash concrete after 1 year under-continuous moist or fog curing compared to only 18–25% increase for the control or plain concrete under similar curing conditions. Under the other two curing regimes, one with 7-day moist curing followed by air drying and the other with continuous dry curing, the corresponding increase in strength of fly ash

**Fig. 1.9** The effectiveness of steam curing [126]



**Table 1.14** Rate of strength development of 28-day strength [117]

Age (days)	Strength (MPa)								
	20			40			60		
	Fog	Dry	7F + D	Fog	Dry	7F + D	Fog	Dry	7F + D
1	19	–	–	25	–	–	34	–	–
7	55	71	–	67	80	–	68	79	–
28	100	100	100	100	100	100	100	100	100
150	176	125	104	140	119	105	135	123	117
270	197	114	110	150	125	116	140	113	121
365	209	118	106	162	122	107	146	116	118

7F + D = 7 days fog followed by air dry curing

concrete after 1 year varied between 6 and 22% of the 28-day strength of the reference concrete.

Haque et al. [44] reported that mixes with Alberta fly ashes replacing up to 50% cement showed smaller reduction in strength at lower ash contents when curing was done at 50% relative humidity at room temperature of about 23°C.

Gifford et al. [42] studied the effect of dry curing on unprotected concrete specimens at 0 and 5°C made with 40% cement replacement with fly ash. They found that within 50 h after casting, about 30 and 60% of the mixing water was lost through evaporation from unprotected surfaces on curing at 50 and 10% relative humidity, respectively. In addition to strength loss due to evaporation of water, it was reported that the combination of low curing temperature and the cooling effect of concomitant evaporation of water at low humidity would significantly retard the rate of hydration and thereby strength development. The importance of curing concrete in an enclosed environment particularly at low temperatures is therefore stressed in order to mitigate the effect of water evaporation during the initial hours after the placing of concrete.

Langley et al. [68] reported that minimum duration of moist curing for fly ash concrete was 3 days after which normal curing practices as for ordinary plain concrete might be employed without any significant adverse effects. They also pointed out that long-term strength development in mass fly ash concrete was less influenced by dry curing than much smaller test specimens used in the laboratory.

Gopalan [43] studied the effect of curing conditions on the compressive strength of concretes made with fly ash. Compressive strength was determined for three grades (designated as M1, M2 and M3) of cement concrete having water cement ratios of 0.53, 0.62 and 0.88. Each grade of concrete was then incorporated with two levels (20 and 40%) of fly ash as cement replacement by weight. Cylinders of size 200 × 100 mm were cast. Samples were subjected to standard fog curing at 23°C ± 2°C and relative humidity of 95 ± 3% for 7 days. Samples were also cured (dry curing) at 23°C ± 2°C and relative humidity of 50 ± 3%. Compressive strength results are given in Table 1.15. It is evident from these results that fly ash replacements up to 20% did not have a significant impact on the long term strength of fog cured mixes. The results from the fog cured samples showed that the rate of

**Table 1.15** Compressive strength of fly ash concretes [43]

Mix	Compressive strength (MPa)					
	28 days		91 days		180 days	
	Fog	Dry	Fog	Dry	Fog	Dry
M1-00	49.9	45.1	58.8	61.2	51.9	
M2-00	33.1	31.1	40.2	37.0	42.6	34.3
M3-00	18.9	15.4	21.0	18.6	20.8	16.9
M1-20	36.2	32.1	44.0	40.2	53.9	41.1
M2-20	25.2	22.4	33.1	26.6	42.4	27.4
M3-20	13.6	11.3	17.2	14.0	22.0	13.5
M1-40	20.4	16.7	28.3	21.5	35.8	20.9
M2-40	19.2	16.6	27.5	20.8	35.5	19.6
M3-40	10.3	7.5	13.1	9.5	18.1	9.2

**Table 1.16** Flexural Strength of hardened concrete [19]

Mixture no.	Flexural strength (MPa)		
	14-day	28-day	91-day
Control	4.9	5.4	5.9
F1	4.4	4.4	5.4
F2	3.9	4.8	5.5
F3	4.0	5.0	5.3
F4	4.1	4.4	5.2
F5	3.5	4.4	5.3
F6	3.5	4.6	5.6
F7	3.9	4.5	5.4
F8	4.6	5.0	6.1
F9	4.3	4.2	5.7
F10	4.1	5.1	5.8
F11	4.8	5.3	6.6

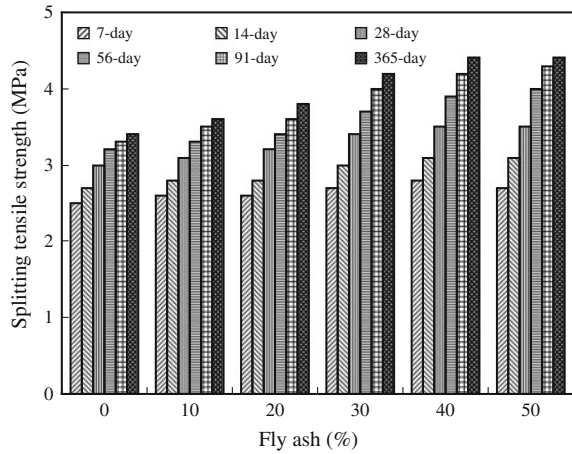
strength-loss was higher for richer mixes. Under drying conditions, there was no noticeable increase in strength after 91 days and strength development pattern did not depend upon the grade of the mix.

### 1.9.4 Tensile Strength Properties

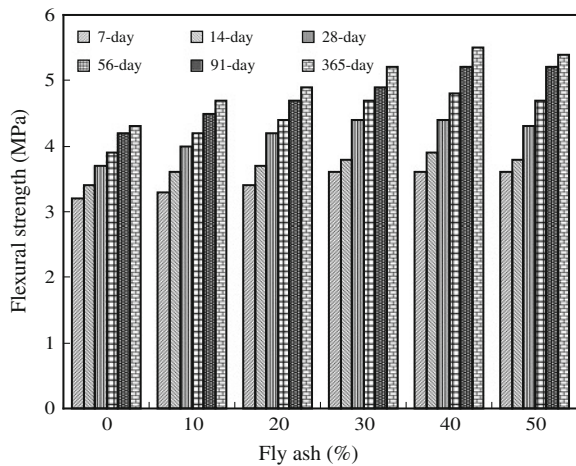
Carette and Malhotra [19] studied the effect of Canadian fly ashes on the flexural strength of concrete mixes up to the age of 91 days (Table 1.16). It is evident that flexural strength continued to increase with age, indicating pozzolanic action of fly ash.

Siddique [112] investigated the effect of partial replacement of fine aggregate (sand) with varying percentages of Class F fly ash on the splitting tensile strength

**Fig. 1.10** Splitting tensile strength versus fly ash percentage [112]



**Fig. 1.11** Flexural strength versus fly ash percentage [112]



and flexural strength of concrete. Fine aggregate (sand) was replaced with five levels of percentages (10, 20, 30, 40, and 50%) of Class F fly ash by weight. A control mix without fly ash was proportioned to have a 28-day cube compressive strength of 26.4 MPa. Tests were performed up to the age of 365 days. Splitting tensile and flexural strength results are shown in Figs. 1.10 and 1.11, respectively. Based on the results, it was concluded that (1) splitting tensile strength, and flexural strength of fine aggregate (sand) replaced fly ash concrete specimens was higher than the plain concrete (control mix) specimens at all the ages. The strength differential between the fly ash concrete specimens and plain concrete specimens became more distinct after 28-days; (2) both splitting and flexural strengths continued to increase with age for all fly ash percentages; (3) at all the ages, the maximum splitting tensile strength was observed with 50% fly ash content. It was

3.5 MPa at 28-day, 4.3 MPa at 91-day, and 4.4 MPa at 365-day; (5) maximum flexural strength was found to occur with 50% fly ash content at all ages. It was 4.3 MPa at 28-day, 5.2 MPa at 91-day, and 5.4 MPa at 365-day.

### ***1.9.5 Elastic Properties***

Lohtia et al. [72], Ghosh and Timusk [41], Lane and Best (1981), Nasser and Marzouk [90], Langley et al. [68] have reported that the effect of fly ash as replacement of cement on modulus of elasticity of concrete is almost the similar as that of compressive strength. The modulus of elasticity of fly ash concrete is generally lower at an early ages and is slightly higher at late ages.

Lohtia et al. [72] reported that as compared to compressive strength gain, the increase in modulus of elasticity was less with the incorporation of 15–25% Class F fly ash in concrete at the age of 90 days. In general, fly ash increased the modulus of elasticity of concrete when concretes of the same strength with and without fly ash are compared. Ghosh and Timusk [41] reported that for all strength levels, the modulus of elasticity of fly ash concrete was generally equivalent to that of the corresponding reference concrete. They also found that the observed modulus exceeded the value given by the ACI formula,  $E_c = 0.043 W(fc)^{3/4}$  MPa, where  $W$  is unit weight of concrete in  $\text{kg/m}^3$  and  $fc$  is compressive strength in MPa.

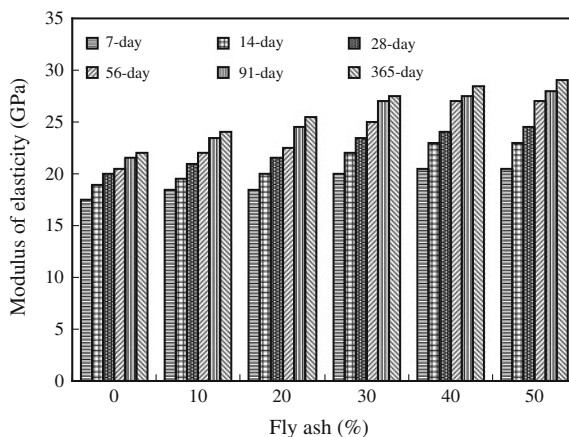
Normally fly ash properties affecting the compressive strength of concrete also influence the modulus of elasticity but to a lower extent. Crow and Dunstan [26] reported that like Portland cement concrete, fly ash concrete had increased modulus of elasticity with age. The modulus of elasticity ranged from a low of 18.8 GPa at 28-day to a high of 39.6 GPa at 365-day. The majority of the fly ash concrete had a 28-day Poisson's ratio ranging from 0.14 to 0.25. At elevated temperatures, the modulus of elasticity of fly ash concrete using Saskatchewan lignite fly ash decreased in a similar way as that of plain concrete. Nasser and Marzouk [90] reported that when fly ash concrete was heated from 21 to 232°C in the sealed containers to prevent loss of moisture, the modulus of elasticity was reduced up to 40%.

Langley et al. [68] found that at the age of 28 days, the modulus of elasticity of concretes made with 50% fly ash constituting the cementitious material varied between 27.9 and 36.1 GPa compared to 31.5–36.8 GPa for control concrete mixes. However, at 365 days, fly ash concrete mixes exhibited significant increase in modulus of elasticity compared to control concrete mixes.

Siddique [112] studied the effect of partial replacement of fine aggregate (sand) with varying percentages of Class F fly ash on the modulus of elasticity of concrete. Fine aggregate (sand) was replaced with five levels of percentages (10, 20, 30, 40, and 50%) of Class F fly ash by weight. A control mix without fly ash was proportioned to have a 28-day cube compressive strength of 26.4 MPa. 150 × 300 mm cylinders were cast for modulus of elasticity. Tests were



**Fig. 1.12** Modulus of elasticity versus fly ash percentage [112]



performed up to the age of 365 days, and results are shown in Fig. 1.12. He concluded that (1) modulus of elasticity of fine aggregate (sand) replaced fly ash concrete specimens was higher than the plain concrete (control mix) specimens at all the ages. The differential between the fly ash concrete specimens and plain concrete specimens became more distinct after 28-days; (2) modulus of elasticity of fine aggregate (sand) replaced fly ash concrete continued to increase with age for all fly ash percentages; and (3) at all ages, the maximum value of modulus of elasticity occurs with 50% fly ash content. It is 24.5 GPa at 28-day, 28.0 GPa at 91-day, and 29.0 GPa at 365-day.

### 1.9.6 Sorptivity and Porosity

Gopalan [43] studied the sorptivity of concretes made with fly ash. Sorptivity measurements based on capillary movement of water were made on three grades (designated as M1, M2 and M3) of cement concrete having water cement ratios of 0.53, 0.62 and 0.88. Each grade of concrete was then incorporated with two levels (20 and 40%) of fly replacement with cement by weight.  $100 \times 25$  mm discs were made for absorption tests. Samples were subjected to standard fog curing at  $23^\circ\text{C} \pm 2^\circ\text{C}$  and relative humidity of  $95 \pm 3\%$  for 7 days. Samples were also cured (dry curing) at  $23^\circ\text{C} \pm 2^\circ\text{C}$  and relative humidity of  $50 \pm 3\%$ . Measured sorptivity results are given in Table 1.17. Based on the test results, he concluded that (1) addition of fly ash influenced the sorptivity of the hardened concrete which strongly depended on the curing conditions. When fog cured concretes of identical strengths were considered, sorptivity of fly ash concretes was found to be lower than that of cement concrete. Under drying-curing conditions, the fly ash concrete had higher sorptivity than cement concrete; (2) addition of fly ash up to 20% did not change the sorptivity characteristics substantially, but for high fly ash concretes, sorptivity was lower than cement concrete of identical strength; under

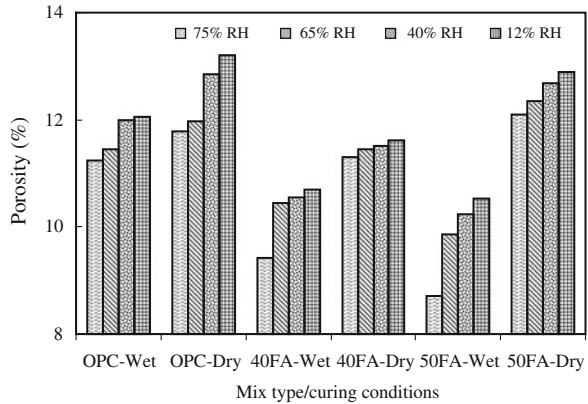
**Table 1.17** Sorptivity ( $\text{mm/h}^{1/2}$ ) of fly ash concretes [43]

Mix	Sorptivity ( $\text{mm/h}^{1/2}$ )					
	28 days		91 days		180 days	
	Fog	Dry	Fog	Dry	Fog	Dry
M1-00	10.4	12.1	10.1	10.6	10.5	10.9
M2-00	10.5	12.8	9.7	11.3	11.4	12.1
M3-00	12.0	14.1	10.4	13.2	12.2	15.2
M1-20	11.0	15.3	9.0	11.7	8.0	12.4
M2-20	11.6	15.6	10.0	14.0	10.2	17.1
M3-20	13.4	15.9	9.7	16.9	9.6	18.2
M1-40	8.5	13.3	5.9	16.7	8.9	18.0
M2-40	9.6	18.9	8.0	17.0	9.3	22.0
M3-40	11.4	17.2	7.9	22.2	9.4	21.5

drying conditions, sorptivity increased by an average of 22%; (3) for fly ash replacement of 20%, there was no noticeable difference between fog cured fly ash and cement concretes; (4) for samples under drying conditions, the increase in sorptivity was 19%; and (5) thus, inadequate curing for a 20% fly ash concrete resulted in an increase of 20% in sorptivity. The corresponding value for 40% fly ash concrete was 60%.

Shafiq and Cabrera [111] investigated the influence of curing conditions on the porosity and degree of saturation of normal concrete (100% OPC) and blended cement concrete (OPC/FA). Three different concrete mixes were prepared using 0, 40, and 50% fly ash content as partial substitution for cement. Mix proportion of control concrete was 1:2.33:3.5. Concrete slabs of dimensions 400-mm long, 250-mm wide, and 40-mm thick, were cast in a wooden mould. After 24 h, the moulds were stripped and slabs were cured for 28 days under two different curing conditions, wet cured (in the fog room) and dry cured (at 65% RH at 20°C). At the end of this initial curing, 50-mm-diameter cylindrical discs were cored out from the slabs. After initial curing, samples were exposed to different climatic conditions (75, 65, 40, and 12% relative humidity at a constant temperature of 20°C) until the equilibrium moisture condition was achieved. Total porosity and degree of saturation was determined using vacuum saturation technique [104]. Porosity of concrete samples is shown in Fig. 1.13. Degree of saturation results are given in Table 1.18. They concluded that (1) initial curing conditions affect the total porosity of concrete mixes. For OPC concrete, total porosity of dry cured samples was 5–10% higher than that of their corresponding wet cured samples. For 40 FA concrete, the total porosity of dry cured samples was increased by 9–20% as compared to that of wet cured samples, whereas a significantly higher porosity value of dry cured 50 FA concrete samples was obtained with respect to the corresponding wet cured samples; it ranged from 23 to 40% higher porosity value; (2) average value of the degree of saturation of wet cured samples equilibrated at 75% RH was obtained as 68%, where as for the corresponding dry cured samples it was determined as 56%. Similarly, an average value of 15 and 13% was determined respectively for wet cured and dry cured samples, those were equilibrated at

**Fig. 1.13** Total porosity of different concrete mixes [111]



**Table 1.18** Degree of saturation of OPC and FA blended cement concrete cured in wet and dry conditions [111]

RH (%)	Measured degree of saturation (%)					
	OPC		40 FA		50 FA	
	Wet	Dry	Wet	Dry	Wet	Dry
75	68.87	59.07	70.24	53.23	66.04	51.45
65	59.34	53.01	61.54	49.04	53.03	47.15
40	34.98	29.97	29.59	28.29	27.97	24.54
12	14.71	13.20	11.69	11.61	15.52	12.89

12% RH; and (3) initial curing condition is one significant factor that controls the porosity and pore network formation of different types of concrete.

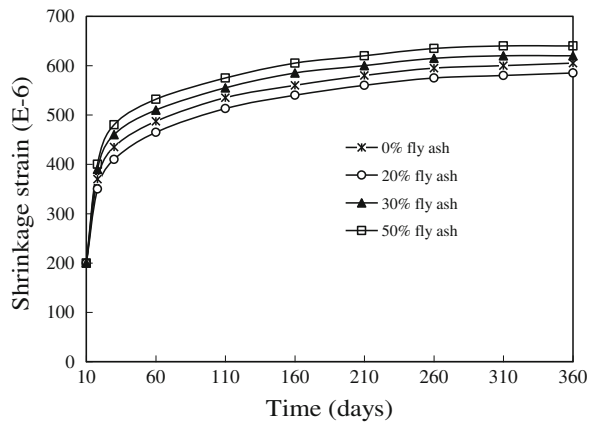
### 1.9.7 Shrinkage

Volume changes in concrete due to hydration reactions, drying, wetting and drying, and thermal variation occur even without application of any loads. Under normal field conditions, drying shrinkage is an important phenomenon which induces time dependent deformations and is sometimes called creep under zero loads.

Klieger and Perenchio [63] found insignificant differences between the shrinkage of concretes made with or with out Class F fly ash blended cements.

Ghosh and Timusk [41] reported that shrinkage of concrete containing fly ash was lower than that of concrete without fly ash for the same maximum size of aggregate and for all strength levels. Munday et al. [83] concluded that incorporation of fly ash did not significantly affect the shrinkage and expansions due to drying, wetting/drying and thermal changes in concrete.

**Fig. 1.14** Drying shrinkage of concretes incorporating high-calcium fly ash [129]



Yuan and Cook [129] reported that fly ash concrete containing 30 and 50% fly ash exhibited more shrinkage than either the control concrete or concrete containing 20% fly ash, as shown in Fig. 1.14.

Nasser and Al-Manasser [91] reported that up to 20% replacement of cement with fly ash did not have significant effect on the drying shrinkage of concrete. Increase in drying shrinkage with fly ash addition may occur from increase in the paste volume if water content is the same. However, when water content was reduced, shrinkage was observed minimal.

Haque et al. [44] investigated the shrinkage of concrete containing 40–75% cement replacement with a bituminous fly ash (CaO 10%). They concluded that drying shrinkage of concrete decreased with increase in fly ash content.

Atis et al. [8] assessed the drying shrinkage of mortar mixtures containing high-calcium nonstandard fly ash up to the age of 5 months. Five mortar mixtures including control Portland cement and fly ash mortar mixtures were prepared. Fly ash replaced cement on mass basis at the replacement ratios of 10, 20, 30 and 40%. Water–cementitious materials ratio was 0.4. Mixtures were cured at 65% relative humidity and  $20 \pm 2^\circ\text{C}$ . They reported that shrinkage of Portland cement mortar at 5 months was 0.1228%. Shrinkage of fly ash mortar decreased with the increase in fly ash content. Shrinkages of mortar containing 10, 20 and 30% fly ash were 25, 37 and 43%, lower than the shrinkage of Portland cement mortar at the end of 5 months. The reduction in shrinkage with the use of fly ash in mortar could be explained by the dilution effect of fly ash. The expansive property of fly ash most probably contributed to the reduction in drying shrinkage.

### 1.9.8 Creep

Creep is the time dependent strain due to sustained loading. The effect of fly ash on creep of concrete are limited primarily to the extent to which fly ash influences the ultimate strength and rate of strength gain. For the same strength concrete made

with and without fly ash, concrete without fly ash would produce less creep strain at all subsequent ages.

Lohtia et al. [71] studied the creep and creep recovery of plain and fly ash concretes at stress-strength ratios of 20 and 35%. Fly ash content was varied between 0 and 25%. They concluded that (1) replacement of 15% of cement with fly ash was optimum with respect to strength, elasticity, shrinkage and creep of fly ash concrete; (2) creep-time curves for plain and fly ash concretes were similar, and creep linearly related to the logarithm of time; (3) with fly ash content up to 15%, increase in creep was negligible. However, slightly higher creep occurred with fly ash content more than 15%; (4) creep coefficients were similar for the materials with fly ash content in the range of 0–25%; and (5) creep recovery was found to vary from 22 to 43% of the corresponding 150-day creep. For replacement beyond 15%, the creep recovery was smaller. No definite trend of creep recovery as a function of stress-strength ratio was observed.

Ghosh and Timusk [41] concluded that fly ash concrete proportioned for equivalent 28-day strength of plain concretes ranging from 20 to 55 MPa exhibited lesser creep than that of the plain concrete. This was possibly because of the favorable effect of pozzolanic reactions due to fly ash which caused higher rate of strength gain after the time of loading. Yuan and Cook [129] showed that high strength concretes containing 20 to 50% high-calcium fly ash exhibited opposite trend in that fly ash concrete containing 30 to 50% ash had more creep than control concrete. However, the 20% fly ash concrete exhibited about the same creep as control concrete.

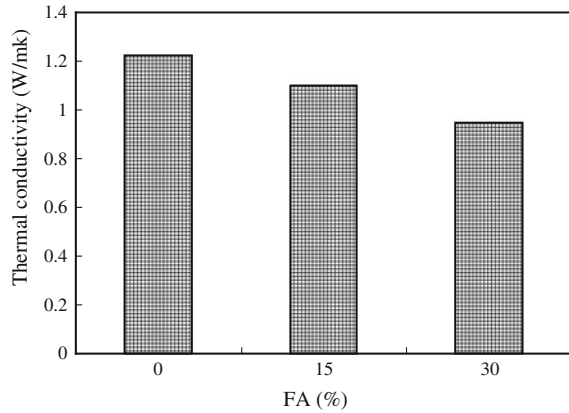
Nasser and Marzouk [90] observed that creep of concrete with 20% fly ash under sealed conditions showed a continuing reduction with an increase in temperature except at 177°C, while that of unsealed specimens increased with temperature up to 71°C and decreased thereafter within the range of temperature between 21.4 and 232°C.

Nasser and Al-Manasser [91] concluded that concrete containing 20% fly ash in unsealed conditions had on average 72% greater creep than the equivalent sealed concrete for stress-strength rates varying from 10 to 60%. However concrete with 50% fly ash had 13% less creep for unsealed specimens and 39% less for sealed ones. Similar behavior was reported by Carette and Malhotra [20] with various types of Canadian fly ashes including Saskatchewan fly ash. In their study, concrete with 20% fly ash produced consistently lower creep compared to that of control concrete.

### ***1.9.9 Thermal Conductivity***

Thermal conductivity (TC) and other thermal transport properties of construction materials are essential in predicting the temperature profile and heat flow through the material. Mineralogical character of the aggregate greatly influences the TC of concrete [92]. Thermal conductivity of concrete depends upon (1) aggregate type;

**Fig. 1.15** Thermal conductivity of concrete with fly ash [27]



(2) moisture content; and (3) porosity. Aggregate with crystalline structure shows higher heat conduction than amorphous and vitreous aggregate of the same composition. Porosity and moisture content are other important factors that influence the TC of concrete.

Demirboğa [27] studied the influence of partial replacement of cement with fly ash on the TC of concrete. Cement was replaced with 0, 15, and 30% fly ash. Variation of thermal conductivity with fly ash is shown in Fig. 1.15. It can be seen from this figure that TC decreased with the increase in fly ash content. For 15 and 30% FA replacement, the reductions were 12 and 23%, respectively, compared to the corresponding control specimens.

Demirboğa et al. [28] investigated the TC of HVFA concrete at the age of 28 days. Cement was replaced with 0, 50, 60, and 70% of Class C fly ash. They concluded that TC of concrete decreased to 32, 33, and 39% for 50, 60 and 70% fly ash replacement, respectively.

## 1.10 Durability Properties of Concrete made with Fly Ash

### 1.10.1 Permeability

Permeability is the key to the durability of concrete exposed to harsh environments. Permeability of concrete is very important in determining the rates of mass-transport relevant to destructive chemical action. Mehta [79] identified water as either the agent of destruction or a necessary participant in many different types of deterioration in concrete such as frost damage, leaching of CH, acid attack, sulfate attack, corrosion of reinforcement, and alkali–aggregate reaction.

The permeability of concrete primarily depends on the size, distribution and continuity of the pores of the hydrated paste of the concrete. The important factors

which control the pore structure of the paste are degree of hydration and water cement ratio.

In ordinary Portland cement concrete, calcium hydroxide formed during hydration of Portland cement can be leached out over a period of time. This creates channels available for the ingress of water and deleterious salt solutions. However, when fly ash is incorporated, it reacts with the calcium hydroxide in the water filled capillary channels to produce calcium silicate and aluminate hydrates of the same or similar type that are formed in the normal hydration of cement. Thus the calcium hydroxide is consumed in the pozzolanic reactions and converted to water insoluble hydration products. The reactions reduce the risk of leaching calcium hydroxide. The reaction products also tend to fill capillaries, thereby reducing permeability to aggressive fluids such as chloride or sulfate solutions.

The addition of fly ash results in considerable pore refinement. It transforms bigger pores into smaller ones due to the formation of pozzolanic reaction products concomitant with the progress of cement hydration. Since strength and impermeability are inversely related to the volume of pores larger than 100 Å in the hydrated paste, the phenomenon of pore refinement in fly ash concrete leads to the improvement in these characteristics.

Permeability of concrete containing fly ash can be determined by following methods

- Water permeability
- Rapid chloride permeability
- Air/gas permeability

### 1.10.1.1 Water Permeability

Rodway and Fedriko [105] investigated the water permeability of concrete incorporating Class C fly ash for 68% cement replacement. They reported permeability of fly ash concrete as  $3.65 \times 10^{-12}$  m/s. Ellis et al. [36] observed decrease in permeability of concrete with increase in both either Class C or Class F fly ash contents for a fixed amount of cement. They concluded that (1) concrete containing Class F was more effective than concrete with Class C fly ash in reducing permeability; and (2) permeability values of Class F fly ash concrete were either comparable to or superior to those achieved by using either silica fume or GGBS.

Shafiq and Cabrera [111] investigated the effect of curing conditions on the water permeability of normal concrete and blended cement concrete (OPC/FA). Concrete mixes were made with 0, 40, and 50% fly ash content as partial substitution for cement. Mix proportion of control concrete was 1:2.33:3.5. Concrete slabs of dimensions 400-mm long, 250-mm wide, and 40-mm thick, were cast, and were cured for 28 days under two different curing conditions, wet cured (in the fog room) and dry cured (at 65% RH at 20°C). cylindrical discs of 50-mm diameter were cored out from the slabs after the initial curing. Samples were then exposed

**Table 1.19** Coefficient of water permeability,  $K_{op}$  ( $\times 10^{-19}$  m<sup>2</sup>) and permeability ratio of OPC and fly ash blended cement concrete cured in wet and dry conditions [111]

RH (%)	Concrete type/curing condition								
	OPC			40 FA			50 FA		
	Wet	Dry	Dry/wet	Wet	Dry	Dry/wet	Wet	Dry	Dry/wet
75	11.0	210.0	19.1	2.8	442.0	157.9	10.0	3080.0	309.5
65	35.0	305.0	8.7	11.4	468.0	41.1	20.9	5140.0	245.9
40	166.0	658.0	3.9	22.8	678.0	29.7	62.0	12300.0	198.4
12	764.0	3870.0	5.1	425.0	6830.0	16.1	231.0	13300.0	57.6

to different climatic conditions (75, 65, 40, and 12% relative humidity at a constant temperature of 20°C) until the equilibrium moisture condition was achieved. Water permeability of concrete was determined by a penetration method. Coefficients of water permeability are given in Table 1.19. Based on the test results, they concluded that (1) water permeability ratio as calculated for OPC and fly ash blended concrete followed a similar trend but on different scales. For initially dry cured OPC concrete, the coefficients of water permeability were 2–19 times higher than the coefficients obtained for the initially wet cured concrete samples. In contrast, the coefficients of water permeability of dry cured fly ash blended cement concrete were 16–210 times greater than the coefficients of the corresponding wet-cured concrete samples; (2) a large difference in the coefficient of fluid permeability and/or diffusion between the dry cured and wet cured concrete was observed when concrete samples were equilibrated at 75% RH. In contrast a small difference between the fluid transport coefficients of dry cured and wet cured concrete samples was observed when they were equilibrated at 40 and 12% relative humidity (RH); and (3) there was approximately 12% difference between the average degree of saturation of dry cured concrete samples equilibrated at 75% RH and the average degree of saturation of the corresponding wet cured concrete samples, which resulted in the much higher values of the fluid permeability and diffusion coefficients of dry cured samples relative to wet-cured samples. This is probably due to the fact that the wet cured concrete samples when equilibrated at higher RH, have a tight pore network with small pore diameters and exhibit very high degree of saturation.

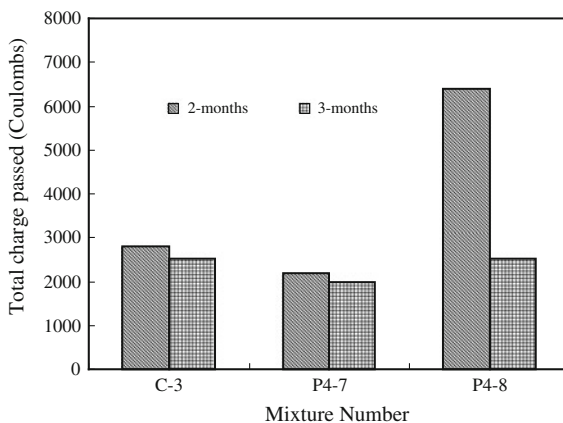
### 1.10.1.2 Chloride Permeability

Bilinear and Amphora (1992) measured water and chloride permeability of concretes having 55–60% cement replacement with various sources of fly ash. They reported coefficient of water permeability of fly ash concretes in the range of  $1.6 \times 10^{-14}$  to  $5.7 \times 10^{-13}$  m/s. The values of chloride were less than 650 C at 91 days.

Naik et al. [86] evaluated the influence of addition of large amounts (50 and 70% cement replacement) of Class C fly ash on the chloride permeability of



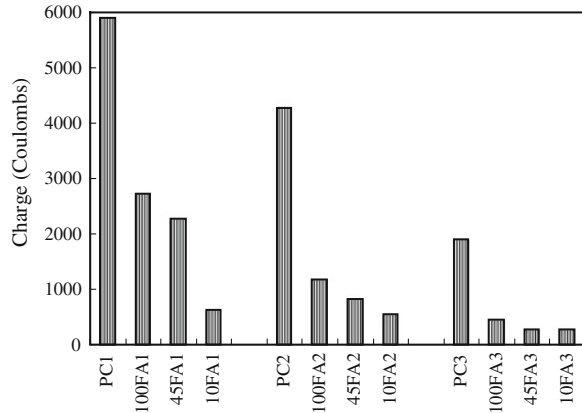
**Fig. 1.16** Effect of fly ash addition on chloride permeability of concrete [86]



concrete. Concrete mixtures were designated as C-3 (0% fly ash), P4-7 (50% fly ash) and P4-8 (70% fly ash). Chloride permeability was determined in accordance with ASTM C1202, and chloride permeability results are shown in Fig. 1.16. Chloride permeability decreased with age. At the age of 2 months, all concrete mixtures except the 70% fly ash mixture exhibited moderate (2,000–4,000 C) permeability in accordance with ASTM C1202 specifications. The 50% fly ash concrete mixture showed lower permeability relative to the no-fly ash concrete at all ages. The 70% fly ash mixture also performed better than that of the no-fly ash concrete after 3 months.

Chindaprasirt et al. [22] examined the effect of fly ash fineness on the chloride permeability of concrete. Three fly ash finenesses: coarse, medium and fine were used. The coarse fly ash was 100% original fly ash (100 FA). 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 (10 FA). Three concrete mix series viz. a low, normal 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 PC mixes. For the high strength concrete, the water-to-cement ratio was 0.25 with the use of superplasticizer. Rapid chloride permeability (Coulomb charge) test was conducted at the age of 28 days as per ASTM C1202, and test results are shown in Fig. 1.17. Based on the test results they concluded that (1) coulomb charge for the PC concrete was higher than those of the fly ash concrete in the same group; (2) for low-strength concrete, the coulomb charge of the PC1 concrete was 5,800 indicating a rather poor chloride penetration characteristic. Incorporation of fly ashes resulted in drastic reductions in the coulomb charges. The Coulomb charge of the original fly ash concrete (100FA1) was reduced to 2,700, indicating moderate chloride penetration resistance. The charge was further reduced with the increase in the fly ash fineness. The charges of the 45FA1 and 10FA1 concrete are reduced to 2,300 and 700, respectively; (2) for the normal strength concrete, the coulomb charge of the PC2 concrete was 4,200 and the charges of the fly ash concrete were 1,250, 800 and 500 for the 100FA2, 45FA2

**Fig. 1.17** Coulomb charge of concrete at the age of 28 days [22]



and 10FA2 mixes, respectively; and (3) for the high strength concrete group, the coulomb charge of the PC3 concrete was slightly higher than 1,000 and the charges of the fly ash concrete were only 500, 250 and 240 for the 100FA3, 45FA3 and 10FA3 mixes, respectively. Even at this high strength level, the reduction in the coulomb charge owing to the incorporation of the fly ash especially with the fine fly ashes was quite evident.

### 1.10.1.3 Gas permeability

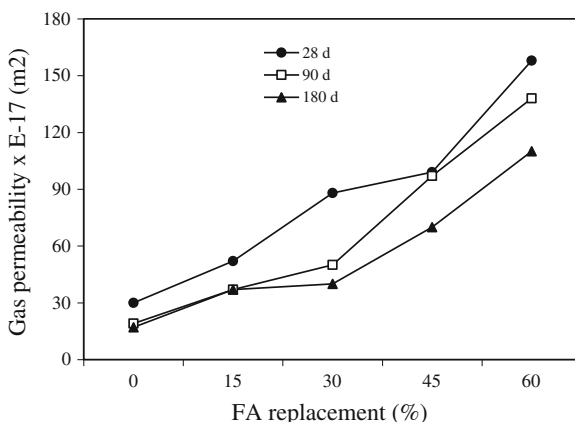
Kasai et al. [60] studied the air/gas permeability of mortar made with blended cements containing fly ash and blast furnace slag. The study was important from durability aspects of concrete with respect to carbonation. Up to the age of 7 days, blended cement mortars exhibited more permeability than plain cement mortars. However, as curing age increased, the permeability of blended cement mortars decreased. In general terms, the permeability was found to be directly related to the compressive strength development of the mortars.

Shafiq and Cabrera [111] investigated the effect of curing conditions on the oxygen permeability of normal concrete (100% OPC) and blended cement concrete (OPC/FA). Mix proportion of control concrete was 1:2.33:3.5. Fly ash content was 0, 40, and 50% as partial substitution for cement. The gas permeameter developed by Cabrera and Lynsdale [18] was used to measure the oxygen permeability of cylindrical concrete samples of 50-mm diameter and 40-mm thick. Water permeability of concrete was determined by a penetration method. Coefficients of oxygen permeability are given in Table 1.20. Based on the test results, they concluded that (1) oxygen permeability ratios as calculated for OPC and fly ash blended concrete followed a similar trend but on different scales. For initially dry cured OPC concrete, the coefficients of oxygen permeability were 2–19 times higher than the coefficients obtained for the initially wet cured concrete samples. In contrast, the coefficients of oxygen permeability of dry cured fly ash blended

**Table 1.20** Coefficient of oxygen permeability,  $K_o \times 10^{-19} \text{ m}^2$  and permeability ratio of OPC and fly ash blended cement concrete cured in wet and dry conditions [111]

RH (%)	Concrete type/curing condition								
	OPC			40 FA			50 FA		
	Wet	Dry	Dry/wet	Wet	Dry	Dry/wet	Wet	Dry	ry/wet
75	13.3	230.0	17.3	2.5	518.0	208.9	4.1	906.0	220.4
65	62.1	308.0	5.0	18.2	665.0	36.5	31.8	1070.0	33.6
40	192.0	486.0	2.5	104.0	1720.0	16.5	91.8	2270.0	24.7
12	337.0	772.0	2.3	136.0	2210.0	16.3	117.0	2690.0	23.0

**Fig. 1.18** Influence of FA on nitrogen gas permeability of HPC [48]



cement concrete were 16–210 times greater than the coefficients of the corresponding wet cured concrete samples; (2) a large difference in the coefficient of fluid permeability and/or diffusion between the dry cured and wet cured concrete was observed when concrete samples were equilibrated at 75% RH.

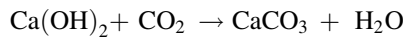
Hui-sheng et al. [48] examined the influence of fly ash on the nitrogen gas permeability of high-performance concrete (HPC) up to the age of 180 days. Control mixture contained cement (550 kg/m<sup>3</sup>), fine aggregate (687 kg/m<sup>3</sup>), and coarse aggregates (1,030 kg/m<sup>3</sup>). Fly ash replacement levels were 0, 15, 30, 45 and 60% by weight of cement, with water-binder ratio of 0.30. Influence of FA on gas permeability of HPC is shown in Fig. 1.18. It can be observed that gas permeability coefficients significantly increased with the increase in FA replacement. According to Bamforth [13] and McCarthy and Dhir [77], fly ash can have significant reduction in permeability of normal concrete, however, their effects on HPC were not obvious. For instance, Thomas (1992) reported that fly ash had a significant reduction in gas permeability of normal concrete. However, according to Khan [62], incorporation of fly ash in HPC only had marginal reduction in oxygen permeability. The underlying mechanism may be attributed to the fact that HPC is much denser and hydrates slower than normal concrete, thus the filler

effect and pozzolanic effect in HPC may not work as well as that in normal concrete.

Thomas and Matthews [122] investigated oxygen permeability of fly ash concrete. Concrete mixtures were made with 15, 30 and 50% fly ash as cement replacements, exhibited reduction in the permeability values by 50, 60 and 86%, respectively, compared to concrete with out fly ash.

### 1.10.2 Carbonation

Carbonation is a chemical reaction that takes place between portlandite and  $\text{CO}_2$ . Portlandite is present in the hydrated cement. The gas  $\text{CO}_2$  is present in the atmosphere. When  $\text{CO}_2$  penetrates into the hardened concrete, it reacts with portlandite in the presence of moisture forming  $\text{CaCO}_3$ . This is expressed as



Carbonation requires the presence of water because  $\text{CO}_2$  must dissolve in water and form  $\text{H}_2\text{CO}_3$ . According to Taylor [120],  $\text{OH}^-$  and  $\text{Ca}^{2+}$  ions required by these reactions are obtained by the dissolution of CH and decomposition of the hydrated silicate and aluminate phases. Decalcification of the C–S–H is evidenced initially by a reduction in the Ca/Si ratio, and ultimately by conversion into a highly porous form of silica. Phenolphthalein tests show that the pH falls to 8.5 or below, accelerating the rate of corrosion.

The rate at which concrete carbonates depends upon (1) its permeability; (2) degree of saturation with water; and (3) mass of calcium hydroxide available for reaction; (4) relative humidity; and (5) temperature of the environment where concrete is placed.

Gebauer [39] reported that an increase in water–cement ratio of concrete mix resulted in an increase in the depth of carbonation. Kasai et al. [60] studied the carbonation of mortar specimens made with different types of cement and fly ash after 7 days of moist curing. It was observed that (1) carbonation was observed to progress rapidly up to 3 months and after that it slowed down; and (2) greater the coefficient of permeability of the specimen, the greater was its susceptibility of  $\text{CO}_2$  attack manifested in terms of increased depth of carbonation. The specimens made with fly ash cement exhibited greater carbonation effect than ordinary Portland cement specimens.

Nagataki and Ohga [85] found that rate of carbonation increases with fly ash content of mortars. However, longer curing periods reduce the rate of carbonation, and mortars with greater fly ash contents are more sensitive to the length of the curing period. These results are consistent with the slower hydration and development of a discontinuous pore system in fly ash cement pastes.

Schubert [110] believed that the consumption of  $\text{Ca(OH)}_2$  in the pozzolanic reaction acts to increase the rate of carbonation, while the blocking of capillary pores to acts to decrease it. Kokubu and Nagataki [64] reported the 20-year data on

outdoor exposure of concretes at various locations show that the carbonation depth increases with water-to-cementitious ratio, slump, and level of fly ash replacement. Carbonation depth also increases with reductions in the total content of cementitious materials.

Ho and Lewis [46] investigated the carbonation rates of three types of concrete mixes (1) plain concrete; (2) the second containing a water reducing admixture; and (3) third in which fly ash was used to replace part of the cement. Accelerated carbonation was induced by storing specimens in an enriched CO<sub>2</sub> atmosphere (4%) at 20°C and 50% RH for 8 weeks. One week under these conditions was approximately equivalent to 1 year in a normal atmosphere (0.003% CO<sub>2</sub>). They concluded that (1) concretes having the same strength and water-to-cement ratio do not necessarily carbonate at the same rate; (2) concrete containing fly ash showed significant improvement in quality when curing was extended from 7 to 90 days. This improvement was much greater than that achieved for the plain concrete; and (3) depth of carbonation is a function of the cement content for concretes moist-cured for 7 days. However, with further curing to 90 days, concrete containing fly ash showed a slower rate of carbonation as compared to plain and water-reduced concretes.

Nagataki et al. [84] reported a direct relationship between 28-day compressive strength and depth of carbonation irrespective of fly ash replacement in concrete, and also mentioned that the extent of carbonation decreased with an increase in compressive strength.

Buttler et al. [17] studied the carbonation behavior of cement sand mortars made with 25% pulverized fuel ash or fly ash replacing cement and at water cement ratios of 0.35 to 0.55. They concluded that more carbonation occurred at lower water contents when the fly ash concrete was desiccated with calcium chloride (CaCl<sub>2</sub>). However, in the case of non-desiccated specimens, the effect of fly ash on carbonation at lower water content was insignificant. Of course in non-desiccated specimens, more carbonation was observed at high water cement ratios.

Joshi et al. [59] found that up to about 7 days, the extent of carbonation measured by the affected depth from the outer surface in concrete, after subjecting the specimen to 4% CO<sub>2</sub> at 20°C and 50% RH, was more in concrete containing fly ash than the control concrete without fly ash. However, after 90 days curing, the trend reversed in that the fly ash concrete exhibited less carbonation than the control concrete.

Atis [7] carried out an accelerated carbonation test (using a controlled environment) to assess the carbonation of fly ash (FA) concrete. The concrete mixtures were made with 0, 50 and 70% replacement of normal Portland cement (NPC) with fly ash. Water-cementitious material ratios ranged from 0.28 to 0.55. The proportions of the control NPC concrete mixture (M0) were: 1:1.5:3 NPC, sand and gravel, respectively. The quantity of NPC was 400 kg/m<sup>3</sup>, w/c was 0.55. M0 mixture was conventional Portland cement concrete. M1, M2, M3 and M4 concrete mixtures were made with fly ash. M1 and M3 mixtures also contained superplasticizer. Test results are given in Table 1.21. It is evident from these results that fly ash concrete made with 70% replacement ratio was carbonated

**Table 1.21** Accelerated carbon depth of concrete cured at 100% RH with 20°C [7]

Mix name	Accelerated carbon depth (mm)			
	3 days	7 days	28 days	3 months
M0 (0% FA, w/c 0.55)	9.10	7.40	4.50	3.30
M1(70% FA, w/c 0.28)	13.30	10.90	6.50	4.60
M2(70% FA, w/c 0.29)	13.80	11.70	7.30	5.00
M3(50% FA, w/c 0.33)	8.70	8.40	3.20	1.80
M4(50% FA, w/c 0.30)	9.60	7.50	2.10	1.60

**Table 1.22** Experimental results of carbonation of concrete [52]

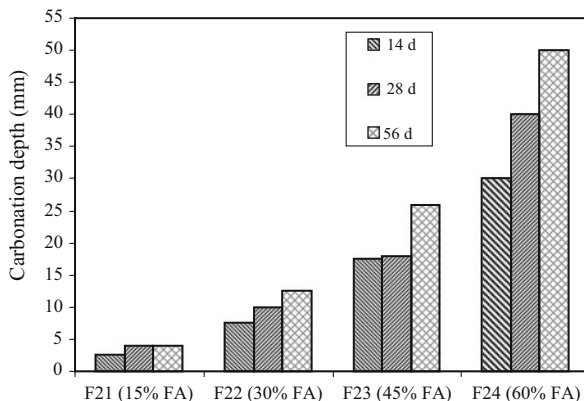
Mix no	Depth of carbonation (mm)							
	Concentration of CO <sub>2</sub> (20%)				Concentration of CO <sub>2</sub> (20%)			
	3d	7d	14d	28d	3d	7d	14d	28d
C1	7.7	10.4	12.7	14.8	7.8	11.2	12.3	13.8
C2	12.2	15.7	19.4	22.4	11.3	14.1	15.8	17.7
C3	10.3	12.4	14.1	15.9	8.1	11.4	12.4	13.7

more than that of 50% fly ash replacement concrete and normal Portland cement (NPC) concrete. In contrast, 50% fly ash replacement concrete showed lower or similar carbonation to NPC concrete. Before exposing the concrete to the accelerated carbonation testing, the longer initial curing period resulted in lower carbonation depth. The effect is more marked with moist curing.

Jiang et al. [52] studied the carbonation of concrete incorporating large volumes of low-quality fly ash (LVLQFA). Three mixtures were prepared. First mixture (C1) was control, second mixture (C2) and third mixture (C3) contained 40% fly ash of the total cementitious materials. Third mixture (C3) also contained activator (11.6%). Tests were conducted up to the age of 28 days with two concentrations of CO<sub>2</sub>. Carbonation results are given in Table 1.22. It is evident that at the 20% CO<sub>2</sub> concentration, carbonation depth of the LVLQFA concrete was greater than of control concrete, especially at the early-age carbonation. The activator can improve the carbonation resistance of LVLQFA concrete. At 28 days, the carbonation depth of the LVLQFA concrete was close to the control concrete. At the concentration of 3% CO<sub>2</sub>, the depth of carbonation of LVLQFA concrete without an activator was greater than others. The carbonation depth of LVLQFA concrete with an activator was close to the control concrete. It is seen, therefore, that the concentration of CO<sub>2</sub> used in the experiment has considerable effect on estimating the carbonation resistance of LVLQFA concrete.

Hui-sheng et al. [48] studied the influence of fly ash on the carbonation of high-performance concrete up to the age of 56 days. Cement, fine aggregate, and coarse aggregates contents were 550, 687, and 1,030 kg/m<sup>3</sup>, respectively. Fly ash replacement levels were 0, 15, 30, 45 and 60% by weight of cement, with water-binder ratio of 0.30. Influence of fly ash on carbonation resistance of HPC is shown in Fig. 1.19. Carbonation phenomenon of the control HPC was not observed at the

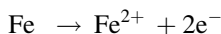
**Fig. 1.19** Influence of FA on carbonation depth of HPC at w/b ratio of 0.30 [48]



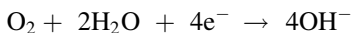
end of each carbonation period. It can be seen that the incorporation of fly ash decreased the carbonation resistance of HPC, but at significantly different levels. For HPC with fly ash at w/b of 0.30, carbonation depth significantly increased with the increase of fly ash replacement.

### 1.10.3 Corrosion Resistance

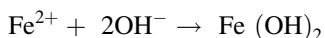
The corrosion of reinforcement is one of the most widespread causes of deterioration in concrete [120]. Nielsen (1979) has given the anodic equation for the corrosion of ions as:



And the cathodic equation as



For the usual case when oxygen is available for reaction. Corrosion in the absence of oxygen is much slower. Thus, the availability of both oxygen and water is critical to the corrosion process. The net reaction is



Corrosion of reinforcing steel embedded in fly ash concrete has great cause of concern for applications of concrete in the construction of reinforced and pre-stressed concrete structures, particularly, those subject to chloride induced corrosion of steel caused by the use of deicing salts or sea water exposure of structures in a marine environment. The bond between the surrounding concrete and steel reinforcement and the high alkalinity of the concrete provide protection from corrosion.

In a hydrated Portland cement paste, about 20%  $\text{Ca(OH)}_2$  by weight of the hydration products is present to provide the reserve basicity for steel protection. Diamond [29] reported that the high alkalinity of the pore solution in cement paste primarily results from the presence of sodium and potassium ions rather than from the presence of calcium hydroxide alone. In the two fly ash systems examined, it was observed that pH of pore solution was reduced from 13.75 in a control system to about 13.55 in the presence of fly ash. Under highly alkaline conditions i.e. pH larger than 11.5 of pore solution in concrete, a protective iron oxide film forms on the surface of reinforcing steel that makes it passive against further corrosion. This passive iron oxide layer is susceptible to the attack by chloride ions in concrete or to carbonation when the pH of the surrounding concrete is reduced below 11.0. Once this passive layer is destroyed, a galvanic cell can form between different areas on reinforcing bars causing reduction at anodic area. Furthermore, the rate and extent of corrosion of embedded steel depends on the electrical conductivity of the surrounding concrete and the permeation of moisture and air through the concrete. In practice, adequate cover of high quality and impervious concrete over the reinforcing steel has been found to provide adequate protection against corrosion.

Saraswathy et al. [107] investigated the influence of activated fly ash on the corrosion resistance of mortar by using anodic polarization technique. Mortar specimens with 0, 10, 20, 30, 40 and 50% fly ash as replacement of cement w/c ratio of 0.45, were subjected to anodic polarization. Mild steel rods were embedded in cylindrical mortar (1:3) specimens of size 58 mm diameters and 60 mm height. Anodic polarization studies have been carried out in 3% NaCl solution. The current flowing at +300 and +600 mV were recorded for mild steel embedded in OPC and OPC replaced by various fly ash systems at 10, 20, 30, 40 and 50% replacement levels and the corresponding magnitude of current for a fixed duration of 12 h are given in Table 1.23. From the table it can be seen that for OPC, the current measurement was 0.43 and 1.04 mA. For as-received fly ash (AFA), the current measurement at 30% replacement was 0.34 and 0.99 mA. On the other hand thermally activated fly ash (TFA) and chemically activated fly ash (CFA) systems showed superior properties even up to 50% replacement level. For example in the case of CFA system, the current measured was found to be 0.40 and 0.56 mA at 50% replacement level. These data clearly illustrated that activated fly ashes improved the corrosion-resistance properties even up to 50% replacement level.

Andrade [4] tested concrete mixes with and without fly ash for corrosion using polarization resistance techniques. The addition of fly ash promoted the corrosion of steel in mortars but had no effect on concrete specimens. The decrease in the alkalinity due to introduction of fly ash was reported to have a major effect in promoting corrosion in fly ash mortar mixes.

Jiang et al. [52] studied the carbonation of concrete incorporating large volumes of low-quality fly ash (LVLQFA). They concluded that (1) corrosion resistance of LVLQFA concrete in 5%  $\text{Na}_2\text{SO}_4$  and 5% HCl solution was better than that of the control concrete; and (2) an activator can improve the corrosion resistance of steel



**Table 1.23** Anodic polarization test parameters for OPC and various activated fly ash blended cement concrete in 3% NaCl solution [107]

System	As-received fly ash (AFA)		Physically activated fly ash (PFA)		Thermally activated fly ash (TFA)		Chemically activated fly ash (CFA)	
	+300 mV shift current (mA)	+600 mV shift current (mA)	+300 mV shift current (mA)	+300 mV shift current (mA)	+300 mV shift current (mA)	+300 mV shift current (mA)	+300 mV shift current (mA)	+300 mV shift current (mA)
OPC (100%)	0.43	1.04	0.43	1.04	0.43	1.04	0.43	1.04
OPC + 10% FA	0.24	0.55	0.16	0.40	0.06	0.08	0.05	0.07
OPC + 20% FA	0.27	0.75	0.21	0.62	0.09	0.14	0.07	0.10
OPC + 30% FA	0.34	0.99	0.30	0.83	0.18	0.26	0.11	0.15
OPC + 40% FA	0.46	1.08	0.38	0.99	0.24	0.40	0.19	0.20
OPC + 50% FA	1.26	2.50	1.00	1.50	0.40	0.66	0.40	0.56

reinforcement in LVLQFA concrete caused by carbonation and seawater. The corrosion resistance of steel reinforcement in LVLQFA concrete with an activator was close to the control concrete.

Chalee et al. [21] studied the effect of W/C ratio on covering depth required against the corrosion of embedded steel of fly ash concrete in marine environment up to 4-year exposure. Fly ash was used to partially replace Portland cement type I at 0, 15, 25, 35, and 50% by weight of cementitious material. Water-to-cementitious material ratios (w/c) of fly ash concretes were varied at 0.45, 0.55, and 0.65. Tests were conducted for corrosion of embedded steel bar after being exposed to tidal zone for 2, 3, and 4 years. Based on the tests, they concluded that (1) covering depth required for the initial corrosion of embedded steel bar in concrete could be reduced with fly ash; (2) decrease in W/C ratio resulted in reducing the covering depth required for initial corrosion, and generally affected the cement concrete rather than the fly ash concrete; (3) fly ash concretes with 35 and 50% replacements and W/C ratio of 0.65, provided the result of corrosion resistance at 4-year exposure as good as cement concrete with W/C ratio of 0.45; and (4) concrete with compressive strength of 30 MPa could reduce the covering depth from 50 to 30 mm by using fly ash to replace Portland cement of 50%.

#### ***1.10.4 Freezing and Thawing Resistance***

Freezing–thawing resistance of concrete depends on both cement paste and aggregate. The actual behaviour in a particular situation depends upon the location of escape boundaries, pore structure of the system, degree of saturation, the soundness of aggregate, degree of hydration, strength of binding paste, and tensile strength of the paste. Escape boundaries are provided by entraining numerous air bubbles in the paste. The pore structure is controlled by the water–cement ratio and curing.

Schiepl and Hardtle [108] concluded that main effect of pozzolanic reactions due to fly ash addition is to change the pore size distributions, the total porosity remaining mostly uncharged. In particular, the capillary water along with calcium hydroxide liberated during cement hydration is largely consumed in pozzolanic reactions. The phenomenon of pore refinement as a result of pozzolanic reactions leads to the breaking of continuity of the capillary pore structure. Malhotra et al. [74] reported that the pozzolanic reactions alter the pore structure of the cement paste and thus densify the transition zone between the paste and aggregates.

Air entrainment has the greater role on freeze–thaw durability of concrete mixtures. Perencho and Klieger [98] found that resistance to freezing and thawing in water was comparable and excellent for air-entrained concretes made with either Type I or Type II cements containing fly ash. Majko and Pistilli [73] found that properly air-entrained concretes made with Class C fly ash showed excellent freeze/thaw durability even at high fly ash contents.

Gebler and Klieger [40] investigated the influence of air entrainment on the air-void parameters of hardened concretes made with both Class C and Class F fly ashes. The concretes were cast after 30, 60 and 90 min of initial mixing. They found that air void spacing factors were almost constant for the majority of concretes containing fly ash which were cast after 90 min. At early periods of casting concretes with Class F fly ash exhibited greater variability in air void parameters than concretes with Class C fly ash.

Yuan and Cook [129] found that up to 400 freeze–thaw cycles, there was no significant difference in mass loss or dynamic modulus for air-entrained concrete with or without Class C fly ash. Concrete with 20% fly ash exhibited better frost resistance than the control concrete. After 400 cycles, concrete made with 50% fly ash showed significant scaling damage. Virtanen [124] evaluated the freezing and thawing resistance concrete made with fly ash. They concluded that (1) air content has the greatest influence on the freeze–thaw resistance of concrete; (2) addition of fly ash had no major influence on the freeze–thaw resistance of concrete if the strength and air content are kept constant.

Carette and Malhotra [19] conducted freeze–thaw tests on concrete mixes with number of Canadian fly ashes. Chemical composition of fly ashes has already been given in Table 1.7. Durability factor for fly ash concrete mixes was determined at 300 cycles and results are given in Table 1.24. It can be seen that with constant air content around 6.4%, all the fly ash concretes had about the same durability factor as control concretes.

Joshi [55] investigated the freezing and thawing resistance of concrete made with 50% fly ash as partial replacement of cement. He concluded that (1) no significant differences were observed in freeze–thaw performance of air-entrained high volume fly ash concrete, and the concrete containing both air-entraining and water-reducing agents; (2) it exhibited relative dynamic modulus of elasticity values in excess of 60% after 300 cycles; and (3) fly ash concrete mixes showed

**Table 1.24** Freeze–thaw durability factors for fly ash concretes [19]

Mix no.	Cement (kg/m <sup>3</sup> )	Air (%)	Durability factor
Control	295	6.4	98.1
F1	236	6.2	96.4
F2	237	6.2	98.8
F3	237	6.2	96.8
F4	238	6.3	98.8
F5	237	6.4	97.2
F6	238	6.5	96.8
F7	239	6.1	97.6
F8	236	6.2	96.9
F9	236	6.4	97.6
F10	237	6.5	97.2
F11	237	6.6	95.8

some scaling after 150 to 200 freeze thaw cycles and exhibited about 2% weight loss at the end of the 300 cycles.

Malhotra et al. [75] examined the durability of high volume Class F fly ash concretes and concluded that superplasticized and air-entrained HFCC showed satisfactory durability against freeze–thaw attack. Schmidt [109] reported that mass loss of concrete cubes subjected to 100 cycles of freezing and thawing was higher for the concretes made with inter-ground fly ash cement than for the Portland cement controls.

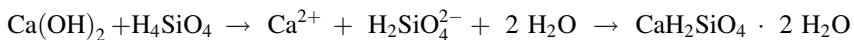
Joshi et al. [58] investigated freezing and thawing resistance of air-entrained and superplasticized concretes containing with 40 to 60% fly ash as partial replacement of cement. The specimens were moist cured for 14 days prior to freeze–thaw tests. The air content of the mixes was maintained at  $6 \pm 1\%$ . The use of fly ash in concrete increased the air entraining agent demand to maintain constant air content. They concluded that most of the mixes had relative dynamic modulus of elasticity values in excess of 60% after 300 freeze–thaw cycles. In general, all the concrete mixes containing Alberta fly ash and with air content more than 5% exhibited acceptable freeze–thaw durability performance.

### ***1.10.5 Alkali–Silica Reaction***

Alkali–silica reaction (ASR) is caused by a reaction between the hydroxyl ions in the alkaline cement pore solution in the concrete and reactive forms of silica in aggregate such as chert, quartzite, opal, strained quartz crystals. Alkali ions ( $\text{Na}^+$  and  $\text{K}^+$ ) from cement, mixing water increase the concentration of  $\text{OH}^-$  ions in the pore solution. The  $\text{OH}^-$  dissolves amorphous silica ( $\text{SiO}^{-2}$ ) in the aggregate, forming a gel of variable chemical composition. The gel imbibes water from the environment, expanding and generating hydraulic stresses in the cement paste which may cause cracking.

According to Mehta [79], the solubility of alkali silicate gel in water accounts for its mobility from the interior of the aggregate to micro-cracked regions within the aggregate or the cement paste. Continued availability of water to the gel causes further expansion, resulting in further crack growth.

The ASR reaction is the same as the Pozzolanic reaction which is a simple acid–base reaction between calcium hydroxide, also known as Portlandite, or ( $\text{Ca}(\text{OH})_2$ ), and silicic acid [ $\text{H}_4\text{SiO}_4$ , or  $\text{Si}(\text{OH})_4$ ]. For the sake of simplicity, this reaction can be schematically represented as following:



This reaction causes the expansion of the altered aggregate by the formation of a swelling gel of calcium silicate hydrate (CSH). This gel increases in volume with water and exerts an expansive pressure inside the material, causing spalling and loss of strength of the concrete, finally leading to its failure.

Alkali–silica reaction is also known as alkali–aggregate reaction (AAR). The conditions required for ASR to occur are:

- Sufficiently high alkali content of the cement
- A reactive aggregate, such as chert
- Water—ASR will not occur if there is no available water in the concrete, since alkali–silica gel formation requires water

The mechanism of ASR causing the deterioration of concrete can be described as:

- Alkaline solution attacks the siliceous aggregate to convert it to viscous alkali silicate gel.
- Consumption of alkali by the reaction induces the dissolution of  $\text{Ca}^{2+}$  ions into the cement pore water. Calcium ions then react with the gel to convert it to hard calcium silicate hydrate.
- Penetrated alkaline solution converts the remaining siliceous minerals into bulky alkali silicate gel. The resultant expansive pressure is stored in the aggregate.
- Accumulated pressure cracks the aggregate and the surrounding cement paste when the pressure exceeds the tolerance of the aggregate.

However, ASR can be mitigated in concrete by following approaches:

- Limiting the alkali metal content of the cement.
- Limiting the reactive silica content of the aggregate: certain volcanic rocks are particularly susceptible to ASR because they contain volcanic glass and should not be used as aggregate.
- Addition of very fine siliceous materials: to neutralize the excessive alkalinity of cement with silicic acid by voluntarily provoking a controlled pozzolanic reaction at the early stage of the cement setting. Convenient pozzolanic materials to add to the mix may be, e.g., pozzolan, silica fume, fly ashes, or metakaolin.

The use of pozzolans such as fly ash in the concrete mix as a partial replacement of cement can reduce the likelihood of ASR occurring as they reduce the alkalinity of the pore fluid. Numerous early studies suggested the effectiveness of fly ash in inhibiting or reducing expansion resulting from ASR [97, 116].

Stanton [116] recognized the deterioration of concrete because of reaction between the alkaline hydroxyl ions in the pore water of concrete and certain forms of silica occasionally present in the aggregate. Investigation was conducted using aggregates containing opaline material and cement with acid soluble alkali content of more than 0.6%. Deleterious expansion due to the alkali–silica reaction could be reduced or eliminated by the addition of finely divided mineral admixtures including fly ash containing siliceous material.

Dunstan [34] identified aggregates and their mineralogical constituents that can react with alkalis in concrete. They are (1) silica materials—opaline or chalcocindic cherts, tridymite, cristobalite, siliceous limestone; (2) glassy to crypocrystalline rhyolites, dacites, and their tuffs; (3) zeolite and neulandite; and

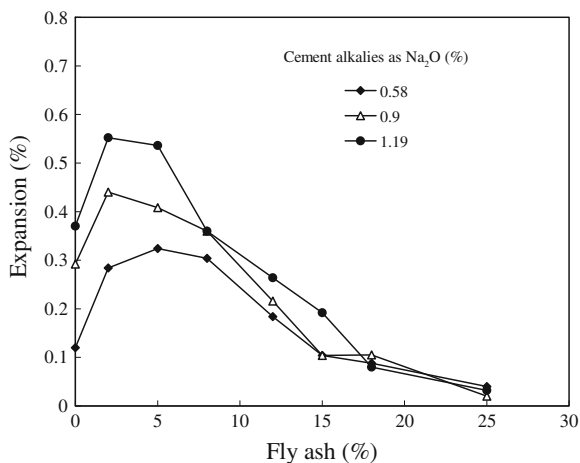
(4) certain phylites. An effect of cement alkalies and fly ash on alkali–aggregate reaction as reported by Dunstan [34] is shown in Fig. 1.20.

Hobbs [47] studied the effect of different Class F fly ashes on the alkali silica reactivity of mortars made with opaline aggregates and high alkali cement. Based on the test results, he concluded that (1) partial replacement of a high-alkali cement with fly ash reduced the long-term expansion due to alkali–silica reactivity but, even when 30 or 40% of the cement was replaced, most of the blended cement mortars cracked at earlier or similar ages as compared to the Portland cement mortars; (2) where part of the cement was replaced by fly ash, the lowest mortar alkali content, expressed as equivalent  $\text{Na}_2\text{O}$ , at which cracking was observed was  $2.85 \text{ kg/m}^3$ . This related only to acid soluble alkalis contributed by the Portland cement and compared with  $3.5 \text{ kg/m}^3$  for a Portland cement mortar; (3) if it is assumed that fly ash acts effectively like a cement with an alkali content of 0.2% by weight, the lowest alkali content at which cracking was observed was  $3.4 \text{ kg/m}^3$ ; and (4) fly ash acts as alkali diluters, slag being more effective in reducing damage due to alkali–silica reactivity than fly ash.

Oberholster and Westra [93] observed that fly ash addition effectively suppressed expansion at cement replacement levels of 20% or more on an equal volume basis. Mehta [78] concluded that alkali–silica reaction progresses slowly and the continuous formation of swelling type gel causes internal disruption and cracking of concrete. The damage to concrete due to this reaction is appreciably aggravated when other causes of deterioration such as weathering effects of freeze–thaw, sulfate attack, and other aggressive physical and chemical processes are concurrently active.

Perry et al. [99] investigated the influence of 12 different Canadian fly ashes on the alkali–aggregate reaction of mortar mixes made with reactive opaline aggregate. Replacement levels of cement with fly ash were 20–40%. They concluded that reduction in expansion after 1 year ranged from 5 to 81 at 20% replacement

**Fig. 1.20** Effects of cement alkalies and fly ash on alkali–aggregate reaction [34]



level, 34 to 89 at 30% replacement level, and 47 to 92% at 40% replacement level, respectively, compared to that of control mortar mix (no fly ash).

Idorn [49] reported that in field cases of deleterious silica reaction, the cement paste is chemically unaffected while the reacting aggregate particles are internally fractured and/or partially dissolved. High alkaline Portland cements generally having more than 0.6% sodium equivalent alkali content is highly vulnerable to attack by aggregates containing reactive amorphous as well as crystalline silica such as chalcedony, crypto-crystalline fibrous, and tridymite. Alkalies in most cases are derived from Portland cement itself, but they can also be augmented by their presence in the mixing water, admixtures, salt contaminated aggregate and deicing salts used on concrete.

### ***1.10.6 Resistance to Aggressive Chemicals***

Loss in durability of concrete by chemical attack can occur either due to the decomposition of cement paste or due to the disruptive internal expansion caused by chemical reactions in the paste or by combination of both the actions. Deleterious chemicals can react with  $\text{Ca}(\text{OH})_2$  to form water soluble salts that can be leached out of the concrete over a period of time, thereby increasing the permeability of concrete and aggravating the damage by increased and faster ingress of harmful chemicals. Sulfates react with  $\text{Ca}(\text{OH})_2$  and calcium aluminate compounds in concrete to form gypsum and calcium sulpho-aluminate, ettringite that can cause internal disruption of the concrete by concomitant volume increase of the paste.

### ***1.10.7 Sulfate Resistance***

Portland cement mortar and concrete are attacked by solutions containing sulfates (sodium or magnesium sulfate). Sulfate attack can lead to expansion, cracking, strength loss, and disintegration. The constituents of hydrated cement paste taking part in the expansive reactions are monosulfoaluminate hydrate, calcium aluminate hydrate, and calcium hydroxide.

Use of fly ash in concrete increases its resistance to sulfate attack and potentially corrosive salts that penetrate into the concrete and cause steel corrosion with accompanying cracking and spalling of concrete. It is well established that the reaction of fly ash with calcium hydroxide released during cement hydration results in the formation of additional calcium aluminosilicate hydrates and accompanying reduction in permeability of the concrete.

Dunstan [32, 33] investigated the sulfate resistance of concrete mixes made with lignite and sub-bituminous fly ashes. He concluded that lignite and sub-bituminous Class C fly ash generally reduced sulfate resistance when used in

normal proportion. Dustan reported that as the calcium oxide in the fly ash increased above a lower limit of 5% and the ferric oxide ( $\text{Fe}_2\text{O}_3$ ) decreased, sulfate resistance was reduced. He proposed the use of an indicator 'R' defined as  $R = \% \text{CaO} - 5/\% \text{Fe}_2\text{O}_3$ .

For the fly ashes used by Dunstan [33], those having 'R' values of 1.5 or less generally improved sulfate resistance while those with higher values did not. The general applicability of the 'R' factor to predict sulfate resistance of all fly ashes is further required to be investigated. With the use of fly ash at 25% cement replacement level, the sulfate resistance of concrete made with ASTM Type II cement at 0.45 water cement ratio has been related to the 'R' factor as follows:

<i>R</i> limits	Sulfate resistance
<0.75	Greatly improved
0.75 to 1.5	Moderately improved
1.5 to 3.0	No significant change
>3.0	Reduced

Mehta [79] 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.

Joshi [55] reported that with the incorporation of Alberta fly ash at 15% replacement level by weight of cement, the sulfate resistance of cement-sand mortar was improved significantly when exposed to sodium sulfate and magnesium sulfate solutions of concentration below 10%. For higher sulfate concentrations, the mortars made with Type-V cement and 15% Alberta fly ash developed adequate sulfate resistance.

Larsen [69] reported that the change in the pore structure of cement paste as a result of fly ash addition can not be the sole reason for the observed favorable performance of fly ash concrete subject to chemical attack, particularly sulfate attack. He observed the favorable effect of the fly ash on sulfate resistance of concrete mixes even at ages when the pozzolanic reaction of fly ash was still not particularly high. Accordingly, it is suggested that additional chemical-mineral interaction including the reduction in tricalcium aluminate ( $\text{C}_3\text{A}$ ) and calcium hydroxide content contribute to sulfate resistance. The fly ash may combine with some alumina phases such as  $\text{C}_3\text{A}$  in the cement during the first few days of cement hydration to form primary ettringite, thus reducing the potential for expansive sulfate-alumina reactions responsible for sulfate attack. With the increased conversion of  $\text{C}_3\text{A}$  in the initial stages, less of the aluminate containing phase is available for reaction during subsequent sulfate attack.



Fay and Pierce [38] conducted a study on air-entrained fly ash concrete. They used three fly ashes from the United States, representing a range of CaO contents of 11 to 28.8% and used 10 to 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<sub>2</sub>SO<sub>4</sub> solution or subjected to cyclic soaking and drying phases in 2.1% Na<sub>2</sub>SO<sub>4</sub> solution to generate data by accelerated test. The test results showed that (1) both low-calcium Class C and Class F fly ashes can be effective cement replacements in controlling sulfate expansion; (2) Class F fly ash was the most effective in reducing sulfate expansion at the lower cementitious content (251.5 kg/m<sup>3</sup>). Likewise at the higher cementitious content (387 kg/m<sup>3</sup>), Class F fly ash at 30% replacement level was found to be the most effective; (3) high-calcium Class C fly ash concrete mixes, with fly ash replacement levels below 50%, generally exhibited more expansion than the control mixes, opposite to the behavior observed with low-calcium class F concrete; (4) 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; (5) the replacement level for a particular type of fly ash was found to depend on cementitious material content of the mix. With lower cementitious material content, 50% or more, while for richer mixes 50% or less Class C was suggested for improving the sulfate resistance of concrete; and (6) 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 the investigation. The high-calcium Class C fly ash concretes generally performed much worse than the control mix under sulfate attack indicating the least effectiveness of these types of ash in reducing expansion.

Mehta [81] concluded that fly ashes are amongst the group of pozzolans that significantly increase the life expectancy of concrete exposed to sulfate attack. In general, Class F type fly ash meeting the specification requirements will improve the sulfate resistance of any concrete/mortar mix in which it is included, although the degree of improvement may vary with either the cement used or the fly ash. The situation with Class C fly ash is different. A few studies indicated that some Class C fly ashes may rather reduce sulfate resistance when used in normal proportions.

Prunsinski and Carrasquillo [100] found that sulfate resistance of concretes made with class C fly ash was strongly influenced by the gypsum content of the mix. In their studies, fly ash was inter-ground and blended in varying quantities (25–75%) with Type I and II cements. In some blends, additional gypsum was inter-ground to supply the fresh concrete with sufficient sulfate ions to stabilize the ettringite. Increasing the gypsum content decreased the expansion of the specimens, specifically, mixes having gypsum contents of twice the sulfation point had lower expansions than the controls made with Type II cement alone, while specimens made with Class C fly ash and Type II cement with out additional gypsum failed.

### 1.10.7.1 Resistance to Sulfuric Acid

Sulfuric acid is a very aggressive acid that reacts with the free lime  $\text{Ca}(\text{OH})_2$ , in cement paste forming gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). This reaction is associated with an increase in volume of the concrete by a factor of 2.2 [10]. Another destructive action is the reaction between calcium aluminate present in cement paste and gypsum crystals. These two products form the less soluble reaction product, ettringite ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ ). These very expansive compounds cause internal pressure in the concrete, which leads to the formation of cracks. The reacted surface becomes soft and white. Because of these, concrete structure loses its mechanical strength. Another important phenomenon where sulfuric acid is responsible for concrete corrosion is biogenic sulfuric acid corrosion, which occurs often in sewer systems. Due to different chemical and microbiological reactions, hydrogen sulfide releases into the atmosphere of sewer structures above the water level. This gas reacts with oxygen to form elemental sulfur, which is deposited on the walls of the sewer structures. In the slime layer coating these walls, aerobic sulfur-oxidizing bacteria (*Thiobacillus* spp.) metabolize the sulfur to sulfuric acid. Repair and sometimes complete replacement of the damaged structures becomes necessary after this acid attack. Pozzolans combine and stabilize the calcium hydroxide liberated during the hydration of cement in concrete, to form additional cementitious compound, mainly in the form of calcium silicate hydrate (CSH). The resultant binder matrix is more chemically resistant, by virtue of its denser microscopic pore structure.

Aydin et al. [11] investigated the effect of Class C fly ash on the sulfuric acid resistance of concrete. Cement was replaced with fly ash up to 70%. Cylinders (100 × 200 mm) and cubes (71 mm) were cast. After 28 days of water curing, specimens were immersed in a 5% sulfuric acid ( $\text{H}_2\text{SO}_4$ ) solution for 60 days in a plexiglass container. After 60 days of exposure, acid-attacked surfaces of the specimens were cleaned with distilled water. Chemical resistance was evaluated by determining the weight loss (WL) and compressive strength loss (SL) of the specimens. Based on the results, it was concluded that (1) loss in compressive strength was related with the FA content. The FA replacement seemed to improve the acid resistance of the steam-cured samples as loss percentages dropped to 21% (FA70) from 58% (FA0); (2) negligible differences in weight-loss were observed for standard cured concrete with increasing FA content. Similar trends have been observed in terms of weight loss for both curing cases. Weight loss dropped from 5% (FA0) to 3.3% (FA70) for standard curing and 8.3% (FA0) to 1.1% (FA70) for SC conditions; and (3) strength loss and weight loss of Portland cement concrete cured in water were lower than that of steam-cured ones due to somewhat higher permeability of steam-cured samples. However, over 30 and 40% FA replacement levels, weight and strength losses of steam-cured concrete were lower than water-cured ones, respectively. In other words, sulfuric acid resistance of steam-cured concrete could be improved significantly by incorporation of FA. The positive effect of FA on acid resistance may arise from pozzolanic reaction between FA and

calcium hydroxide liberated during the hydration of cement, which forms additional cementitious compound, mainly CSH.

### ***1.10.8 Abrasion Resistance***

Abrasion occurs due to rubbing, scraping, skidding or sliding of objects on its surface. Abrasion resistance of concrete is influenced by number of factors such as water-cement ratio, types of aggregates, air-entrainment, compressive strength, surfacing finish, types of hardeners, and curing.

In general, hardened paste has low abrasion resistance. The use of hard aggregates and low water to cement ratio has been found to be quite effective in increasing abrasion/erosion resistance of both types of concrete, i.e., with and without fly ash. With the use of fly ash in concrete the quality of cement paste is improved, and the leachability of calcium hydroxide is impeded with age. Because of the dense structure of cement paste and good bonding characteristics of fly ash concrete, it is believed that the tendency of coarse aggregate to be plucked out of the binding matrix by abrasive action is reduced. At equal compressive strengths, properly cured and finished concrete with and without fly ash will exhibit essentially equal resistance to abrasive-erosive forces. Use of fly ash thus affects this aspect of durability only to the extent that it usually improves compressive strength of concrete due to its pozzolanic activity with time.

Liu [70] compared the abrasion resistance of non-fly ash concrete with a fly ash concrete made with 25% cement replacement. He concluded that abrasion of concrete with or without fly ash was similar up to 36 h of abrasion testing, but after 72 h of testing, the fly ash concrete lost about 25% more weight than the concrete without fly ash. Tikalsky et al. [123] concluded that concrete containing Class C fly ash possessed superior abrasion resistance compared to either ordinary Portland cement concrete or concrete containing Class F fly ash.

Nanni [89] investigated the abrasion resistance of roller-compacted concrete using laboratory and field specimens made by replacing cement with 50% Class C fly ash. He concluded that (1) testing under air-dry conditions produced 30–50% less wear than under wet conditions; addition of steel or synthetic fibers did not cause any appreciable change in the abrasion resistance of concrete; and (3) improper moist-curing conditions produced more negative effects on the surface quality than the compressive strength of concrete.

Langan et al. [67] investigated the influence of compressive strength on the durability of concrete containing 50% fly ash as replacement of cement, and concluded that the presence of fly ash at high levels of cement replacement increased the weight loss due to abrasion at all ages relative to concrete without fly ash.

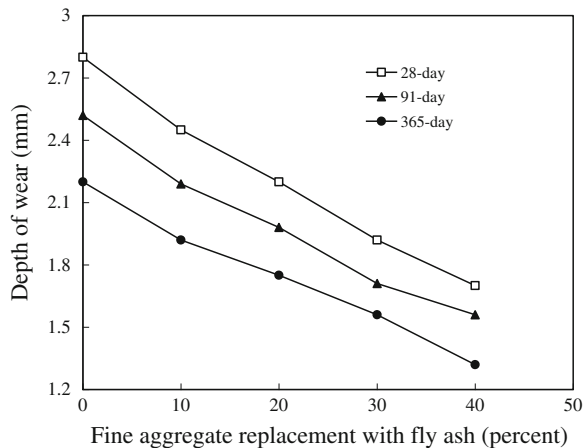
Dhir et al. [31] concluded that near surface characteristics such as absorption, intrinsic permeability and vapour diffusivity are closely related with the abrasion

resistance of concrete. Bilodeau and Malhotra [14] investigated the abrasion resistance of concrete incorporating high volumes of Class F fly ash. Superplasticized mixtures were developed with 55 to 60% fly ash of total cementitious materials. Test results showed that fly ash concrete had poorer abrasion resistance than concrete without fly ash.

Naik et al. [87] evaluated the abrasion resistance of concrete containing five levels of cement replacements (15, 30, 40, 50, and 70%) with one source of Class C fly ash. Test results showed that abrasion resistance of concrete having cement replacement up to 30% was comparable to the reference concrete with out fly ash, but beyond 30% cement replacement, fly ash concrete exhibited slightly lower resistance to abrasion relative to non-fly ash concretes. Naik et al. [88] reported that blending of Class C fly ash with Class F fly ash showed either comparable or better abrasion resistance results than either the control mixture with out fly ash or the unblended Class C fly ash.

Siddique [113] studied the abrasion resistance of concrete proportioned to have four levels of fine aggregate replacement (10, 20, 30 and 40%) with Class F fly ash. A Control mixture with ordinary Portland cement was designed to have 28 days compressive strength of 26 MPa. Concrete specimens of size  $65 \times 65 \times 60$  mm were made for the purpose. The abrasion resistance of concrete mixtures was determined at the ages of 28, 91, and 365 days in accordance with Indian Standard Specifications [50]. It was measured in term of depth of wear. Figure 1.21 shows the variation of depth of wear versus percentage of fine aggregate replacement with Class F fly ash, at 60 min of abrasion time. It is evident that with the increase in fly ash content, depth of wear decreased, which indicated that the abrasion resistance of concrete increased with the increase in fly ash content. This showed that for a particular percentage of fine aggregate replacement with fly ash, depth of wear decreased with increase in age, which means that abrasion resistance increased with age. This could be primarily attributed to the increase in compressive strength resulting from increased maturity of concrete with age.

**Fig. 1.21** Depth of wear at 60 min of abrasion versus fine aggregate replacement with fly ash [113]



Yazici and İnan [127] developed a relationship between mechanical properties (compressive strength and splitting tensile strength) and abrasion resistance of high strength concretes (HSC) having compressive strength between 65 and 85 MPa. They concluded that abrasion resistance of high strength concrete can be estimated from compressive and splitting tensile strength results.

Yen et al. [128] established equations based on effective compressive strength and effective water-to-binder ratios, which were modified by cement replacement and developed to predict the 28- and 91-day abrasion resistance of concretes with compressive strengths ranging from approximately 30–100 MPa. The predicted results compared favourably with the experimental results.

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