# Mineral Admixtures


## 2.1 Fly Ash

### Introduction

Fly ash is a byproduct of the combustion of pulverized coal in thermal power plants. A dust-collection system removes the fly ash, as a fine particulate residue, from combustion gases before they are discharged into the atmosphere (Figure 2.1). The types and relative amounts of incombustible matter in the coal used determine the chemical composition of fly ash. More than 85% of most fly ashes is comprised of chemical compounds and glasses formed from the elements silicon, aluminum, iron, calcium, and...

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* Scientist Emeritus at CANMET, Natural Resources Canada, Ottawa, Canada; prolific author, editor, and researcher who has received many awards and honors from the ACI, ASTM, and other institutions throughout the world.
magnesium. Generally, fly ash from the combustion of subbituminous coals contains more calcium and less iron than fly ash from bituminous coal; also, fly ash from subbituminous coals contains very little unburned carbon. Plants that operate only intermittently (peak-load stations) and that burn bituminous coals produce the largest percentage of unburned carbon. Fly-ash particles are typically spherical, ranging in diameter from $<1\ \mu m$ up to $150\ \mu m$.

Fly ashes exhibit pozzolanic activity. The American Society for Testing and Materials (ASTM) (ASTM, 1975) defines a pozzolan as “a siliceous or siliceous and aluminous material which in itself possesses little or no cementitious value but which will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties.” Fly ashes contain metastable aluminosilicates that will react with calcium ions, in the presence of moisture, to form calcium silicate hydrates.

The term fly ash was first used in the electrical power industry around 1930. The first comprehensive data on the use of fly ash in concrete in North America were reported by Davis et al. (1937). The first major practical application was reported in 1948 with the publication of the U.S. Bureau of Reclamation's data on the use of fly ash in the construction of the Hungry Horse Dam. Worldwide acceptance of fly ash as a component of concrete slowly followed these early efforts, but interest was particularly noticeable in the wake of the rapid increases in energy costs (and hence cement costs) that occurred during the 1970s.

In recent years, it has become evident that fly ashes differ in significant and definable ways that reflect their combustion and, to some extent, their origin. The ASTM recognizes two general classes of fly ash:

- Class C, normally produced from lignite or subbituminous coals
- Class F, normally produced from bituminous coals

Several publications are available that discuss in detail the properties and use of fly ash in concrete (ASTM, 1978; Berry and Malhotra, 1978; Malhotra and Mehta, 1996; Malhotra and Ramezanianpour, 1994), and Table 2.1 shows the estimated production and use of coal ash in major coal-using countries (Malhotra and Ramezanianpour, 1994).
2.1.2 Physical, Chemical, and Mineralogical Properties of Fly Ash

2.1.2.1 Physical Properties

Fly ash is a fine-grained material consisting mostly of spherical, glassy particles. Some ashes also contain irregular or angular particles. The size of particles varies depending on the sources. Some ashes may be finer or coarser than Portland cement particles. Figure 2.2 and Figure 2.3 show scanning electron

![SEM micrograph of a subbituminous ash: backscattered electron image of a polished section of the dispersed sample. (From Malhotra, V.M. and Ramezanianpour, A.A., *Fly Ash in Concrete*, MSL 94-45(IR), Canada Center for Mineral and Energy Technology (CANMET), Ottawa, 1994.)](image)

**TABLE 2.1** Coal Ash Production and Use in Major Coal-Using Countries

<table>
<thead>
<tr>
<th>Country</th>
<th>Fly Ash (kt/yr)</th>
<th>Coarse Ash (kt/yr)</th>
<th>Total Ash (kt/yr)</th>
<th>Use (kt/yr)</th>
<th>Use (%)</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia</td>
<td>7050</td>
<td>850</td>
<td>7900</td>
<td>800</td>
<td>10</td>
<td>1990</td>
</tr>
<tr>
<td>Belgium</td>
<td>930</td>
<td>160</td>
<td>1090</td>
<td>795</td>
<td>73</td>
<td>1989</td>
</tr>
<tr>
<td>Canada</td>
<td>3830</td>
<td>1420</td>
<td>5250</td>
<td>1575</td>
<td>30</td>
<td>1987</td>
</tr>
<tr>
<td>France</td>
<td>2200</td>
<td>405</td>
<td>2605</td>
<td>1300</td>
<td>50</td>
<td>1987</td>
</tr>
<tr>
<td>Germany</td>
<td>7480</td>
<td>4120</td>
<td>11,600</td>
<td>6465</td>
<td>56</td>
<td>1989</td>
</tr>
<tr>
<td>Italy</td>
<td>1300</td>
<td>135</td>
<td>1435</td>
<td>900</td>
<td>63</td>
<td>1988</td>
</tr>
<tr>
<td>Japan</td>
<td>3480</td>
<td>445</td>
<td>3925</td>
<td>1920</td>
<td>49</td>
<td>1989</td>
</tr>
<tr>
<td>Spain</td>
<td>7390</td>
<td>1305</td>
<td>8695</td>
<td>1220</td>
<td>14</td>
<td>1987</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>9950</td>
<td>2590</td>
<td>12,540</td>
<td>6120</td>
<td>49</td>
<td>1989</td>
</tr>
<tr>
<td>United States</td>
<td>48,430</td>
<td>16,750</td>
<td>65,190</td>
<td>15,895</td>
<td>24</td>
<td>1989</td>
</tr>
<tr>
<td>China</td>
<td>—</td>
<td>—</td>
<td>82,500</td>
<td>16,200</td>
<td>26</td>
<td>1989</td>
</tr>
<tr>
<td>Czechoslovakia</td>
<td>—</td>
<td>—</td>
<td>18,100</td>
<td>400</td>
<td>8</td>
<td>1989</td>
</tr>
<tr>
<td>East Germany (former GDR)</td>
<td>—</td>
<td>—</td>
<td>19,100</td>
<td>7200</td>
<td>38</td>
<td>1989</td>
</tr>
<tr>
<td>Hungary</td>
<td>—</td>
<td>—</td>
<td>4100</td>
<td>1100</td>
<td>27</td>
<td>1987</td>
</tr>
<tr>
<td>India</td>
<td>—</td>
<td>—</td>
<td>40,000</td>
<td>6750</td>
<td>17</td>
<td>1991</td>
</tr>
<tr>
<td>Poland</td>
<td>—</td>
<td>—</td>
<td>29,500</td>
<td>4500</td>
<td>15</td>
<td>1989</td>
</tr>
<tr>
<td>Romania</td>
<td>—</td>
<td>—</td>
<td>27,000</td>
<td>700</td>
<td>3</td>
<td>1989</td>
</tr>
<tr>
<td>Former Soviet Union</td>
<td>—</td>
<td>—</td>
<td>125,000</td>
<td>11,500</td>
<td>9</td>
<td>1989</td>
</tr>
<tr>
<td>Others</td>
<td>—</td>
<td>—</td>
<td>116,470</td>
<td>3660</td>
<td>3</td>
<td>1989</td>
</tr>
</tbody>
</table>

*Note:* In 2007, the total production of fly ash in China, India, and the United States exceeded 80,000, 130,000, and 70,000 kilotons a year, respectively.


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microscope (SEM) micrographs of polished sections of subbituminous and lignite fly ashes, and Figure 2.4 shows a secondary electron SEM image of bituminous fly-ash particles. Some of these particles appear to be solid, whereas other larger particles appear to be portions of thin, hollow spheres containing many smaller particles.
TABLE 2.2 Fineness of Fly Ashes

<table>
<thead>
<tr>
<th>Fly Ash Source</th>
<th>Type of Coal</th>
<th>Specific Gravity (Le Chatelier Method)</th>
<th>Blaine Specific Surface (m²/kg)</th>
<th>Fineness (% Retained on 45-µm Sieve)</th>
<th>Physical Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Wet Sieving³</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Dry Sieving³ (Alpine Jet)</td>
</tr>
<tr>
<td>1</td>
<td>B</td>
<td>2.53</td>
<td></td>
<td>17.3 (14.9)</td>
<td>12.3</td>
</tr>
<tr>
<td>2</td>
<td>B</td>
<td>2.58</td>
<td></td>
<td>14.7 (12.7)</td>
<td>10.2</td>
</tr>
<tr>
<td>3</td>
<td>B</td>
<td>2.88</td>
<td></td>
<td>25.2 (21.7)</td>
<td>18.0</td>
</tr>
<tr>
<td>4</td>
<td>B</td>
<td>2.96</td>
<td></td>
<td>19.2 (16.6)</td>
<td>14.0</td>
</tr>
<tr>
<td>5</td>
<td>B</td>
<td>2.38</td>
<td></td>
<td>21.2 (18.3)</td>
<td>16.1</td>
</tr>
<tr>
<td>6</td>
<td>B</td>
<td>2.22</td>
<td></td>
<td>40.7 (35.1)</td>
<td>30.3</td>
</tr>
<tr>
<td>7</td>
<td>SB</td>
<td>1.90</td>
<td></td>
<td>33.2 (28.7)</td>
<td>26.4</td>
</tr>
<tr>
<td>8</td>
<td>SB</td>
<td>2.05</td>
<td></td>
<td>19.4 (16.7)</td>
<td>14.3</td>
</tr>
<tr>
<td>9</td>
<td>SB</td>
<td>2.11</td>
<td></td>
<td>46.0 (39.7)</td>
<td>33.0</td>
</tr>
<tr>
<td>10</td>
<td>L</td>
<td>2.38</td>
<td></td>
<td>24.9 (21.5)</td>
<td>18.8</td>
</tr>
<tr>
<td>11</td>
<td>L</td>
<td>2.53</td>
<td></td>
<td>2.7 (2.4)</td>
<td>2.5</td>
</tr>
</tbody>
</table>

a B, bituminous; L, lignite; SB, subbituminous.
b Values in parentheses do not include sieve correction factor.


2.1.2.2 Fineness

Dry- and wet-sieving methods are commonly used to measure the fineness of fly ashes. ASTM C 311-77 recommends determining the amount of the sample retained after it is wet sieved on a 45-µm sieve, in accordance with ASTM C 430, except that a representative sample of the fly ash or natural pozzolan is substituted for hydraulic cement in the determination. Dry sieving on a 45-µm sieve can be performed according to a method established at the Canada Center for Mineral and Energy Technology (CANMET) (Malhotra and Wallace, 1993). Table 2.2 shows the fineness of 11 fly ashes as determined by wet and dry sieving. The particle-size distribution of fly ash can be determined by various means, such as x-ray sedigraph, laser particle-size analyzer, and Coulter counter. In some cases, agglomeration of a number of small particles may form a large particle. In most cases, fly ashes contain particles greater than 1 µm in diameter. Mehta (1994), using an x-ray sedimentation technique, reported particle-size distribution data for several U.S. fly ashes. Mehta found that high-calcium fly ashes were finer than low-calcium fly ashes, and he related this difference to the presence of larger amounts of alkali sulfates in the high-calcium fly ashes.

2.1.2.3 Specific Surface

The specific surface of fly ash, which is the area of a unit of mass, can be measured by various techniques. The most common technique is the Blaine specific-surface method, which measures the resistance of compacted particles to air flow. ASTM C 204 describes this method for measurement of the surface area of Portland cement.

2.1.2.4 Specific Gravity

The specific gravity of hydraulic cements is determined according to ASTM C 188. This method can also be used to determine the specific gravity of fly ashes. If fly ashes contain water-soluble compounds, the use of a nonaqueous solvent, instead of water, is recommended. The specific gravity of different fly ashes varies over a wide range. In the CANMET investigation of 11 fly ashes (Carette and Malhotra, 1986), the specific gravity ranged from a low value of 1.90 for a subbituminous ash to a high value of 2.96 for an iron-rich bituminous ash. Three subbituminous ashes had a comparatively low specific gravity of ~2.0, and this suggested that hollow particles, such as cenospheres or plerospheres, were present in significant proportions in the three ashes.
In general, the physical characteristics of fly ashes vary over a significant range, corresponding to their source. Attempts have been made to correlate the physical properties of different fly ashes. In one CANMET investigation, no apparent relationship was found between type of fly ash and fineness, as determined by the percentage retained on a 45-µm sieve. Fineness is probably influenced more by factors such as coal combustion and ash collection and classification than by the nature of the coal itself (Carette and Malhotra, 1986). Similarly, the type of fly ash showed no apparent influence on the specific surface as measured by the Blaine technique. Moreover, except in one or two cases, there was very little relationship between the specific surface as measured by the Blaine technique and the fineness as determined by percentage retained on a 45-µm sieve.

2.1.3 Chemical and Mineralogical Composition

2.1.3.1 Chemical Composition

Several authors have reported the chemical composition of various fly ashes produced in North America. In their study of 11 Canadian fly ashes, Carette and Malhotra (1986) reported a wide range of chemical compositions (Table 2.3). Manz et al. (1989) examined 19 North American lignite fly ashes, and their data are given in Table 2.4. The results of the CANMET investigations (Carette and Malhotra, 1986) and the data reported by Manz et al. (1989) on bituminous, subbituminous, and lignite ashes obtained from various coal-powered plants in North America show significant differences in the chemical composition of fly ashes.

2.1.3.2 Mineralogical Composition

In general, both the type and source of fly ash influence its mineralogical composition. Due to the rapid cooling of burned coal in the power plant, fly ashes consist of noncrystalline particles (≤90%), or glass and a small amount of crystalline material. Depending on the system of burning, some unburned coal may be collected with ash particles. In addition to a substantial amount of glassy material, each fly ash may contain one or more of the four major crystalline phases: quartz, mullite, magnetite, and hematite. In subbituminous fly ashes, the crystalline phases may include C₃A, C₄A₃S, calcium sulfate, and alkali sulfates (Mehta, 1989). Table 2.5 shows the mineralogical composition of some selected fly ashes. The reactivity of fly ashes is related to the noncrystalline phase or glass. The reasons for the high reactivity of high-calcium fly ashes may lie partially in the chemical composition of the glass. Mehta (1989) pointed out that the composition of glass in low-calcium fly ashes is different from that in high-calcium fly ashes.

2.1.4 Proportioning Concretes Containing Fly Ash

In most applications, 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
• Obtaining reduced heat of hydration
• Improving workability
• Attaining required levels of strength in concrete at ages >90 days
• Improving durability

The properties of any particular fly ash will greatly affect the properties of the concrete in which it is used. The mixture-proportioning method can minimize the effects that the inclusion of different fly ashes has on concrete performance. In practice, fly ash can be introduced into concrete in one of two ways:

• A blended cement containing fly ash may be used in place of Portland cement.
• Fly ash may be introduced as an additional component at the concrete-mixing stage.

The use of blended cement is the simpler of the two, as it is free from the complication of batching additional materials and may ensure more uniform control. The relative proportions of fly ash and cement are predetermined, and this limits the range of mixture proportions.
### TABLE 2.3 Chemical Composition of Fly Ashes

| Fly-Ash Source | Type of Coal | Chemical Composition (wt%)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>SiO₂</td>
</tr>
<tr>
<td>1</td>
<td>B</td>
<td>47.1</td>
</tr>
<tr>
<td>2</td>
<td>B</td>
<td>44.1</td>
</tr>
<tr>
<td>3</td>
<td>B</td>
<td>35.5</td>
</tr>
<tr>
<td>4</td>
<td>B</td>
<td>38.3</td>
</tr>
<tr>
<td>5</td>
<td>B</td>
<td>45.1</td>
</tr>
<tr>
<td>6</td>
<td>B</td>
<td>48.0</td>
</tr>
<tr>
<td>7</td>
<td>SB</td>
<td>55.7</td>
</tr>
<tr>
<td>8</td>
<td>SB</td>
<td>55.6</td>
</tr>
<tr>
<td>9</td>
<td>SB</td>
<td>62.1</td>
</tr>
<tr>
<td>10</td>
<td>L</td>
<td>46.3</td>
</tr>
<tr>
<td>11</td>
<td>L</td>
<td>44.5</td>
</tr>
</tbody>
</table>

a B, bituminous; L, lignite; SB, subbituminous.
b By inductively coupled argon plasma (ICAP) technique, except for Na₂O, K₂O, SO₃, and LOI.
c 105 to 750°C.

### TABLE 2.4 Chemical Analyses for North American Lignite Fly Ashes

<table>
<thead>
<tr>
<th>Bulk Chemical Analysis (wt%)</th>
<th>Available Alkalis (%)</th>
<th>Loss on Ignition (LOI) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly Ash</td>
<td>SiO₂</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>North Dakota and Montana lignite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>81–271</td>
<td>25.7</td>
<td>15.0</td>
</tr>
<tr>
<td>81–560</td>
<td>30.2</td>
<td>12.5</td>
</tr>
<tr>
<td>82–179</td>
<td>42.1</td>
<td>12.0</td>
</tr>
<tr>
<td>83–275</td>
<td>45.6</td>
<td>15.5</td>
</tr>
<tr>
<td>85–352</td>
<td>39.6</td>
<td>14.0</td>
</tr>
<tr>
<td>87–139</td>
<td>27.9</td>
<td>10.7</td>
</tr>
<tr>
<td>86–305</td>
<td>35.2</td>
<td>20.3</td>
</tr>
<tr>
<td>Saskatchewan lignite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>85–147</td>
<td>50.4</td>
<td>21.4</td>
</tr>
<tr>
<td>86.805</td>
<td>46.4</td>
<td>24.5</td>
</tr>
<tr>
<td>87–144</td>
<td>47.9</td>
<td>21.9</td>
</tr>
<tr>
<td>Texas and Louisiana lignite</td>
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<td></td>
</tr>
<tr>
<td>87–146</td>
<td>50.3</td>
<td>20.2</td>
</tr>
<tr>
<td>87–147</td>
<td>57.9</td>
<td>26.3</td>
</tr>
<tr>
<td>87–154</td>
<td>62.3</td>
<td>20.9</td>
</tr>
<tr>
<td>87–155</td>
<td>52.2</td>
<td>18.0</td>
</tr>
<tr>
<td>87–156</td>
<td>55.5</td>
<td>18.6</td>
</tr>
<tr>
<td>87–159</td>
<td>57.5</td>
<td>20.6</td>
</tr>
<tr>
<td>87–219</td>
<td>62.0</td>
<td>20.1</td>
</tr>
<tr>
<td>87–239</td>
<td>48.9</td>
<td>18.5</td>
</tr>
<tr>
<td>87–157</td>
<td>52.8</td>
<td>23.6</td>
</tr>
</tbody>
</table>

*Note:* ASTM C 618 specification limits: Class F fly ash, SiO₂ + Al₂O₃ + Fe₂O₃ = 70%; SO₃ = 5% max.; LOI = 5% max. Class C fly ash, SiO₂ + Al₂O₃ + Fe₂O₃ = 50%; SO₃ = 5% max.; LOI = 5% max.

The addition of fly ash at the concrete-mixing stage is flexible and allows for more complete exploitation of the qualities of fly ash as a component of concrete. It does, however, demand that the unique properties of fly ash be considered in determining the proportions of the mixture. In current trends, fly ash plays more than one role in concrete. In freshly mixed concrete, it generally acts as a fine aggregate and to some degree may reduce the demand for water. In hardened concrete, because of the pozzolanic nature of fly ash, it becomes a component of the cementitious matrix and influences strength and durability. Thus, the use of fly ash in a concrete introduces a number of complexities regarding proportioning, if the accepted relationships among workability, strength, and the water/cement ratio are taken into account.

Two common assumptions are made when selecting an approach to mixture proportioning of fly-ash concrete:

- Fly ash usually reduces the strength of concrete at early ages.
- For equal workability, concrete incorporating fly ash usually requires less water than concrete containing only Portland cement.

Neither assumption is universally true, and both are influenced by the presence of other common concrete components; however, both assumptions have strongly influenced the approach to mixture proportioning of fly-ash concrete. As with any other type of concrete, the mixture proportions for a fly-ash concrete can be selected either by reference to some standard concrete (excluding fly ash) or on the basis of the ways in which all the concrete components (including fly ash) will behave in fresh and hardened states.

Throughout the more than 40 years that fly ash has been used in concrete, common practice has been to use some plain concrete as a standard of comparison for the mixture proportions of fly-ash concretes. Similarly, the properties of both fresh and hardened concrete usually have been compared with those of a reference concrete. Thus, fly ash has generally been considered to be a replacement for cement, rather than a component that complements the functions of the cement, sand, or water. The trend now is to consider the components of fly-ash concrete as a whole and to treat it as a unique material without reference to an equivalent plain-concrete mixture.

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

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

- The ash may be cementitious (high calcium).
- Fly ash may contain sulfates that react with cement in the same way as the gypsum added to Portland cement does.

<table>
<thead>
<tr>
<th>Fly-Ash Source</th>
<th>Type of Coal</th>
<th>Glass (%)</th>
<th>Quartz (%)</th>
<th>Mullite (%)</th>
<th>Magnetite (%)</th>
<th>Hematite (%)</th>
<th>Loss on Ignition (LOI) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 B</td>
<td></td>
<td>72.1</td>
<td>4.0</td>
<td>12.6</td>
<td>6.2</td>
<td>1.6</td>
<td>3.5</td>
</tr>
<tr>
<td>4 B</td>
<td></td>
<td>70.1</td>
<td>3.2</td>
<td>3.3</td>
<td>17.2</td>
<td>4.7</td>
<td>1.5</td>
</tr>
<tr>
<td>5 B</td>
<td></td>
<td>55.6</td>
<td>6.2</td>
<td>19.8</td>
<td>5.6</td>
<td>3.1</td>
<td>9.7</td>
</tr>
<tr>
<td>6 B</td>
<td></td>
<td>54.2</td>
<td>8.3</td>
<td>23.5</td>
<td>4.4</td>
<td>2.1</td>
<td>7.5</td>
</tr>
<tr>
<td>7 SB</td>
<td></td>
<td>90.2</td>
<td>2.9</td>
<td>6.1</td>
<td>—</td>
<td>—</td>
<td>0.8</td>
</tr>
<tr>
<td>8 SB</td>
<td></td>
<td>83.9</td>
<td>4.1</td>
<td>10.2</td>
<td>—</td>
<td>1.4</td>
<td>0.4</td>
</tr>
<tr>
<td>9 SB</td>
<td></td>
<td>79.8</td>
<td>8.7</td>
<td>11.5</td>
<td>—</td>
<td>—</td>
<td>0.8</td>
</tr>
<tr>
<td>10 L</td>
<td></td>
<td>94.5</td>
<td>4.6</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.9</td>
</tr>
</tbody>
</table>

*α B, bituminous; L, lignite; SB, subbituminous.

• The fly-ash–cement mortar may contain less water as a consequence of the presence of fly ash, and this will influence the rate of stiffening.
• The ash may absorb surface-active agents added to modify the rheology (water reducers) of concrete, and, again, this influences the stiffness of the mortar.
• Fly-ash particles may act as nuclei for crystallization of cement hydration products.

There seems to be general agreement in the literature that low-calcium fly ashes retard the setting of cement. In experiments conducted at CANMET (Carette and Malhotra, 1986), the data show that all but 2 of the 11 ashes significantly increase both the initial and final setting times.

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

The small size and the essentially spherical form of low-calcium fly-ash particles influence the rheological properties of cement pastes, causing a reduction in the water required or an increase in workability compared with that of an equivalent paste without fly ash. As Davis et al. (1937) noted, fly ash differs from other pozzolans that usually increase the water requirement of concrete mixtures. The improved workability allows a reduction in the amount of water used in concrete. According to Owens (1979), the major factor influencing the effects of ash on the workability of concrete is the proportion of coarse material (>45 mm) in the ash. Owens has shown, for example, that substitution of 50% by mass of the cement with fine particulate fly ash can reduce the water requirement by 25%. A similar substitution using ash with 50% of the material larger than 45 mm has no effect on the water requirement.

2.1.7 Effects of Fly Ash on Air Entrainment in Fresh Concrete

Cycles of freezing and thawing are extremely destructive to water-saturated concretes that are not properly proportioned. Concrete will be frost-resistant if it is made with sound, coarse aggregate and is properly protected until some maturity is attained. To obtain the number of correctly spaced air voids in hardened concrete necessary for frost resistance, an air-entraining admixture (AEA) is added (at a prescribed dosage) to the concrete during mixing. Two attributes are important: (1) the AEA must produce the required volume of air bubbles of the desired size and spacing in the concrete, and (2) it must do so in a manner that allows the air content to remain stable while the concrete is mixed, transported, and placed. The use of some fly ashes causes an increase in the quantity of AEA required to produce a given level of air entrainment in fresh concrete. Larson (1994), writing on the use of fly ash in air-entrained concrete and reviewing the work of other investigators, concluded that the primary effect of fly ash was on the AEA requirement rather than on the air entrainment as such.

Gebler and Klieger (1983) examined 10 different fly ashes representing a range of chemical and physical properties. Carbon content was 0.14 to 4.19%, total organics were 0.09 to 1.04%, CaO was 1.2 to 9.0%, and fineness (as a percentage retained on a 45-µm sieve) was 11.24 to 38.45%. Concretes were proportioned by simple replacement of 25% of the cement by fly ash (by mass). All mixtures were proportioned to have 75 ± 25-mm slump and 6 ± 1% air. Neutralized Vinsol™ resin was the only AEA used. The AEA requirement as a percentage of that for the control concrete (for 6% air content) showed the following results:

• For ashes containing >10% CaO, the range of AEA requirements was 126 to 173%.
• For ashes containing <10% CaO, the range of AEA requirements was 170 to 553%.

Gebler and Klieger (1983, p. 107) offered the following summary of the findings and conclusions relevant to air entrainment in fresh concrete:

• Generally, concretes containing Class C fly ash require less air-entraining admixture than those concretes with Class F fly ash. All concretes with fly ash required more air-entraining admixture than Portland cement concretes without fly ash.
- Plastic concretes containing Class C fly ash tended to lose less air than concretes with Class F ash.
- As the air-entraining admixture requirement increases for a concrete containing fly ash, the air loss increases.
- Air contents in plastic concrete containing Class F fly ash were reduced as much as 59%, 90 minutes after completion of mixing.
- As the organic matter content, carbon content, and loss-on-ignition of fly ash increase, the air-entraining admixture requirement increases, as does the loss of air in plastic concrete.
- Generally, as the total alkalis in fly ash increase, the air-entraining admixture requirement decreases.
- As the specific gravity of a fly ash increases, the retention of air in the concrete also increases. Concrete containing a fly ash that has a high lime content (Class C fly ash) and less organic matter tends to be less vulnerable to loss of air.
- Generally, as the SO₃ content of fly ash increases, the retained air in concrete increases.

2.1.8 Effects of Fly Ash on Properties of Hardened Concrete

2.1.8.1 Strength Development in Fly-Ash Concrete

As discussed earlier, the main factors determining strength in concrete are the amount of cement used and the water/cement ratio. In practice, these are established as a compromise between the need for workability in the freshly mixed state, strength and durability in the hardened state, and cost. The degree and manner in which fly ash affects workability are major factors in its influence on strength development. As was shown earlier, a fly ash that permits a reduction in the total water requirement in concrete will generally present no problems in selection of mixture proportions and permit any rate of strength development. Many variables influence the strength development of fly-ash concrete; the most important are the following:

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

2.1.8.2 Effect of Fly-Ash Type on Concrete Strength

The first difference among fly ashes is that some are cementitious even in the absence of Portland cement; these are the so-called ASTM Class C, or high-calcium, fly ashes, usually produced at power plants that burn subbituminous or lignitic coals. In general, the rate of strength development in concretes tends to be only marginally affected by high-calcium fly ashes. Concrete incorporating high-calcium fly ashes can be made on an equal-weight or equal-volume replacement basis without any significant effect on strength at early ages. Yuan and Cook (1983) examined the strength development of concretes with and without high-calcium fly ash (CaO = 30.3 wt%). The data from their research are shown in Figure 2.5 and Figure 2.6. Using a simple replacement method of mixture proportioning (Table 2.6), they found the rate of strength development of fly-ash concrete to be comparable to that of the control concrete, with or without air entrainment. Low-calcium fly ashes, the so-called ASTM Class F fly ashes, were the first to be examined for use in concrete. Most of what has been written on the behavior of fly-ash concrete examines concretes that use Class F ashes. In addition, the ashes used in much of the early work came from older power plants and were coarse in particle size, contained unburned fuel, and were often relatively inactive pozzolans. Used in concrete and proportioned by simple replacement, these ashes showed exceptionally slow rates of strength development. This led to the erroneous view that fly ash reduces strength at all ages. Gebler and Klieger (1986) evaluated the effect of ASTM Class F and Class C fly ashes from 10 different sources on the compressive strength development of concretes under different curing conditions, including effects of low temperature and moisture availability. Their tests indicated that concrete containing fly ash had the potential to produce satisfactory compressive strength development. The influence of the class of fly ash on the long-term compressive strength of concrete was not significant. In general,
Compressive strength development of concretes containing Class F fly ash was more susceptible to low curing temperature than concretes with Class C fly ash or the control concretes. Gebler and Klieger concluded that Class F fly-ash concretes required more initial moist curing for long-term, air-cured compressive strength development than did concretes containing Class C fly ashes or the control concretes.

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

When concrete made with Portland cement is cured at temperatures greater than 30°C, an increase in strength occurs at early ages but a marked decrease in strength in the mature concrete. Concretes containing fly ash and control concretes behave significantly differently. Figure 2.7 shows the general way in which the temperature maintained during the early ages of curing influences the 28-day strength of concrete (Williams and Owens, 1982).

2.1.8.4 Effect of Fly-Ash on Elastic Properties of Concrete

Published data indicate that fly ash has little influence on the elastic properties of concrete. Abdun-Nur (1961) made the following observation:

The modulus of elasticity of fly ash concrete is lower at early ages and higher at later ages. In general, fly ash increases the modulus of elasticity of concrete when concretes of the same strength with and without fly ash are compared.
2.1.8.5 Effect of Fly Ash on Creep Properties of Concrete

Data on creep of fly-ash concrete are limited. Ghosh and Timusk (1981) examined bituminous fly ashes of different carbon contents and fineness values in concretes at nominal strength levels of 20, 35, and 55 MPa (water/cement ratio of 1.0, 0.4, and 0.2, respectively). Each concrete was proportioned for equivalent strength at 28 days. Fly-ash concretes showed less creep in the majority of specimens than the reference concretes. This was attributed to a relatively higher rate of strength gain after the time of loading for the fly-ash concretes than for the reference concretes. Yuan and Cook (1983) investigated creep of high-strength concrete containing a high-calcium fly ash and showed that concrete containing 30 and 50% fly ash exhibited more creep than either the control concrete or a concrete with 20% fly ash.

2.1.8.6 Effect of Fly Ash on Volume Changes of Concrete

It has been generally reported that the use of fly ash in normal proportions does not significantly influence the drying shrinkage of concrete. Typical of the conclusions of most researchers in this area are those made by Davis et al. (1937), who commented as follows:

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

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

2.1.9 Effects of Fly Ash on the Durability of Concrete

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

2.1.9.1 Effects of Fly Ash on Permeability of Concrete

A number of investigations have studied the influence of fly ash on the relative permeability of concrete pipes containing fly ash substituted for cement in amounts of 30 to 50%. In a study by Davis (1954), permeability tests were made on 150 × 150-mm cylinders at the ages of 28 days and 6 months. The results of these tests are shown in Table 2.7. It is clear from these data that the permeability of the concrete was directly related to the quantity of hydrated cementitious material at any given time. After 28 days of curing, at which time little pozzolanic activity would have occurred, the fly-ash concretes were more permeable than the control concretes. At 6 months, this was reversed. Considerable imperviousness had developed, presumably as a result of the pozzolanic reaction of fly ash. Short and Page (1982) reported on the diffusion of chloride ions in solution into Portland blended cement pastes and found the following values of diffusion coefficient ($D_c$) for different cement types:

<table>
<thead>
<tr>
<th>Type</th>
<th>Percent (%) by Weight</th>
<th>W/(C + F) by Weight</th>
<th>Relative Permeability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>—</td>
<td>0.75</td>
<td>100</td>
</tr>
<tr>
<td>Chicago</td>
<td>30</td>
<td>0.70</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.65</td>
<td>1410</td>
</tr>
<tr>
<td>Cleveland</td>
<td>30</td>
<td>0.70</td>
<td>320</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.69</td>
<td>1880</td>
</tr>
</tbody>
</table>

Note: W/(C + F) = water/cement + fly ash ratio.

Source: Davis, R.E., Pozzolanic Materials With Special Reference to Their Use in Concrete Pipe, Technical Memo, American Concrete Pipe Association, Irving, TX, 1954.
It was concluded from these data that slag and fly-ash cements were more effective in limiting chloride diffusion in pastes than were normal or sulfate-resisting cements.

### 2.1.9.2 Effects of Fly Ash on Carbonation of Concrete

In moist conditions, calcium hydroxide, and to a lesser degree, calcium silicates and aluminates in hydrated Portland cement react with carbon dioxide from the atmosphere to form calcium carbonate. The process, termed carbonation, occurs in all Portland cement concretes. The rate at which concrete carbonates is determined by its permeability, the degree of saturation, and the mass of calcium hydroxide available for reaction. Well-compacted and properly cured concrete, at a low water/cement ratio will be sufficiently impermeable to resist the advance of carbonation beyond the first few millimeters. If carbonation progresses into a mass of concrete, two deleterious consequences may follow: shrinkage may occur, and carbonation of concrete immediately adjacent to steel reinforcement may reduce the resistance of steel to corrosion.

Nagataki et al. (1986) reported the long-term results of experiments carried out since 1969 that investigated the depth of carbonation in concrete with and without fly ash. The authors concluded that the initial curing period affects the carbonation of concrete cured indoors; hence, it is necessary for fly-ash concrete to have a longer curing period in water at early ages. The carbonation of concrete cured outdoors is not affected by the initial curing period in water, provided it is cured in water for a period of 7 days.

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

It is generally accepted, other criteria also being met, that air entrainment renders concrete frost resistant. Fly ashes, in common with other finely divided mineral components in concrete, tend to cause an increase in the quantity of admixture required to obtain specified levels of entrained air in concrete. In some instances, the stability of the air or the rate of air loss from fresh concrete is also affected. In general, the observed effects of fly ash on freezing and thawing durability support the view expressed by Larson (1994):

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

Klieger and Gebler (1987) also evaluated the durability of concretes containing ASTM Class F and Class C fly ashes. Their test results indicated that air-entrained concretes, with or without fly ash, that were moist cured at 23°C generally showed good resistance to freezing and thawing. For specimens cured at a low temperature (4.4°C), air-entrained concretes with Class F fly ash showed slightly less resistance to freezing and thawing than similar concretes made with Class C fly ash.

Bilodeau et al. (1991), in an investigation carried out at CANMET, determined the scaling resistance of concrete incorporating fly ashes. Water/cement + fly ash ratios of 0.35, 0.45, and 0.55 were used. Concrete without fly ash and concretes containing 20 and 30% fly ash as replacement by mass for cement were made. The results of Bilodeau et al. showed that the concrete containing ≥30% fly ash performed satisfactorily under the scaling test with minor exceptions (Table 2.8).

Carette and Langley (1990) studied the performance of fly ash concrete subjected to 50 freezing and thawing cycles in the presence of deicing salts. They concluded that the incorporation of fly ash in concrete mixtures with ≤30% replacement of Portland cement did not show significant difference in salt-scaling resistance in the presence of a 4% calcium chloride solution when examined by visual rating of surface

<table>
<thead>
<tr>
<th>Type of Cement</th>
<th>$D_i$ Value ($\times 10^{-9}$ cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Portland</td>
<td>44.7</td>
</tr>
<tr>
<td>Sulfate-resisting</td>
<td>100.0</td>
</tr>
<tr>
<td>Fly-ash/Portland</td>
<td>14.7</td>
</tr>
<tr>
<td>Slag/Portland</td>
<td>4.1</td>
</tr>
</tbody>
</table>
deterioration. In the measurement of weight loss due to surface deterioration, which they believed was a meaningful way to assess surface deterioration, concretes containing fly ash showed greater weight loss than control concrete. Carette and Langley stated that the surface scaling appeared not to be sensitive to the length of time that specimens were moist cured or air dried subsequent to initial moist curing, at least within the periods investigated.

2.1.9.4 Abrasion and Erosion of Fly-Ash Concrete

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

Carrasquillo (1987) examined the abrasion resistance of concretes containing no fly ash, 35% ASTM Class C fly ash, or 35% ASTM Class F fly ash. Specimens tested were cast from concretes having similar strengths, air contents, and cementitious materials contents. The abrasion resistance of concrete containing Class C fly ash was greater than that of concrete containing Class F fly ash or no fly ash. The latter two exhibited approximately equal abrasion resistance; measurement was based on the depth of wear.

Naik et al. (1992) carried out an investigation of the compressive strength and abrasion resistance of concrete containing ASTM Class C fly ash. They proportioned concrete mixtures to have cement replacement in the range of 15 to 70 wt% fly ash. The water/cementitious materials ratio varied from 0.31 to 0.37. Their results showed that the abrasion resistance of concrete containing ≤30% fly ash was similar to that of the control concrete; however, the abrasion resistance of concretes containing >40% fly ash was lower than that of control concrete without fly ash.

2.1.9.5 Effects of Fly Ash on Sulfate Resistance of Concrete

In 1967, Dikeou (1970) reported the results of sulfate-resistance studies on 30 concrete mixtures made with Portland cement, Portland fly-ash cement, or fly ash. From this work, it was concluded that all of the 12 fly ashes tested greatly improved sulfate resistance. Kalousek et al. (1972) studied the requirements of concretes for long-term service in a sulfate environment. From their study, they drew the following conclusions:

<table>
<thead>
<tr>
<th>Time of Moist Curing (days)</th>
<th>Time of Air Drying (weeks)</th>
<th>Mass of Scaling Residue (kg/m²)</th>
<th>W/(C + F) = 0.35 (Percentage of Fly Ash)</th>
<th>W/(C + F) = 0.45 (Percentage of Fly Ash)</th>
<th>W/(C + F) = 0.55 (Percentage of Fly Ash)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>3</td>
<td>0.195</td>
<td>0.149</td>
<td>0.123</td>
<td>0.139</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.122</td>
<td>0.178</td>
<td>0.126</td>
<td>0.144</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.076</td>
<td>0.091</td>
<td>1.131</td>
<td>0.174</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.100</td>
<td>0.105</td>
<td>0.129</td>
<td>0.192</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>0.154</td>
<td>0.135</td>
<td>0.160</td>
<td>0.147</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.147</td>
<td>0.158</td>
<td>0.172</td>
<td>0.098</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.098</td>
<td>0.114</td>
<td>0.119</td>
<td>0.192</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.192</td>
<td>0.169</td>
<td>0.118</td>
<td>0.120</td>
</tr>
<tr>
<td>14</td>
<td>3</td>
<td>0.139</td>
<td>0.188</td>
<td>0.517</td>
<td>0.144</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.144</td>
<td>0.126</td>
<td>0.131</td>
<td>0.174</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.174</td>
<td>0.135</td>
<td>0.162</td>
<td>0.168</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.168</td>
<td>0.117</td>
<td>0.286</td>
<td>0.064</td>
</tr>
</tbody>
</table>

Note: Each value represents the average of results from two slabs.

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• Eighty-four percent of ASTM Types V and II cement concretes without pozzolan showed a life expectancy of <50 years.
• Certain pozzolans very significantly increased the life expectancy of concrete exposed to 2.1% sodium sulfate solution. Fly ashes meeting current specifications were prominent among the group of pozzolans showing the greatest improvements.
• Concretes for long-term survival in a sulfate environment should be made with high-quality pozzolans and a sulfate-resisting cement. The pozzolan should not increase significantly but should preferably decrease the amount of water required.
• Cement to be used in making sulfate-resisting concrete with pozzolan of proven performance should have a maximum C₃A content of 6.5% and maximum C₆AF content of 12%. Restriction of cements to those meeting present-day specifications for Type V cement does not appear justified.

The fly-ash samples examined by Dikeou (1970) and those examined by Kalousek et al. (1972) originated from bituminous coals.

Dunstan (1976) reported the results of experiments on 13 concrete mixtures made with fly ashes from lignite or subbituminous coal sources. On the basis of this work, he concluded that lignite and subbituminous fly-ash concrete generally exhibited reduced resistance to sulfate attack. The Concrete Manual published by the U.S. Bureau of Reclamation gives options for cementitious materials for producing sulfate-resistant concretes (Bureau of Reclamation, 1981; Pierce, 1982).

2.1.9.6 Effects of Fly Ash on Alkali–Aggregate Reactions in Concrete

Shortly after Stanton (1940) discovered that alkali–aggregate reactions (AARs) caused expansion and damage in some concretes, he reported that the effects could be reduced by adding finely ground reactive materials to the concrete mixture. Subsequently, a variety of natural and artificial pozzolans and mineral admixtures, including fly ash, were found to be effective in reducing the damage caused by AARs. The effectiveness of fly ash (and other mineral admixtures) in reducing expansion due to AARs appears to be limited to reactions involving siliceous aggregates. A form of AAR known as the alkali–carbonate reaction (Poole, 1981) is relatively unresponsive to the addition of pozzolans (Swenson and Gillott, 1960). The role of fly ashes in reducing expansion by AAR can be summarized as follows:

• Substantial published data show that low-calcium fly ashes with alkali contents of less than about 4% are effective in reducing expansion caused by alkali–silica reactions when the fly ashes are used at a replacement level in the range of 25–30%. High-volume fly ash concrete is very effective in this regard.
• The use of high-calcium ashes has received less attention; hence, the background information relevant to their use is less well developed. If they are to be used, there is some indication that effective replacement levels may be higher than those for low-calcium ashes.
• The mechanism and details of the control of expansion caused by alkali–silica reactions are not fully understood. Much research remains before a satisfactory understanding can be developed.

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

Recently, an issue of concern has been the corrosion of steel reinforcement in fly-ash concrete structures exposed to chloride ions from deicing salts or seawater. If the concrete cover over steel reinforcement is sufficiently thick and impermeable, it will normally provide adequate protection against corrosion. The protective effect of the concrete cover is of both a physical and a chemical nature and functions in three ways:

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

Under alkaline conditions (pH higher than ~11.5), a protective oxide film will form on a steel surface, rendering it immune to further corrosion.
When concrete carbonates and the depth of carbonation reach the steel–concrete boundary, passivation may be reduced and corrosion may occur if sufficient oxygen and moisture reach the metal surface. Chlorides or other ions may also undermine the protective effect of passivation and encourage corrosion.

The Réunion internationale des laboratoires d’essais et de recherches sur les matériaux et les constructions (RILEM) Technical Committee on Corrosion of Steel in Concrete (1974) made the following statement, which gives perspective to this issue:

The efficiency of the (concrete) cover in preventing corrosion is dependent on many factors which collectively are referred to as its “quality.” In this context, the “quality” implies impermeability and a high reserve of alkalinity which satisfies both the physical needs and chemical requirements of the concrete cover. If the concrete is permeable to atmospheric gases or lean in cement, corrosion of the reinforcement can be anticipated and good protection should be attempted by the use of dense aggregate and a well-compacted mix with a reasonably low water/cement ratio. …If chloride corrosion is excepted, it is now usually agreed that carbonation of concrete cover is the essential condition for corrosion of reinforcement.

As discussed in the Effects of Fly Ash on Carbonation of Concrete section above, the issue of carbonation of fly-ash concrete has received some attention in recent years; however, it is our belief that the carbonation of fly-ash concrete is not a matter of concern, provided attention is paid to obtaining adequate impermeability in the concrete mass.

2.1.9.8 Effects of Fly Ash on Concrete Exposed to Seawater

Exposure of concrete to the marine environment subjects it to an array of severely aggressive factors, including most of those discussed in the preceding sections of this chapter. Concrete in tidal zones is the most severely attacked, subjected as it is to alternating wetting and drying, wave action, abrasion by sand and debris, frequent freezing and thawing cycles, and corrosion of reinforcement—all occurring in a chemically aggressive medium. Permanently immersed concrete is less severely affected.

Very little direct observation of fly-ash concrete in seawater has been reported in the literature, although some research in this area has been reported (Malhotra et al., 1980). In 1978, CANMET (Malhotra et al., 1988, 1992) initiated a long-term project on marine-environment performance of concretes incorporating supplementary cementing materials. Test specimens were exposed to repeated cycles of wetting and drying and up to approximately 100 freezing and thawing cycles per year. Even under exposure to severe marine conditions, concretes incorporating 25% fly ash from a bituminous source were in satisfactory condition after 15 years. The only exceptions were the specimens with a water/cement + fly ash ratio of 0.60. It was concluded that fly-ash concrete at a 25% cement replacement level (by mass) can be satisfactory under such conditions of exposure, provided the water/cementitious materials ratio is ≤50.

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

2.2 Blast-Furnace Slag

2.2.1 Ground, Granulated, or Pelletized Blast-Furnace Slag

Blast-furnace slag is a byproduct of iron manufacture. When it is rapidly quenched with water to a glassy state and finely ground, it develops the property of latent hydraulicity. Most of the slags so produced are, in themselves, cementitious materials to a certain degree, whereas others become so in the presence of activators such as Portland cement and calcium sulfate. Their performance in concrete,
however, is independent of whether they are inherently cementitious or not. Figure 2.8 shows a flow chart for the production of pig iron and blast-furnace slag (Kim, 1975). The technology for utilization of granulated blast-furnace slags in concrete is now well established worldwide. In the early 1970s, a pelletizing process to produce glassy slag was introduced in southern Ontario. This process uses considerably less water than granulation techniques. The molten slag is first expanded by treatment with water sprays, and the material is then passed over a rotating finned drum. The semimolten material is then thrown into the air for cooling and pelletization (Figure 2.9). Several pelletization plants are in operation worldwide (Hooton, 1987a).

**FIGURE 2.8** Flowchart showing production of pig iron and blast-furnace slag. (From Kim, C.S., Waste and Secondary Product Utilization in Highway Construction, M.S. thesis, McMaster University, Hamilton, Ontario, 1975.)

**FIGURE 2.9** Diagram of a typical slag pelletizer. (From Hooton, R.D., in *Supplementary Cementing Materials*, Malhotra, V.M., Ed., Canada Center for Mineral and Energy Technology (CANMET), Ottawa, Ontario, 1987, pp. 247–330.)
2.2.2 Mixture Proportions and Properties of Fresh Concrete Incorporating Blast-Furnace Slag

2.2.2.1 Mixture Proportions
The proportions of ground, granulated, or ground, pelletized, blast-furnace slag used in concrete depend on the job requirements. In normal ready-mixed concrete operations, in which the primary aim is to conserve cement, the usual proportions vary from 25 to 50% by weight of cement on a cement-replacement basis; however, if the purpose is to enhance some aspect of concrete durability (for example, sulfate resistance), then the slag content is at least 50% of the total cementitious material. As each slag has a unique chemical composition, glass content, and fineness, it is necessary to perform exploratory laboratory investigations with the cement, aggregates, and chemical admixtures to be used at a project to determine the correct percentage of slag to be incorporated into the concrete. This aspect cannot be overemphasized. The specific gravity of slags ranges from 2.85 to 2.95, compared with 3.15 for Portland cements; thus, a given replacement of cement by slag on a weight basis results in a higher volume of paste in a concrete mixture. This result is of little consequence at lower percentages of cement replacement. If, however, 50 to 75% cement replacements are being considered, this will affect the rheology of the concrete mixtures and may allow some increase in the volume of coarse aggregate to be used, especially in mixtures incorporating higher amounts of cement.

2.2.2.2 Time of Setting
The incorporation of slag as a replacement for Portland cement in concrete normally results in increased setting time. Final setting time can be delayed up to several hours depending on the ambient temperature, concrete temperature, and mixture proportions. At temperatures lower than 23°C, considerable retardation in setting time can be expected for slag concretes compared with control concrete, which has serious implications in winter concreting. At higher temperatures (>30°C), there is little or no change in the setting time of slag concrete as compared to control concrete. Data by Hogan and Meusel (1981) on initial and final setting for concrete incorporating granulated slag are shown in Table 2.9.

2.2.2.3 Bleeding
Few published data are available on the bleeding of slag concretes. Slags are generally ground to a higher fineness than normal Portland cement; therefore, a given mass of slag has a higher surface area than the corresponding mass of Portland cement. As the bleeding of concrete is governed by the ratio of the surface area of solids to the volume of water, in all likelihood the bleeding of slag concrete will be lower than that of the corresponding control concrete. The slags available in Canada and the United States have fineness, as measured by the Blaine method, greater than 4500 cm²/g, compared with that of about 3000 cm²/g for Portland cement. Thus, in concrete in which a given mass of Portland cement is replaced by an equivalent mass of slag, bleeding should not be a problem.

2.2.2.4 Dosage of Air-Entraining Admixtures
The dosage requirement of an air-entraining admixture to entrain a given volume of air in slag concrete increases with increasing amounts of slag. The increased demand for the admixture is, once again, probably due to the higher total surface area of the slag particles compared with that of the Portland cement particles. In an investigation reported by Malhotra (1979), the admixture dosage required to entrain about 5% air increased from 177 mL/m³ for the control concrete to 562 mL/m³ for a concrete mixture incorporating 65% pelletized slag. The water/cement + slag ratio was 0.30.

*Granulated slag implies that the slag is granulated by rapid-water quenching of the molten slag, whereas pelletized slag implies that the granulation is achieved by a pelletizing process. Hereafter, these are referred to either as granulated or pelletized slag or only as slag when reference is made to both types.
2.2.2.5 Rates of Slump Loss

Meusel and Rose (1979) have shown that the rate of slump loss of concrete incorporating granulated slag at 50% cement replacement was comparable to that of the control concrete.

2.2.3 Properties of Hardened Concrete

2.2.3.1 Color

Concrete incorporating slags is generally lighter in color than normal Portland cement concrete, due to the lighter color of slags. When concrete is tested for compression or flexure, the interior of the broken specimens exhibit a deep blue–green color. After sufficient exposure to air, the color disappears. The degree of color, which results from the reaction of sulfides in the slag with other compounds in cement, depends on the percentage of slag used, curing conditions, and the rate of oxidation.

2.2.3.2 Curing

The rate and degree of hydration of cement paste, and consequently its strength, are affected significantly by lack of proper curing because of the slow formation of strength-producing hydrates. This effect becomes more pronounced when the paste incorporates high percentages of slag. To ensure proper strength and durability of concretes incorporating high percentages of slag (>30%), it is important that they be given more curing than concretes without slag. Such extended curing is especially important during winter concreting in Canada and the northern United States. The increase in curing time would depend on the ambient temperature, the concrete temperature, the type and amount of cement used, and the percentage of cement replacement.

2.2.3.3 Compressive Strength

The compressive strength development of slag concrete depends primarily on the type, fineness, activity index, and proportions of slag used in concrete mixtures. Other factors that affect the performance of slag in concrete are the water/cementitious materials ratio and the type of cement used. In general, the strength development of concrete incorporating slags is slow at 1 to 5 days, compared to that of the control concrete. Between 7 and 28 days, the strength approaches that of the control concrete.

### TABLE 2.9 Data on Time of Setting for Air-Entrained Concrete Incorporating Granulated Slag

<table>
<thead>
<tr>
<th>Properties</th>
<th>Control, No Slag</th>
<th>Slag Content (%)</th>
<th>Control, No Slag</th>
<th>Slag Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water/(cement + slag)</td>
<td>0.40</td>
<td>40</td>
<td>0.55</td>
<td>40</td>
</tr>
<tr>
<td>Cement factor (cement and slag) (kg/m³)</td>
<td>413</td>
<td>413</td>
<td>272</td>
<td>272</td>
</tr>
<tr>
<td>Fine aggregate/coarse aggregate</td>
<td>33/67</td>
<td>33/67</td>
<td>46/54</td>
<td>46/54</td>
</tr>
<tr>
<td>Air content (%)</td>
<td>5.4</td>
<td>3.4</td>
<td>3.5</td>
<td>6.0</td>
</tr>
<tr>
<td>Unit weight (kg/m³)</td>
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<td>2350</td>
<td>2355</td>
<td>2310</td>
</tr>
<tr>
<td>Slump (mm)</td>
<td>75</td>
<td>75</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>Air-entraining admixture (mL/kg cement)</td>
<td>4.4</td>
<td>4.4</td>
<td>4.4</td>
<td>4.4</td>
</tr>
<tr>
<td>Initial set at 21.1°C (70°F) (hr:min)</td>
<td>4:06</td>
<td>4:02</td>
<td>5:02</td>
<td>5:10</td>
</tr>
<tr>
<td>Final set at 21.1°C (70°F) (hr:min)</td>
<td>5:34</td>
<td>5:40</td>
<td>6:40</td>
<td>8:10</td>
</tr>
<tr>
<td>Initial set at 32.2°C (70°F) (hr:min)</td>
<td>3:30</td>
<td>3:45</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Final set at 32.2°C (70°F) (hr:min)</td>
<td>4:30</td>
<td>4:50</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

concrete, and beyond this period the strength of slag concrete exceeds the strength of the control concrete. Figure 2.10 and Figure 2.11 show compressive strength development with age for granulated slag concrete for water/cement + slag ratios of 0.40 and 0.55. Note that the highest strength gain at 28 days was for concrete with a slag content of 40% cement replacement.

Malhotra et al. (1985) reported investigations in which small amounts of condensed silica fume were added to pelletized slag concrete to increase the early-age strength. Figure 2.11 illustrates the strength development of concrete from 1 to 180 days. The authors concluded that:

**FIGURE 2.10** Age vs. compressive strength relationship for air-entrained concrete: \( W/(C + S) = 0.40 \). (From Hogan, F.J. and Meusel, J.W., ASTM Cement, Concrete, Aggregates, 3(1), 40–52, 1981.)

**FIGURE 2.11** Age vs. compressive strength relationship for concrete incorporating condensed silica fume and pelletized slag, water/cement + blast-furnace slag \( W/(C + BFS) = 0.50 \). (From Malhotra, V.M. et al., in Proceedings of the RILEM/ACI Symposium on the Technology of Concrete When Pozzolans, Slags and Chemical Admixtures Are Used, Monterey, Mexico, 1985, pp. 395–414.)
Mineral Admixtures

- The low early-age strength of Portland cement concrete incorporating blast-furnace slag can be increased by the incorporation of condensed silica fume. The gain in strength is generally directly proportional to the percentage of the fume used.
- At 3 days, the increase in strength is generally marginal, especially for concrete with high W/C + blast-furnace slag (BFS) ratios. However, at the age of 14 days and beyond, with minor exceptions, the loss in compressive strength of concrete due to the incorporation of BFS can be fully compensated for with a given percentage of condensed silica fume, regardless of the W/(C + BFS). This is also true for the flexural strength.
- The continuing increase in strength at 56, 91, and 180 days of the concrete incorporating BFS and condensed silica fume indicates that sufficient lime (liberated during the hydration of Portland cement) is present at these ages for the cementitious reaction to continue.

2.2.3.4 Flexural Strength

In general, at 7 days and beyond, the flexural strength of concrete incorporating slag is comparable to, or greater than, the corresponding strength of control concrete; however, in one instance, the reverse was reported for a water/cement + slag ratio of 0.38. The increased flexural strength of slag concrete is probably due to the stronger bonds in the cement–slag–aggregate system because of the shape and surface texture of the slag particles.

2.2.3.5 Young's Modulus of Elasticity

According to Stutterheim (1960), at the same strength level, there is little, if any, difference between the modulus of elasticity of the control concrete and a concrete containing a granulated slag of South African origin. No published data are available on Young's modulus of elasticity of slags currently available in North America. Investigations performed by Nakamura et al. (1986) on a Japanese slag showed no significant difference between the values of the Young's modulus of elasticity of concrete incorporating granulated slag and that of the control concrete.

2.2.3.6 Drying Shrinkage

Hogan and Meusel (1981) showed that drying shrinkage of concrete incorporating granulated slag is more than that of control concrete. The increase in shrinkage is attributed to increased paste volume in concrete when slag is used as replacement for Portland cement on an equal weight basis because of the lower specific gravity of the slag. This finding may or may not be true for other slags, and further research is needed to confirm this. Fulton (1974) suggested that the shrinkage of concrete incorporating granulated slag can be reduced by taking advantage of improved workability to increase the aggregate/cement ratio or by reducing the water/cement ratio of concrete.

2.2.3.7 Creep

Few published data are available on creep of concrete incorporating North American slags. The available data from South Africa and Japan are conflicting (Fulton, 1974). This conflict is due primarily to the fineness of slags used, methods of tests, age of testing, humidity conditions, and the stress/strength ratio employed; for example, it has been shown that the fineness of cement significantly affects the creep strains (Fulton, 1974). Bamforth (1980) has reported limited data on creep strains for concretes with and without fly ash and granulated slags, loaded to a constant stress/strength ratio of 0.25. He found that for concretes loaded at an age greater than 24 hours, the effects of fly ash and slag significantly reduced the magnitude of the creep. Neville and Brooks (1975) showed that, when creep tests are performed at ordinary room temperature and humidity conditions (i.e., 20°C and 60% relative humidity) on test specimens that have been loaded after moist curing for 28 days, the total creep of the concrete incorporating a slag from a British source was greater than that of the control concrete, although not significantly so. The rationale for this finding may be that under such test conditions, the rate of gain of strength of the slag concrete is lower than that of the control concrete.
2.2.3.8 Permeability

The permeability of concrete depends mainly on the permeability of the cement paste, which, in turn, depends on its pore-size distribution. Using mercury-intrusion techniques, several investigators (Mannmohan and Mehta, 1981; Mehta, 1983) demonstrated that incorporating granulated slags in cement paste helps transform large pores into smaller pores, resulting in decreased permeability of the matrix and, hence, of the concrete. The exact mechanism by which the pore refinement occurs in a hydrated slag-cement matrix, however, is not fully understood. Detailed data comparing the permeability of concrete with and without slags are not available, although it has been observed that granulated slag concretes incorporating slags at up to 75% cement replacement have performed satisfactorily when exposed to seawater (Wiebenga, 1980).

2.2.4 Durability of Concrete Incorporating Blast-Furnace Slag

It is believed that the increased durability of Portland cement concrete incorporating blast-furnace slag results from a finer pore structure and a reduction in easily leached calcium hydroxide in the hardened cement paste. Subsequently, the volume previously occupied by calcium hydroxide is filled in with hydration products, resulting in a less-permeable material. Permeability controls the physical and chemical processes of degradation caused by the action of migrating water; therefore, permeability to water determines the rate of deterioration.

2.2.4.1 Resistance to Sulfate Attack

Sulfates attack concrete and affect its coherence and strength. The resistance of concrete to sulfate attack is improved by partially replacing Portland cement with ground granulated blast-furnace slag. In Germany, France, and the Netherlands, cements with a high blast-furnace slag content have been used for many years and are considered appropriate for use in a high-sulfate environment (DIN 1164, 1978; NEN 3550, 1979). Hogan and Meusel (1981) carried out a study that demonstrated high resistance to sulfate attack when the granulated slag proportion exceeded 50% of the total cementitious material; ASTM Type II cements were used. Results of studies carried out by Frearsen (1986) confirmed that ordinary Portland cements and blends of both ordinary and sulfate-resisting Portland cement containing lower levels of granulated slag replacement have inferior resistance to sulfate attack. Sulfate resistance increased with granulated slag content, and a mortar with 70% slag content was found to have a resistance superior to mortars containing sulfate-resisting Portland cements alone. Also, the influence of slag content on sulfate resistance was found to be more significant than the water/cement ratio in the mixtures investigated. According to Ludwig (1989), the cements exhibiting resistance to sulfate attack are:

- Portland cement with $C_3A$ content $\leq 3$ wt%
- Portland cement with $\leq 70\%$ slag content
- Nonstandard cements such as high-alumina and supersulfated cements

Bakker (1983) found that slag concretes with a high slag content display an increased resistance to sulfates because of the low permeability of the concrete to different ions and water, as shown by the various coefficient values in Table 2.10.

Where granulated slag is used in sufficient quantities, several changes occur that improve resistance to sulfate attack. These changes include the following:

- The $C_3A$ content of the mixture is proportionally reduced depending on the percentage of slag used; however, Lea (1970) reported that increased sulfate resistance depends not only on the $C_3A$ content of Portland cement alone but also on the $Al_2O_3$ content of the granulated slag. Lea further reported that sulfate resistance increased where the alumina content of the slag is less than 11%, regardless of the $C_3A$ content of the Portland cement when blends with 20 to 50% granulated slags were used.
Through the reduction of soluble Ca(OH)$_2$ in the formation of calcium silicate hydrates (CSHs), the environment for the formation of ettringite is reduced. Resistance to sulfate attack is greatly dependent on the permeability of the concrete or cement paste. The formation of CSH in pore spaces usually occupied by alkalis and Ca(OH)$_2$ reduces the permeability of the paste and prevents the intrusion of aggressive sulfates.

Mehta (1981) tested pastes incorporating natural pozzolans, rice-husk ash, and granulated slag. The 28-day-old paste of the blended cement containing 70% blast-furnace slag showed excellent resistance to sulfate attack. Few large pores were present in the hydrated paste, although the total porosity (pores >45 Å) was the highest among all the cements tested. The direct relationship between sulfate resistance of a cement and the slope of its pore-size distribution plot in the range of 500 to 45 Å probably shows that the presence of a large number of fine pores is associated with improved sulfate resistance of the material (Figure 2.12). Although the total porosity of the cement containing 30% slag was considerably less than the cement containing 70% slag, the former was not found to be sulfate resistant. On the basis of the test results, Mehta proposed that the chemical resistance of blended Portland cements results mainly from the process of pore refinement, which is associated with the pozzolanic reactions involving the removal of Ca(OH)$_2$.

2.2.4.2 Resistance to Seawater

The action of sulfate in seawater on concrete is rather similar to that of sulfate-bearing groundwater, but in the former case the attack is not accompanied by expansion of the concrete. The absence of expansion is partly due to the presence of a large quantity of chlorides in the seawater that inhibit the expansion; gypsum and calcium sulfoaluminate are more soluble in a chloride solution than in water, so they either do not form or are leached out by the seawater.

Regourd et al. (1977) studied mortar cubes that had been exposed to seawater since 1904 at the port of La Rochelle, France. They concluded that all Portland slag cements with a slag content >60% perform well in seawater. In the case of lower slag content, the MgSO$_4$ reacts with the Ca(OH)$_2$ from C$_3$S and C$_2$S hydration and produces gypsum. The gypsum reacts with the aluminates to form expansive ettringite. Mehta (1989), on the other hand, proposed that the deterioration of concrete by seawater is not characterized by expansion but rather is affected by erosion or loss of the solid constituents from the mass. Mehta suggested that ettringite expansion is suppressed in environments where (OH)$^-$ ions have been replaced by Cl$^-$ ions.
In seawater, well-cured concretes containing large amounts of granulated slag or pozzolan usually outperform reference concretes containing only Portland cement, partly because the former contain less uncombined Ca(OH)$_2$ after curing. In permeable concretes, the normal amount of CO$_2$ present in seawater is sufficient to decompose the cementitious products. The presence of calcium silicocarbonate (thaumasite), calcium carboaluminate hydrate (hydrocalumite), and calcium carbonate (aragonite) have been reported in cement pastes derived from deteriorated concretes exposed to seawater for long periods.

2.2.4.3 Reduction of Expansion Due to Alkali–Silica Reactions

In concrete containing reactive siliceous aggregates, slag cements are preferable to Portland cements, which are rich in alkalis (Regourd, 1980). Research undertaken at the Concrete Research Institute of the Dutch Cement Industry and by other investigators (Smolczyk, 1974, 1975) confirmed that the reason for the high resistance of concretes incorporating slags to the alkali–silica reaction is the low permeability.
of these concretes to various ions and to water. The low permeability is due not only to the amount of gel formed but also to the locality where the gel is precipitated; that is, the gel can block a pore when Portland cement and slag grains are close to each other. The potential alkali–aggregate reactivity for combinations of Portland cement and granulated slag was investigated by Hogan and Meusel (1981) using ASTM Test C 227; the aggregate used was Pyrex® glass, known to be highly reactive. The data indicate that the expansion of mortar bars made with slag-cement mixtures and Pyrex® glass is significantly less than for bars made with Portland cement alone. The cement used for these tests had an alkali content of 0.51% sodium oxide equivalent, which conforms to the ASTM C 150 specification for Portland cement requirement for low-alkali cement. Suppression of the alkali–aggregate reaction by the addition of slag was cited by Mather (1965), who suggested that an alkali limit for Portland slag cements, which have a performance equal to that of 0.60% Na₂O for Portland cements alone, could be as high as 1.20% Na₂O equivalent.

### 2.2.4.4 Resistance to Repeated Cycles of Freezing and Thawing

Many studies have been published in which granulated blast-furnace slag has been used as partial replacement for Portland cement in concrete subjected to repeated cycles of freezing and thawing (Fulton, 1974; Klieger and Isberner, 1967; Mather, 1957). Results of these studies indicated that, when mortar or concrete made with granulated slag and Portland cement were tested in comparison with Type I and Type II cements, their resistance to freezing and thawing (ASTM C 666, Procedure A) was essentially the same, provided the concrete was air entrained. Malhotra (1983b) reported results of tests performed in an automatic unit capable of performing eight freezing and thawing cycles per day (ASTM C 666, Procedure B). The percentage of slag used as replacement for normal Portland cement varied from 25 to 65 wt% of cement. Initial measurements were taken at 14 days. After about every 100 cycles, the specimens were measured, weighed, and tested by resonant frequency and by the ultrasonic-pulse velocity method. The test was terminated at 700 freezing and thawing cycles. Durability of the exposed concrete prisms was determined from weight, length, resonant frequency, and pulse velocity of the test prisms before and after the freezing and thawing cycling, and relative durability factors (ASTM C 666) were calculated. The test results (Table 2.11) indicated that, regardless of the water/cement + slag ratio and whether the concretes were air entrained or air entrained and superplasticized, these specimens performed excellently in freezing and thawing tests, with relative durability factors greater than 91%.

### 2.2.5 Carbonation

Concrete exposed to air will partially release its free water from the layers next to the surface. During evaporation, the pore water in the concrete is replaced by air, and reactions between the CO₂ of the atmosphere and the alkali compounds of the concrete take place. This process between the CO₂ of the atmosphere and the hydration products of the hardened cement paste is called carbonation. The properties of the concrete, as well as its protective properties against corrosion of reinforcing steel, are affected by these reactions. In general, in well-compacted low water/cement ratio slag concrete, carbonation is not a problem; however, if the concrete incorporates a large percentage of slag, is not cured properly, and has a high water/cement + slag ratio, then the depth of carbonation will exceed that for normal Portland cement concrete. Steel in the presence of high concentrations of hydroxyl does not corrode. Bird (1969) suggested that this passivity is the result of the formation of a protective film of gamma ferric oxide on the surface of the steel. As long as this protective film is maintained by a high pH and is not disrupted by aggressive substances, complete protection of the steel against corrosion is assured. Carbonation can reduce the pH to an extent determined by the permeability of the concrete. Hamada (1968) and Meyer (1968) agreed that carbonation proceeds more rapidly in concretes incorporating slag than in those made with ordinary Portland cement; however, this finding was disputed by Schröder and Smolczyk (1968), who pointed out that comparative tests should be based on specimens of equal initial permeability rather than on specimens of equal age.
### TABLE 2.11 Summary of Freeze–Thaw Test Results for Concrete Series B and D

<table>
<thead>
<tr>
<th>Mix Series</th>
<th>W/(C + S)a</th>
<th>Type of Mix</th>
<th>Weight (kg)</th>
<th>Length (mm)b</th>
<th>Longitudinal Resonant Frequency (Hz)</th>
<th>Pulse Velocity (m/sec)</th>
<th>Weight (kg)</th>
<th>Length (Hz)</th>
<th>Longitudinal Resonant Frequency (m/sec)</th>
<th>Pulse Velocity (%)</th>
<th>Durability Factor (%)</th>
<th>Relative Durability Factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B 0.38</td>
<td>Control + AEA</td>
<td>8.703 2.89 5150 4717</td>
<td>8.693 2.90 5200 4747</td>
<td>102 100 100 100 100 100 100 100</td>
<td>100 100 100 100 100 100 100 100</td>
<td>100 100 100 100 100 100 100 100</td>
<td>100 100 100 100 100 100 100 100</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Control + AEA + SP</td>
<td>8.499 2.70 5150 4684</td>
<td>8.486 2.72 5138 4661</td>
<td>99 97 99 97 99 97 99 97</td>
<td>100 100 100 100 100 100 100 100</td>
<td>100 100 100 100 100 100 100 100</td>
<td>100 100 100 100 100 100 100 100</td>
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<tr>
<td></td>
<td>25% slag + AEA</td>
<td>8.697 3.00 5300 4788</td>
<td>8.673 3.05 5225 4788</td>
<td>97 95 97 95 97 95 97 95</td>
<td>100 100 100 100 100 100 100 100</td>
<td>100 100 100 100 100 100 100 100</td>
<td>100 100 100 100 100 100 100 100</td>
<td></td>
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<tr>
<td></td>
<td>25% slag + AEA + SP</td>
<td>8.540 2.96 5125 4684</td>
<td>8.517 3.01 5100 4656</td>
<td>99 97 99 97 99 97 99 97</td>
<td>100 100 100 100 100 100 100 100</td>
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<tr>
<td></td>
<td>65% slag + AEA</td>
<td>8.622 2.74 5140 4684</td>
<td>8.626 2.91 4950 4568</td>
<td>93 91 93 91 93 91 93 91</td>
<td>100 100 100 100 100 100 100 100</td>
<td>100 100 100 100 100 100 100 100</td>
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<tr>
<td></td>
<td>65% slag + AEA + SP</td>
<td>8.302 1.59 5025 4589</td>
<td>8.302 1.68 4875 4531</td>
<td>94 92 94 92 94 92 94 92</td>
<td>100 100 100 100 100 100 100 100</td>
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<td></td>
<td>Control + AEA</td>
<td>8.331 2.56 5000 4568</td>
<td>8.299 2.36 5010 4600</td>
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<td></td>
<td>Control + AEA + SP</td>
<td>8.443 2.76 4980 4568</td>
<td>8.394 2.76 4980 4504</td>
<td>100 100 100 100 100 100 100 100</td>
<td>100 100 100 100 100 100 100 100</td>
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<tr>
<td></td>
<td>25% slag + AEA</td>
<td>8.451 2.85 5000 4573</td>
<td>8.416 2.88 5000 4606</td>
<td>100 100 100 100 100 100 100 100</td>
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</tr>
<tr>
<td></td>
<td>25% slag + AEA + SP</td>
<td>8.544 2.83 5040 4639</td>
<td>8.483 2.91 5050 4622</td>
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<td></td>
<td>65% slag + AEA</td>
<td>8.465 2.61 4950 4546</td>
<td>8.465 2.61 4950 4546</td>
<td>100 100 100 100 100 100 100 100</td>
<td>100 100 100 100 100 100 100 100</td>
<td>100 100 100 100 100 100 100 100</td>
<td>100 100 100 100 100 100 100 100</td>
<td></td>
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<tr>
<td></td>
<td>65% slag + AEA + SP</td>
<td>8.471 2.52 4930 4563</td>
<td>8.471 2.52 4930 4563</td>
<td>100 100 100 100 100 100 100 100</td>
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<td>100 100 100 100 100 100 100 100</td>
<td>100 100 100 100 100 100 100 100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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a Water/(cement + slag) ratio.
b Gauge length of 345 mm should be added to this value to arrive at the exact length.
c Prisms failed at the end of 533 freeze–thaw cycles when the resonant frequency was 3840 Hz.
d Prisms failed at the end of 450 freeze–thaw cycles when the resonant frequency was 4150 Hz.


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2.3 Silica Fume

2.3.1 Production of Silica Fume

Silica fume is a byproduct of the manufacture of silicon or of various silicon alloys produced in submerged electric-arc furnaces. The type of alloy produced and the composition of quartz and coal, the two major components used in the submerged-electric arc furnace, greatly influence the chemical composition of silica fume (Malhotra et al., 1987). Most of the published data on the use of silica fume in cement and concrete are related to silica fume collected during the production of a silicon alloy containing at least 75% silicon.

2.3.1.1 Forms of Silica Fume

Silica fume is available commercially in several forms in both North America and Europe:

- **As-produced silica fume** is silica fume collected in dedusting systems known as bag houses. In this form, the material is very fine and has a bulk density of about 200 to 300 kg/m$^3$, compared with 1500 kg/m$^3$ for Portland cement (Malhotra et al., 1987). As-produced silica fume is available in bags or in bulk. Because of its extreme fineness, this form poses handling problems; in spite of this, the material can be and has been transported and handled like Portland cement.
- **Compacted silica fume** has a bulk density ranging from 500 to 700 kg/m$^3$ and is considerably easier to handle than as-produced silica fume. To produce the compacted form, the as-produced silica fume is placed in a silo, and compressed air is blown in from the bottom of the silo. This causes the particles to tumble, and in doing so they agglomerate. The heavier agglomerates fall to the bottom of the silo and are removed at intervals. The air compaction of the as-produced silica fume is designed so the agglomerates produced are rather weak and quickly break down during concrete mixing. Mechanical means have also been used to produce compacted silica fume.
- **Water-based silica fume slurry** overcomes the handling and transporting problems associated with as-produced silica fume; the slurry contains about 40 to 60% solid particles. Typically, these slurries have a density of about 1300 kg/m$^3$. Some slurries may contain chemical admixtures such as superplasticizers, water reducers, and retarders. One such product (known as Force 10,000®) has been successfully marketed in North America.

2.3.2 Physical and Chemical Characteristics of Silica Fume

2.3.2.1 Physical Characteristics of Silica Fume

Silica fume varies in color from pale to dark gray. The carbon content and, to a lesser extent, the iron content seem to have significant influence on the color of silica fume. The bulk specific weight is of the order of 200 kg/m$^3$ and is 500 kg/m$^3$ when compacted. The specific gravity of silica fume is about 2.20. The particles have a wide range of sizes, but they are perfectly spherical (Figure 2.13). The mean particle diameter is 0.1 $\mu$m, compared with 10 $\mu$m for particles of cement. The specific surface of silica fume ranges from 13,000 to 30,000 m$^2$/kg as measured by the nitrogen adsorption technique; the values for Portland cement are 300 to 400 m$^2$/kg as measured by the Blaine method. Table 2.12 gives values for the fineness, specific surface, pozzolanic activity index, and specific gravity for silica fume from the production of silicon and ferrosilicon alloys (Malhotra et al., 1987). X-ray diffractograms of samples of different types of silica fume have shown them to be vitreous. All the diffractograms exhibit a very wide scattering peak centered at about 4.4 Å, the most important peak of cristobalite (Figure 2.14). When heated to 1100°C, silica fume crystallizes in the form of cristobalite, except the FeSi-50% type, which crystallizes as enstatite, most probably due to the presence of a high amount of iron and magnesium oxide.
2.3.2.2 Chemical Composition of Silica Fume

The chemical composition of silica fume from different furnaces is given in Table 2.13. A change in the type of alloy manufactured may cause changes in the characteristics of the silica fume produced; therefore, it is important that concrete plants using silica fume know of any changes in the source of raw materials used for the furnace or changes in the nature of the alloy being produced by a plant.

2.3.3 Physical and Chemical Mechanisms in the Cement–Silica Fume System

2.3.3.1 Physical Mechanisms

Silica fume enhances the properties of concrete by several physical mechanisms, including increasing the strength of the bond between the paste and aggregate by reducing the size of the CH crystals in the region by: (1) providing nucleation sites for the CH crystals so they are smaller and more randomly oriented, and (2) reducing the thickness of the weaker transition zone (Detwiler and Mehta, 1989; Monteiro and Mehta, 1986). Physical mechanisms also include increasing the density of the composite system due to

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**TABLE 2.12 Physical Characteristics of Silica Fume**

<table>
<thead>
<tr>
<th>Physical Characteristics</th>
<th>Nebesar and Carette Results</th>
<th>Pistilli et al. Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si Silica Fume (24 Samples)</td>
<td>FeSi–75% Silica Fume (24 Samples)</td>
</tr>
<tr>
<td>Fineness by 45 µm sieve (%) passing</td>
<td>94.6</td>
<td>98.2</td>
</tr>
<tr>
<td>Specific surface area (m²/kg)</td>
<td>20,000&lt;sup&gt;a&lt;/sup&gt;</td>
<td>17,200&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Pozzolanic activity index with cement (%)</td>
<td>102.8</td>
<td>96.5</td>
</tr>
<tr>
<td>Water requirement (%)</td>
<td>138.8</td>
<td>139.2</td>
</tr>
<tr>
<td>Pozzolanic activity index with lime (MPa)</td>
<td>8.9</td>
<td>—</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

<sup>a</sup> Nitrogen adsorption.

<sup>b</sup> Blaine permeability.

FIGURE 2.14 X-ray diffractograms of different types of silica fume for concrete with water/cement + silica fume (W/(C + SF)) of 0.64: (a) before heating; (b) after heating at 1100°C. (From Carette, G.G. and Malhotra, V.M., ASTM J. Cement Concrete Aggregates, 5(1), 3–13, 1983.)
the filler packing effect and by providing a more refined pore structure (Bache, 1981; Hjorth, 1982; Sellevold and Nilsen, 1987). For the above mechanisms to take place, it is essential that silica-fume particles be well dispersed in a concrete mixture. To achieve this, the use of high-range water reducers (superplasticizers) becomes almost mandatory.

2.3.3.2 Chemical Mechanisms and Pozzolanic Reactions

Malhotra et al. (1987) have reported extensively on the chemical reactions involved in the cement–silica fume–water system. In the presence of Portland cement, the basic reaction, known as the pozzolanic reaction, involves combining finely divided amorphous silica with lime to form a calcium silicate hydrate.

2.3.4 Properties of Fresh Concrete

2.3.4.1 Color

In general, the color of silica-fume concrete is darker than that of conventional concrete. This color difference is more evident on the surface of wet-hardened concrete and in fresh concrete. Also, in concretes incorporating high levels of silica fume that has high carbon content, the dark color is more pronounced. In investigations of silica-fume concrete made with dark-colored fume, it was observed that the color difference disappeared when concrete specimens were stored in the laboratory environment for extended periods. Presumably, this difference in color was neutralized by drying and perhaps by carbonation.

2.3.4.2 Water Demand

Due to its spherical, small particles, silica fume fills the pores between larger grains of cement and gives a better particle-size distribution, leading to a decrease in water demand in silica-fume concrete; however, the high specific area of the silica-fume particles tends to increase water demand, giving a net effect of increased water demand compared to Portland cement concrete with the same level of workability. Figure 2.15 shows that the increase in water demand is almost directly proportional to the amount of silica fume used in concretes that have an initial water/cement ratio of 0.64 (Carette and Malhotra, 1983). Superplasticizers or high-range water reducers can be used in silica-fume concretes to reduce the water demand. In a study using high-resolution nuclear magnetic resonance (NMR) in combination with thermal analysis (DTA/TG), Justnes et al. (1992) investigated the pozzolanicity of condensed silica fume.
in cement pastes. Their results confirmed that condensed silica fume is a very reactive pozzolan. The conversion rate of condensed silica fume to hydration products after 3 days of curing was higher than for cement at the same age. In a parallel study, Sellevold and Justnes (1992) studied the decrease in relative humidity and chemical shrinkage during hydration for sealed cement pastes. The Portland cement pastes incorporated 0, 8, and 16% condensed silica fume and had water/cement + silica fume ratios of 0.2, 0.3, and 0.40, respectively. They found that the relative humidity (RH) decreased rapidly during the first 2 weeks and reached about 78% after more than a year for the pastes with the lowest water/cement + silica fume ratios; the value for the paste with the highest water/cement + silica fume ratio was about 87% RH. According to the authors, the decrease in RH is the main cause of increased cracking tendency in high-strength concretes that incorporate silica fume.

2.3.4.3 Bleeding

Bleeding of silica fume concretes is generally lower than that of plain Portland cement concrete. The extremely fine silica-fume particles attach themselves to the cement particles, reducing the channels for bleeding and leaving very little free water available in the fresh concrete.

2.3.4.4 Workability

When compared to Portland cement concrete, silica-fume concrete is more cohesive and resistant to segregation due to the increase in the number of solid-to-solid contact points. Silica-fume concrete also tends to lose slump rapidly, and a higher initial slump than that of a conventional concrete is often required. In lean concretes incorporating less than 300 kg/m³ cement, however, workability appears to improve when silica fume is added.
2.3.4.5 Air Entrainment

Because of the extremely high surface area of the silica fume, the dosage of air-entraining admixture required to produce a certain volume of air in silica fume concretes increases considerably with increasing silica-fume dosage. The presence of carbon in the silica fume adds to the increase in air-entraining admixture demand. It has been reported that entrainment of more than 5% air is difficult in concretes that incorporate high amounts of silica fume, even in the presence of a superplasticizer (Carette and Malhotra, 1983).

2.3.4.6 Shrinkage Cracking

Shrinkage cracking occurs in fresh concrete under curing conditions that cause a net removal of water from exposed concrete surfaces, thus creating tensile stresses beyond the low early-age tensile strength capacity of concretes. As concretes containing silica fume show little or no bleeding, thus allowing very little water to rise to the surface, the risk of cracking is high in fresh concrete. Shrinkage cracking can be a very serious problem under curing conditions of elevated temperatures, low humidity, and high winds, which allow rapid evaporation of water from freshly placed concrete. Johansen (1980) and Sellevold (1984) reported that fresh concrete is most vulnerable to shrinkage cracking as it approaches initial set. To overcome this problem, the surface of concrete should be protected from evaporation by covering it with plastic sheets or wet burlap or by using curing compounds and evaporation-retarding admixtures.

2.3.4.7 Setting Time

Ordinary mixtures (with 250 to 300 kg/m^3 cement) that incorporate small amounts of silica fume, up to 10% by weight of cement, exhibit no significant difference in setting times compared with conventional concretes. As silica fume is invariably used in concretes in combination with water reducers and superplasticizers, the effect of silica fume on the setting of concrete is masked by the effects of the admixtures. Investigations by Bilodeau (1985) showed that the addition of 5 to 10% silica fume to superplasticized and nonsuperplasticized concretes had a negligible effect on the setting time of concrete; however, in concrete with a water/cementitious materials ratio of 0.40 and 15% silica fume, there was a noticeable delay in setting time. The high dosage of superplasticizer used because of the high silica-fume content in the concrete could have contributed to the setting delay (Bilodeau, 1985).

2.3.5 Properties of Hardened Concrete

2.3.5.1 Compressive Strength

It is well recognized that silica fume can contribute significantly to the compressive strength development of concrete. This is because of the filler effect and the excellent pozzolanic properties of the material, which translate into a stronger transition zone at the paste–aggregate interface. The extent to which silica fume contributes to the development of compressive strength depends on various factors, such as the percentage of silica fume, the water/cement + silica fume ratio, cementitious materials content, cement composition, type and dosage of superplasticizer, temperature, curing conditions, and age.

Superplasticizing admixtures play an important role in ensuring optimum strength development of silica-fume concrete. The water demand of silica-fume concrete is directly proportional to the amount of silica fume (used as a percentage replacement for Portland cement) if the slump of concrete is to be kept constant by increasing the water content rather than by using a superplasticizer. In such instances, the increase in the strength of silica-fume concrete over that of control concrete is largely offset by the higher water demand, especially for high silica-fume content at early ages. In general, the use of superplasticizer is a prerequisite to achieving proper dispersion of the silica fume in concrete and fully utilizing the strength potential of the fume. In fact, many important applications of silica fume in concrete depend strictly upon its utilization in conjunction with superplasticizing admixtures.

Silica-fume concretes have compressive strength development patterns that are generally different from those of Portland cement concretes. The strength development characteristics of these concretes are
somewhat similar to those of fly-ash concrete, except that the results of the pozzolanic reactions of the former are evident at earlier ages. This is due to the fact that silica fume is a very fine material with a very high amorphous silica content. The main contribution of silica fume to concrete strength development at normal temperatures takes place between the ages of about 3 and 28 days. The overall strength development patterns can vary according to concrete proportions and composition and are also affected by the curing conditions.

Carette and Malhotra (1992) reported investigations dealing with the short- and long-term strength development of silica-fume concrete under conditions of both continuous water curing and dry curing after an initial moist-curing period of 7 days. Their investigations covered superplasticized concretes incorporating 0 and 10% silica fume as a replacement by weight for Portland cement and water/cement + silica fume ratios ranging between 0.25 and 0.40. As expected, the major contributions of silica fume to the strength took place prior to 28 days; the largest gains in strength of the silica-fume concrete over the control concrete were recorded at the ages of 28 and 91 days, although this gain progressively diminished with age. For concretes with water/cement + silica fume ratios of 0.30 and 0.40, the gain largely disappeared at later ages. Under air-drying conditions, the strength development pattern was found to be significantly different from that of water-cured concretes up to the age of about 91 days; thereafter, however, air drying clearly had some adverse effect on the strength development of both types of concrete. The effect was generally more severe for silica-fume concrete, where some reduction in strength was recorded between the ages of 91 days and 3.5 years, especially for concretes with water/cement + silica fume ratios of 0.30 and 0.40. These trends of strength reduction have not yet been clearly explained, but they appear to stabilize at later ages and therefore are probably of little practical significance.

Curing temperatures have also been shown to affect significantly the strength development of silica-fume concrete. This aspect has been examined in some detail by several investigators in Scandinavia. In general, these investigations have indicated that the pozzolanic reaction of silica fume is very sensitive to temperature, and elevated-temperature curing has a greater strength-accelerating effect on silica-fume concrete than on comparable Portland cement concrete. The dosage of silica fume is obviously an important parameter influencing the compressive strength of silica-fume concrete. For general construction, the optimum dosage generally varies between 7 and 10%; however, in specialized situations, up to 15% silica fume has been incorporated successfully in concrete.

### 2.3.5.2 Young’s Modulus of Elasticity

Based on the data published by various investigators, there appears to be no significant differences between the Young’s modulus of elasticity ($E$) of concrete with and without silica fume. Malhotra et al. (1985) reported data on the Young’s modulus of elasticity of Portland cement–blast-furnace slag–silica-fume concrete. They found no significant difference between the $E$ values obtained at 28 days, regardless of the various percentages of silica fume and water/cementitious materials ratios.

### 2.3.5.3 Creep

The published data on the creep strain of silica-fume concrete are sparse; Bilodeau et al. (1989) reported an investigation on the mechanical properties, creep, and drying shrinkage of high-strength concretes incorporating fly ash, slag, and silica fume. The cementitious–material content of the concretes was about 350 kg/m³, and the water/cementitious material ratio was 0.22. In addition to the reference concrete, concretes with silica fume at 7 and 12% cement replacements, fly ash at 25% cement replacement, slag at 40% cement replacement, a combination of 7% silica fume and 25% fly ash, and 7% silica fume and 40% slag were investigated. Specimens of these concretes were subjected to creep loading after 35 days of moist curing and an applied stress equivalent to 35% of the compressive strength. After one year, the creep strains of the reference, 7% silica fume, and 12% silica fume concretes were $1505 \times 10^{-6}$, $713 \times 10^{-6}$, and $836 \times 10^{-6}$, respectively. For concrete with 7% silica fume and 40% slag, the creep strain measured was the lowest at $641 \times 10^{-6}$. The pore structure and minimal quantity of free water in concrete with the highest amount of supplementary materials could have resulted in these very low creep values, about 40% of the creep of the reference concrete.
2.3.5.4 Permeability
The incorporation of supplementary cementing materials such as fly ash, slag, silica fume, and natural pozzolans in concrete results in fine pore structure and changes to the paste-aggregate interface, leading to a decrease in permeability. This decrease is much higher in concretes incorporating silica fume, due to its high pozzolanicity. The filler and pozzolanic activity of the silica fume, as well as the virtual elimination of bleeding, improve the interfacial zone through pore refinement. Plante and Bilodeau (1989) reported that the addition of 8% silica fume significantly reduced the penetration of chloride ions into concrete. With increasing cementitious materials content and decreasing water/cementitious materials ratios, the chloride-ion penetration was reduced further. At a water/cement + silica fume ratio of 0.21 and 500 kg/m³ cement and 40 kg/m³ silica fume, the chloride-ion penetration was found to be 196 coulombs at 28 days, compared to 1246 C for the reference concrete. This reduction is primarily due to the refined pore structure and increased density of the matrix.

2.3.6 Durability Aspects
2.3.6.1 Carbonation
Silica fume, like other pozzolanic materials, reduces the Ca(OH)₂ content of the concrete, and this promotes a faster rate of carbonation. On the other hand, this effect may be offset by the more impermeable nature of silica-fume concrete, which tends to impede the ingress of CO₂ into concrete. The net effect can be somewhat variable, as it depends on various factors such as silica-fume content, water/cementitious materials ratio, and curing conditions, all of which can have a determinant influence on the ultimate Ca(OH)₂ content and permeability of the concrete. Vennesland and Gjørv (1983) reported that using up to 20% silica fume as an addition to cement in concrete, in combination with the use of a plasticizer, reduced the rate of carbonation. The concrete specimens were initially moist cured for a period of 7 days prior to air storage at 60% relative humidity. Carette and Malhotra (1992) compared the rate of carbonation of silica-fume concrete with that of reference Portland cement concrete up to the age of 3.5 years. The test specimens had been initially moist cured for 7 days before being stored under ambient room drying conditions. At a water/cementitious materials ratio of 0.25, they found that all concretes remained free of any noticeable carbonation during a 3.5-year period, whereas at a water/cement + silica fume ratio of 0.40, all specimens exhibited signs of carbonation, the effect being slightly more marked for the silica-fume concrete. In general, however, it is agreed that carbonation is not a problem in adequately cured, high-quality, low water/cement ratio concrete, and this also applies to silica-fume concrete.

2.3.6.2 Chemical Resistance
Chemical attack on concrete causes destructive expansion and decomposition of the cement paste, leading to severe deterioration. A permeating solvent as innocuous as water can result in the leaching of calcium hydroxide liberated from the hydration of cement. The ingress of chemicals and acids into concrete allows them to react with calcium hydroxide to form water-soluble salts that leach out of concrete, increasing the permeability of concrete and allowing further ingress of chemicals. Sulfates react with calcium hydroxide, forming ettringite, which causes expansion and cracking of the concrete. Silica-fume concretes have better resistance to chemicals than comparable Portland cement concretes due to the depletion of calcium hydroxide liberated during the hydration of Portland cement by means of pozzolanic reaction with silica fume, which thus reduces the amount of lime available for leaching, and also due to the decrease in permeability resulting from the refined pore structure of the mortar phase of the concrete.

Mehta (1985) compared the chemical resistance of low water/cement ratio (0.33 to 0.35) concretes exposed to solutions of 1% hydrochloric acid, 1% sulfuric acid, 1% lactic acid, 5% acetic acid, 5% ammonium sulfate, and 5% sodium sulfate. Specimens of a reference concrete, latex-modified concrete, and silica-fume concrete with 15% silica fume by weight of cement were used, and the criteria for failure
was 25% weight loss when fully submerged in the above solutions. The investigation showed that concrete incorporating silica fume better resisted chemical attacks than did the other two types of concrete. The only exception was the silica-fume concrete specimens immersed in ammonium sulfate solution which performed poorly. This was attributed to the ability of the ammonium salts to decompose the calcium silicate hydrate in the hydrated cement paste.

### 2.3.6.3 Freezing and Thawing Resistance

Extensive laboratory and field experience in Canada and the United States has shown that, for satisfactory performance of concrete under repeated cycles of freezing and thawing, the cement paste should be protected by incorporating air bubbles, 10 to 100 µm in size, using an air-entraining admixture. Briefly, the most important parameters concerning the entrainment of air in concrete are the air content, bubble-spacing factor, and specific surface. For satisfactory freezing and thawing resistance, it is recommended that air-entrained concrete should have bubble-spacing factor (L) values of less than 200 µm and specific surface (α) greater than 24 mm⁻¹. Usually, fresh Portland cement concrete incorporating between 4 to 7% entrained air by volume will yield the above values of L and α.

Several investigators have performed studies on the freezing and thawing resistance of silica-fume concrete. These include, among others, Sorensen (1983), Gjov (1983), Carette and Malhotra (1983), Malhotra (1984), Yamato et al. (1986), Hooton (1987b), Hammer and Sellevold (1990), Virtanen (1985), Pigeon et al. (1986), and Batrakov et al. (1992). In one CANMET investigation, the freezing and thawing resistance of non-air-entrained and air-entrained concrete incorporating various percentages of silica fume was compared (Malhotra, 1984). The study led to the following conclusions:

- **Non-air-entrained concrete**: Non-air-entrained concrete, regardless of the water/cement + silica fume ratio and irrespective of the amount of condensed silica fume, shows very low durability factors and excessive expansion when tested in accordance with ASTM C 666 (Procedure A or B). The concrete appears to show somewhat increasing distress with increasing amounts of fume; therefore, the use of non-air-entrained condensed silica-fume concrete is not recommended when it is to be subjected to repeated cycles of freezing and thawing.

- **Air-entrained concrete**: Air-entrained concrete, regardless of the water/cement + silica fume ratio and containing up to 15% condensed silica fume as partial replacement for cement, performs satisfactorily when tested in accordance with ASTM C 666 (Procedures A and B). However, concrete incorporating 30% of the fume and a water/cement + silica fume ratio of 0.42 performs very poorly (durability factors less than 10), regardless of the procedure used. This is probably due to the fact that the hardened concrete has high values of L, or it might be due to the high amount of condensed silica fume in concrete, resulting in a very dense cement matrix system that, in turn, might adversely affect the movement of water. It is difficult to entrain more than 5% air in the above type of concrete, and this amount of air may or may not provide satisfactory L values in hardened concrete for durability purposes. The users are therefore asked to exercise caution when using high percentages of condensed silica fume as replacement for Portland cement in concretes with water/cement + silica fume ratios of the order of 0.40 if these concretes are to be subjected to repeated cycles of freezing and thawing.

### 2.3.6.4 Frost Resistance in the Presence of Deicing Salts

Limited published data are available on the deicing salt scaling resistance of silica-fume concrete. Gagne et al. (1990) reported that the frost resistance of concrete incorporating 6% silica fume as an addition to cement is satisfactory in the procedure of deicing salt scaling tests (ASTM C 672). This was true for both air-entrained and non-air-entrained concrete. The water/cement + silica fume ratio of the concretes ranged from 0.23 to 0.30, and the concretes were air dried for 28 days before being subjected to the deicing salt scaling test. Using the ASTM C 672 tests, Bilodeau and Carette (1989) investigated the deicing salt scaling resistance of Portland cement concrete and concretes incorporating 8% silica fume.
as replacement for cement. In their investigation, superplasticized and nonsuperplasticized concretes were made, with water/cementitious materials ratios ranging from 0.40 to 0.65, all having adequate air-void parameters. They reported that, in general, all concretes performed satisfactorily under the action of deicing salts, although the silica-fume concrete exhibited a slightly inferior performance when compared to that of Portland cement concrete. In particular, silica-fume concrete with a water/cement + silica fume ratio of 0.60 showed appreciable weight loss after 50 cycles.

2.3.6.5 Role of Silica Fume in Reducing Expansion Due to Alkali–Silica Reaction

A number of laboratory investigations have indicated that silica fume, like other pozzolans, is effective in reducing the above-mentioned expansions due to alkali-silica reactions; however, the percentage of silica fume to be incorporated into concrete would depend on the type of reactive aggregate, the exposure conditions, the alkali and silica contents, the silica fume used, the type of cement used, and the water/cementitious materials ratio of the mixture. Published data indicate that the percentage replacement of cement by silica fume may range from about 10 to 15% (Durand, 1991). CANMET-funded studies have indicated that silica fume is not effective in controlling expansions due to alkali-carbonate reactions (Chen and Sunderman, 1990). At present, no significant well-documented data are available as to the long-term effectiveness of silica fume in controlling alkali–silica expansions in actual field structures. Based on current knowledge, it is recommended that those contemplating the use of silica fume to control expansion due to alkali–silica reactions perform accelerated tests in the laboratory, using the materials to be employed on a job site, to determine the percentage of silica fume to be used as replacement for cement.

2.4 Highly Reactive Metakaolin

Highly reactive metakaolin has recently become available as a very active pozzolanic material for use in concrete. Unlike fly ash, slag, or silica fume, this material is not a byproduct but is manufactured from a high-purity kaolin clay by calcination at temperatures in the region of 700 to 800°C (Caldarone et al., 1994). The material, ground to an average particle size of 1 to 2 µm, is white in color. In 1994, a plant was commissioned in Atlanta to produce the material on a commercial scale.

2.4.1 Chemical and Mineralogical Composition

Unlike silica fume, which contains more than 85% SiO₂, highly reactive metakaolin contains equal proportions of SiO₂ and Al₂O₃ by mass. A typical oxide analysis is given below:

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Alkalis</th>
<th>Loss on Ignition</th>
</tr>
</thead>
<tbody>
<tr>
<td>51</td>
<td>40</td>
<td>1</td>
<td>2</td>
<td>0.1</td>
<td>0.5</td>
<td>2</td>
</tr>
</tbody>
</table>

The highly reactive metakaolin derives its reactivity from the combination of two factors—namely, a totally noncrystalline structure and a high surface area. As far as mineralogical character is concerned, like silica fume, metakaolin is composed essentially of noncrystalline aluminosilicate (Si-Al-O) phase. Occasionally, a small amount of crystalline impurities may be present—that is, 1 to 2% of quartz, feldspar, or titania. The material has a specific surface of about 20 m²/g and a specific gravity of 2.5.

2.4.2 Properties of Fresh Concrete

According to the limited published data, the initial and final setting time of concrete incorporating 10% of metakaolin by mass are comparable to those of control concrete and concrete incorporating
Mineral Admixtures

2.4.3 Mechanical Properties of Hardened Concrete

2.4.3.1 Strength Development

Table 2.14 gives some data on strength development and Young’s modulus for concrete made with metakaolin; also, data on the control concrete and silica fume are included for comparison purposes. The faster strength development of the metakaolin concrete at early ages as compared with the silica-fume concrete is probably due to the faster rate of hydration, as discussed earlier.

2.4.3.2 Drying Shrinkage

Zhang and Malhotra (1995) investigated the drying shrinkage of concrete incorporating metakaolin; the data are shown in Figure 2.17, together with data for control and silica-fume concrete. The concretes were exposed to drying shrinkage after 7 days of initial curing in lime-saturated water. The metakaolin concrete had a lower drying shrinkage strain compared with that of the control and silica-fume concrete. After 112 days of drying at a relative humidity of 50%, the metakaolin concrete had a drying shrinkage strain of $427 \times 10^{-6}$ compared with $596 \times 10^{-6}$ for the control concrete.

2.4.4 Durability Aspects of Hardened Concrete

Air-entrained concrete incorporating 10% metakaolin by mass of cement has high resistance to the penetration of chloride ions and excellent durability in regard to repeated cycles of freezing and thawing. Table 2.15 and Table 2.16 show some test results on these above aspects of durability (Zhang and Malhotra, 1995). Limited data on the deicing salt scaling resistance of the metakaolin concrete indicates that its performance in the ASTM deicing salt scaling test (ASTM C 672) is comparable to that of silica-fume concrete but somewhat inferior to that of plain Portland cement concrete.
## TABLE 2.14 Mechanical Properties of Hardened Concrete

<table>
<thead>
<tr>
<th>Mix</th>
<th>MK Content (%)</th>
<th>Silica Fume Content (%)</th>
<th>W/C or W/(C + MK)</th>
<th>Unit Weight (kg/m³)</th>
<th>1 day Compressivea</th>
<th>3 days Compressive</th>
<th>7 days Compressive</th>
<th>28 days Compressive</th>
<th>90 days Compressive</th>
<th>180 days Compressive</th>
<th>28 days Flexurae</th>
<th>28 days Flexura</th>
<th>28 days E Modulus (GPa)d</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>0</td>
<td>0</td>
<td>0.40</td>
<td>2350</td>
<td>20.9</td>
<td>25.5</td>
<td>28.9</td>
<td>36.4</td>
<td>42.5</td>
<td>44.2</td>
<td>2.7</td>
<td>6.3</td>
<td>29.6</td>
</tr>
<tr>
<td>MK10</td>
<td>10</td>
<td>—</td>
<td>0.40</td>
<td>2330</td>
<td>25.0</td>
<td>32.9</td>
<td>37.9</td>
<td>39.9</td>
<td>43.0</td>
<td>46.2</td>
<td>3.1</td>
<td>7.4</td>
<td>32.0</td>
</tr>
<tr>
<td>SF10</td>
<td>—</td>
<td>10</td>
<td>0.40</td>
<td>2320</td>
<td>23.2</td>
<td>28.6</td>
<td>34.7</td>
<td>44.4</td>
<td>48.0</td>
<td>50.2</td>
<td>2.8</td>
<td>7.0</td>
<td>31.1</td>
</tr>
</tbody>
</table>

a Average of three 102 × 203-mm cylinders.
b Average of two 152 × 305-mm cylinders.
c Average of two 102 × 76 × 406-mm prims.
d Average of two 152 × 305-mm cylinders.

Note: MK, metakaolin; W/C, water/cementitious material ratio; SF, silica fume.


![Figure 2.17: Drying shrinkage of control silica fume and metakaolin concrete.](image-url)
### TABLE 2.15 Resistance of Concrete to Chloride-Ion Penetration

<table>
<thead>
<tr>
<th>Mix</th>
<th>Type of Concrete</th>
<th>W/C or W/(C + MK) or W/(C + SF)</th>
<th>Unit Weight (kg/m³)</th>
<th>28-Day Compressive Strength (MPa)</th>
<th>28-Day Resistance to Chloride-Ion Penetration (coulombs)</th>
<th>90-Day Resistance to Chloride-Ion Penetration (coulombs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO-D Control</td>
<td>0.40</td>
<td>2320</td>
<td>36.5</td>
<td>3175</td>
<td>1875</td>
<td></td>
</tr>
<tr>
<td>MK10-D 10% MK</td>
<td>0.40</td>
<td>2330</td>
<td>37.9</td>
<td>390</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>SF10-D 10% SF</td>
<td>0.40</td>
<td>2310</td>
<td>42.8</td>
<td>410</td>
<td>360</td>
<td></td>
</tr>
</tbody>
</table>

*Note: W/C, water/cementitious materials ratio; MK, metakaolin; SF, silica fume.*


### TABLE 2.16 Summary of Test Results after 300 Cycles of Freezing and Thawing

<table>
<thead>
<tr>
<th>Mix</th>
<th>Type of Concrete</th>
<th>28-Day Compressive Strength (MPa)</th>
<th>Air Content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fresh Concrete (%)</td>
</tr>
<tr>
<td>CO-D Control</td>
<td>36.5</td>
<td>5.8</td>
<td>6.6</td>
</tr>
<tr>
<td>MK10-D 10% MK</td>
<td>37.9</td>
<td>5.1</td>
<td>4.9</td>
</tr>
<tr>
<td>SF10-D 10% SF</td>
<td>42.8</td>
<td>5.8</td>
<td>5.0</td>
</tr>
</tbody>
</table>

*Note: L, length; PV, pulse velocity; RF, resonant frequency; W, weight.*

References


Davis, R.E. 1954. Pozzolanic Materials with Special Reference to Their Use in Concrete Pipe, Technical Memo. American Concrete Pipe Association, Irving, TX.


Poole, A.B. 1981. Alkali-Carbonate Reactions in Concrete, paper presented at the 5th International Conference on Alkali–Aggregate Reaction in Concrete, March 30–April 3, Cape Town, South Africa.


(a) Scanning electron micrograph of a polymer concrete fracture surface. (Photograph courtesy of Edward G. Nawy, Rutgers University.)  (b) Chemical admixtures analysis. (Photograph courtesy of Portland Cement Association, Skokie, IL.)