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# Pozzolans and Supplementary Cementitious Materials

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## INTRODUCTION

Pozzolans and supplementary cementitious materials (SCMs), either natural or artificial, are often used as a cement replacement or as an enhancement in concrete. Physical and chemical properties of a material determine their pozzolanic or cementitious properties. Table 1 lists these characteristics for the major pozzolans and SCMs. Pozzolans react with the calcium hydroxide liberated as concrete hardens, forming compounds with cementitious properties (American Geological Institute 1997). The pozzolanic and cementitious properties along with other characteristics make these materials attractive partial substitutes for portland cement in concrete applications or interground with portland cement clinker to create blended cements. Pozzolans can counteract adverse effects of undesirable aggregates used in concretes and help to create a concrete highly resistant to penetration and corrosion.

For centuries, many of the natural pozzolans have been used in concrete or cement. With increasing fuel costs and environmental concerns over the carbon dioxide (CO<sub>2</sub>) emissions associated with the production of portland cement clinker, several pozzolanic by-products of industrial processes are gaining acceptance as admixtures to concrete products. Table 2 lists the major pozzolans and SCMs with production, consumption, and price, where available.

## CLASSIFICATION

Pozzolans are siliceous or siliceous and aluminous materials that alone possess little or no cementitious value, but will, in a finely divided form and in the presence of water, chemically react with calcium hydroxide, such as found in cement at ordinary temperatures, to form compounds possessing hydraulic cementitious properties. SCMs are finely divided and noncrystalline or poorly crystalline materials similar to pozzolans that possess latent cementing properties that are activated in the presence of portland cement and water (Malhotra and Mehta 1996). Pozzolans and SCMs are mineral admixtures when added to concrete or blended cements. (For a complete discussion of cement, refer to the Cement and Cement Raw Materials chapter.)

### Pozzolans

Pozzolans fall into two categories, either natural or artificial, depending on their provenance. Natural pozzolans are either raw or calcined natural materials—such as volcanic ash, opaline chert, tuff, some shale, and some diatomaceous earth—that have pozzolanic properties (American Concrete Institute 2000). The amount of

amorphous or unstructured material often determines the reactivity of the natural pozzolans. There are three categories of natural pozzolans: (1) volcanic ash, called tuff when indurated, in which the amorphous constituent is a glass produced by rapid cooling of magma; (2) those derived from rocks or earth in which the silica is mainly opal, and diatomaceous earth; and (3) some clays and shales. Volcanic glass has a disordered structure because of the relatively quick cooling time and tends to have a porous texture created by escaping gases. Hydrothermally altered volcanic glass can become zeolitic, and when finely ground, zeolitic tuffs become reactive with lime. Deposits of trachyte tuff from a volcanic eruption near the town of Pozzuoli (Italy) are the source of the term *pozzolan*. Romans used this material with lime to form cement for many of their large building projects. Today, volcanic tuffs and pumicite are still used as pozzolans throughout the world and are often referred to as *pozzolana* in the literature.

Moler is a Tertiary-age deposit of diatomaceous earth with significant amounts of clay. These deposits are on the island west of Limfjord, Denmark. Diatomaceous earth is amorphous hydrated silica derived from skeletal remains of diatoms, which are tiny aquatic plants. High-purity diatomaceous earth deposits are pozzolanic, but often they contain large amounts of clays. Depending on the clay content of the deposit, calcination or grinding may be necessary for use as a pozzolan (Flechsigt 1990). Found in France, gaize is a soft, porous, highly siliceous sedimentary rock consisting mainly of opal. Before gaize can be used as a pozzolan, it is calcined at 900°C (American Concrete Institute 2000). Gaize and moler are two examples of natural pozzolans used for their pozzolanic properties. A typical use of moler and gaize is in cement subject to seawater attack.

Although clay and shale are naturally occurring, calcination enhances their pozzolanic characteristics. Calcining is necessary to destroy existing crystal structure and to form an amorphous or disordered aluminosilicate structure. As an example, metakaolin, derived from high-purity kaolin that undergoes low-temperature calcination and grinding to a fine particle size, is a highly reactive product having excellent pozzolanic properties. Not all clays and shales, however, are suitable as pozzolans, even when calcined.

### Artificial Pozzolans

Artificial pozzolans used today are mostly from by-product materials. Silica fume is a by-product of the reduction of high-purity quartz with coal in electric arc furnaces in the production

**Table 1. Physical and chemical properties of pozzolans and SCMs**

Properties	Silica Fume	Ground, Granulated Blast Furnace Slag (GGBFS)	Fly Ash (Class C and Class F)	Calcined Clay, Shale	Diatomite	Rice Hull Ash
Physical	Very fine, tiny spheres (0.1 μm), high surface area—acts as filler	Angular, ground to <45 μm	Fine-grained, spherical, <45 μm	<45 μm rough texture because of grinding	Very fine-grained (1 μm). Porous skeletal remains of single-cell plants	Highly cellular, creating large surface area, >45 μm
Chemical	Amorphous silica	Silicate glass, high in calcium	Aluminosilicate	Aluminosilicate glass; may contain quartz, feldspar, mica	Amorphous silica	Pure silica, noncrystalline

Adapted from Malhotra and Mehta 1996; Lohtia and Joshi 1995.

**Table 2. Statistics for major pozzolans and SCMs in the United States as raw materials**

Pozzolan or SCMs	Consumed as Clinker (2003), kt	Consumed as Blended Cement (2003), kt	Price, US\$	Production, kt
Diatomite, and other microcrystalline silica (silica fume)	129	49	Diatomite, † 970/t	Diatomite, 0.003
Burned clays and shales, other natural pozzolans	na <sup>‡</sup>	25	na	na
Pumice and pumicite <sup>§</sup>			27/t	42
Fly ash	2,250	39	18–41/t	63,682
Granulated blast furnace slag**	17	333	60/t (ground) 30/t (unground)	3,800 <sup>††</sup>

Adapted from van Oss 2003a, 2003b, 2004; Bolen 2003; ACAA 2004a, 2004b.

\* Material used as raw feed; does not have pozzolanic or cementitious properties.

† Includes absorbents and silicate admixtures (Dolley 2003).

‡ na = not available.

§ Use listed as concrete admixture and aggregate combined (Bolen 2003).

\*\* Includes both ground and unground material.

†† van Oss estimates GGBFS sales 20% of total slag market (van Oss 2004).

of ferrosilicon alloys and silicon metal. The silicon dioxide (SiO<sub>2</sub>) that vaporizes during this process condenses to very fine (0.1-μm diameter) noncrystalline spheres (Malhotra and Mehta 1996). Use of these pozzolanic spheres in blended cement or as a mineral admixture produces a high-strength concrete. Rice hull (or husk) ash, when burned in the production of electricity or milling, produces a high-silica ash. This ash has potential as a pozzolanic admixture in concrete.

Fly ash is a by-product of burning finely ground coal either for industrial application or in the production of electricity. The largest producers of fly ash are electricity-generating stations. The amount of fly ash available is greater than for any of the other by-product materials used in cement or concrete. The composition of fly ash is dependent on the composition of the coal feed and the efficiency of the combustion process. Most fly ash particles are spherical and glassy, and possess pozzolanic properties.

### Supplementary Cementitious Materials

SCMs include ground, granulated blast furnace slag (GGBFS) and high-calcium fly ash. Blast furnace slag, a by-product of pig-iron production, when rapidly cooled yields a granulated product that is high in calcium content (35%–40%; Malhotra and Mehta 1996). GGBFS mixed with portland cement has hydraulic properties, creating cement that will harden under water.

### Other Considerations

With the exception of silica fume, natural pozzolans and industrial by-products generally cost less than portland cement. The cost savings and beneficial properties of pozzolans and SCMs have increased the use of these products. Most natural rock material used as pozzolans undergo some processing, either grinding or calcination, to improve their reactivity. The percentage of amorphous

**Table 3. Natural and artificial pozzolans and SCMs classified by reactivity**

Degree of Reactivity	Material
Cementitious and pozzolanic	GGBFS (cementitious) High-calcium fly ash (cementitious and pozzolanic)
Highly active pozzolans	Silica fume Rice hull (or husk) ash from electrical generation
Normal pozzolans	Low-calcium fly ash Natural pozzolans—clay, shale, diatomaceous earth, opaline cherts
Weak to very weak pozzolans	Slowly cooled blast furnace slag Bottom ash Boiler slag Field burnt rice hull ash

Adapted from Malhotra and Mehta 1996.

material in the pozzolan often determines the reactivity of a natural pozzolan. Many of the by-products of manufacturing or electrical generation have acquired pozzolanic or cementitious characteristics during these mechanized processes, and for a few, grinding enhances these properties. The degree of pozzolanic reactivity can vary depending on the method of processing. Rice hulls burned in a furnace reach higher temperatures than those burned in the rice fields and yield a more reactive product. The quality of the original feed, or the combustion and cooling method, can also determine the pozzolanic or cementitious properties (Table 3).

## NATURAL POZZOLANS

### Industry Structure

Cement companies or businesses specializing in mineral admixtures mine, process, and market natural pozzolans. Depending on the raw material, processing may include grinding, drying, purifying, and calcining. Many of the rocks or minerals used for their pozzolanic properties also have other uses such as lightweight aggregate, soil amendments, filters, or fillers. The product sold as a pozzolan can be a minor fraction of the total end use. In the United States, using natural pozzolans is economic when locally available for bulk concrete construction or in the manufacturing of concrete products. The use of natural pozzolans is more widespread in Europe and Asia than in the United States (American Concrete Institute 2000); the four largest producers of natural pozzolans are Italy, Chile, Greece, and Cameroon (Table 4). Home construction techniques in Europe use less gypsum sheetrock and more stone and concrete than in North America. Prefabricated lightweight concrete walls using pumice as a cement admixture are shipped to the construction site. Pumice as a lightweight pozzolan works well for the European style of construction (Bolen 2003).

### Raw Materials and Processing

Natural pozzolans such as calcined siliceous clay and shale, diatomaceous earth or diatomite, and volcanic tuff can be used either as a mineral admixture in concrete or interground with clinker to create blended cements. Most of these raw materials have a variety of applications. The respective commodity chapters in this volume provide more detail on the mining and processing of these materials. Clay, shale, volcanic tuffs or pumicite, and diatomite are commonly quarried with rippers, dozers, and front-end loaders, and then transported to a processing plant. Most of the pumicite mined in the United States comes from western states, including Arizona, California, Idaho, Kansas, Nevada, New Mexico, and Oregon (Bolen 2004). California and Nevada have large diatomite deposits. One location in Nevada is a combination of diatomaceous earth and a dacitic pumicite. The diatomite or diatomaceous earth is processed near the mine site because of the expense of transporting a raw material with high water content. This raw material goes through a series of crushing, drying, and comminution steps. Calcining in a rotary kiln and classifying by particle size with heated air are common processes used to produce a pozzolanic material from diatomite (Dolley 2002).

Water processing of kaolin removes impurities to lighten color and control particle size. Calcining the purified material at 600° to 900°C results in dehydroxylation and a disordered and essentially amorphous state. The product is then pulverized to 1–2- $\mu$ m diameter creating a highly reactive pozzolanic product called metakaolin. The use of metakaolin as a mineral admixture has been growing since the mid-1980s (American Concrete Institute 2000). Heating other siliceous clays and shales at 700°–800°C makes them reactive by destroying the crystalline structure of the clays and other minerals in shales. Heating increases the pozzolanic reactivity of zeolites as well (Virta 2002).

### Specifications

The American Society for Testing and Materials (ASTM) C311-02 (2003a) specifies the methods for testing raw or calcined natural pozzolans and fly ash for use in portland cement concrete. ASTM C618-03 (2003b) outlines the specifications for use in concrete of natural pozzolans and fly ash, dividing these into Class N for natural pozzolans and Class C and F for fly ash. Comparing the requirements for natural pozzolans to the fly ash classifications,

Table 4. World production of pozzolan in 2003

Country	Commodity	Production, kt
Algeria	Pozzolan	400.0
Austria	Trass	5.0
Cameroon	Pozzolan	600.0
Cape Verde*	Pozzolan	1.0
Chile	Pumice and pozzolan	830.0
Ecuador	Pozzolan	23.0
France*	Pozzolan and lapilli	450.0
Greece*	Pozzolan	750.0
Honduras	Pozzolan	190.0
Italy*	Pozzolan	4,000.0
Saudi Arabia*	Pozzolan	160.0
Tanzania	Pozzolan materials	43.3
Uganda	Pozzolan materials	12.4
<b>Total pozzolan production†</b>		<b>6,180.0</b>

Adapted from Bolen 2003.

\* Estimated.

† Total is rounded; may not add to totals shown. Total is taken directly from Table 4 of Bolen 2003.

there are few differences between low-calcium fly ash (Class F) and natural pozzolans (Class N). The major differences are (1) the maximum loss on ignition (LOI), or amount of unburned carbon, is greater for natural pozzolans; and (2) the maximum water requirement is greater for natural pozzolans (see section on Fly Ash in this chapter for specifications table). ASTM specifications are not the only standards used in the United States or the world. Almost every country has a different set of specifications for pozzolans used in concrete. Within the United States, each state has its own specifications for use of pozzolans in portland cement concrete for road construction.

### Finished Product Uses

A major use of natural pozzolans is in mass concrete, such as dams, where there are large pours and the risk of thermal cracking from the heat produced from the chemical reactions during hydration of portland cement minerals. For example, the Los Angeles Aqueduct (rhyolitic pumicite), the Glen Canyon Dam (pumice; Figure 1), and Flaming Gorge Dam were all constructed using natural pozzolans (American Concrete Institute 2000). Adding natural pozzolans slows down the cementation process, reducing the temperature. Many of the natural pozzolans also improve the workability of the concrete pour, which is beneficial in massive concrete structures. Grouts and mortars are another market for natural pozzolans.

### Finished Product Marketing

Markets for natural pozzolans are in blended cements, intergrinding the pozzolan with the portland cement clinker, and as a mineral admixture for concrete. Mining a deposit for a particular project that is nearby and closing the pit when the project is completed is a typical strategy for using natural pozzolans. Natural pozzolans that do not require calcining are the most attractive for marketing beyond a local market. Calcined clay and shale tend to be marketed for blended cements and therefore are used directly by the cement companies. Cement companies have a local market area, because the transportation costs are a limiting factor. Companies mining and marketing diatomite and pumicites as pozzolans often sell these materials as mineral admixtures.

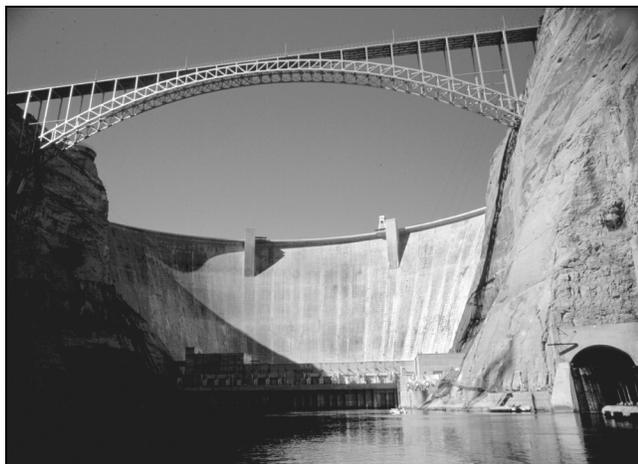


Photo by L. Greer Price.

**Figure 1.** Glen Canyon Dam (concrete in dam was made with pumice from Arizona, used as pozzolan admixture)

## ARTIFICIAL POZZOLANS AND SCMS

### Industry Structure

Prevalent use of by-products in the cement and concrete industries is a recent development, particularly in the United States. Using by-products reduces the need for portland cement and uses a product created from expending energy to create another product or electricity. When the by-products are not used, they must be disposed of, which has environmental implications as well. Market barriers for many of these by-products include the wide variety of state regulations regarding their use. If a marketer is transporting the material from one state to another, problems can arise because of the lack of standardization of regulations.

For pozzolanic or cementitious materials such as GGBFS, silica fume, and fly ash, the companies producing the iron or energy generally contract with a mineral admixture marketer or slag processor to handle their by-products. Trade associations such as the Slag Cement Association, the Silica Fume Association, and the American Coal Ash Association (ACAA) represent marketers of these products. These associations promote the product by providing information and technical reports to the buyers and marketers. A discussion for each of the major by-products being used today as a pozzolan or SCM follows. Included is a brief discussion of rice hull ash, although it is not marketed to any extent in the United States.

### Silica Fume

Silica fume is a by-product of producing silicon metal or ferrosilicon alloys by reduction of high-purity quartz with coal or coke and wood chips in an electric arc furnace (Figure 2). The silica fume is condensed from gases escaping from the furnace. During the production of silicon metals and alloys, baghouse filters collect the silica fume from the furnace gases. The gas has a very high content of amorphous  $\text{SiO}_2$ . Depending on the process, silica fume is 94%–98%  $\text{SiO}_2$  from silicon production and 85%–90%  $\text{SiO}_2$  from ferrosilicon production (Harben 2002). Silica fume is a very fine, gray powder consisting of glassy spherical particles in the size range of 0.1–0.2  $\mu\text{m}$  with surface areas of 20–23  $\text{m}^2/\text{g}$ . As a comparison, fly ash is typically less than 45  $\mu\text{m}$  in diameter. The chemical composition, size, and surface area of these particles create a



Courtesy of Silica Fume Association.

**Figure 2.** A silicon metal furnace

**Table 5.** ASTM C1240-03 chemical and physical requirements for silica fume as a mineral admixture

Chemical Requirements	
$\text{SiO}_2$ , minimum	85.0%
Moisture content, maximum	3.0%
LOI, maximum	6.0%
Physical Requirements	
Oversize:	
Retained on 45- $\mu\text{m}$ (325) sieve, maximum	10%
Retained on 45- $\mu\text{m}$ (325) sieve, maximum percentage variation from average*	5%
Accelerated pozzolanic strength activity index:†	
With portland cement at 7 days, minimum percentage of control	105%
Specific surface, minimum	15 $\text{m}^2/\text{g}$

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\* Average is determined by the average of 10 preceding tests or all preceding tests if less than 10.

† A measure of the reactivity (not compressive strength) of given silica fume with a given cement and may vary with the source of both silica fume and cement.

very reactive pozzolanic material. The limited availability of silica fume increases the cost of the finished concrete when added to portland cement, limiting its use to projects where cost is not a primary consideration and the improved performance of silica fume, such as high compressive strength and increased resistance to sulfate attack, are required in the concrete application.

**Specifications.** ASTM C1240-03 (2003c) outlines the standards for silica fume as a mineral admixture. Table 5 lists the chemical and physical requirements for silica fume. A minimum 85%  $\text{SiO}_2$  is required with a maximum of 6% LOI. Physical requirements are concerned with the size and strength when added to mortar. The ASTM requirements also include optional physical requirements for air-entrained concrete, reactivity with alkalis, and sulfate resistance expansion.

Silica fume is the one mineral admixture not considered a lower-cost partial replacement for portland cement in concrete; the cost of silica fume is equal to or greater than portland cement. Using silica fume for its high reactivity creates a high-compressive-strength product that is very durable and can reduce the amount of reinforcing steel required in concrete applications.

**Finished Product Uses and Marketing.** Concrete admixture suppliers market silica fume. Silica fume in the United States comes from a few producers; the Silica Fume Association lists five member producers. Silica fume products include a fine powder (Figure 3), a densified form, a slurry form with water, or a pelletized form for intergrinding with portland cement. The as-produced fine powder is difficult to handle and is generally used in bagged products such as grouts or repair mortars (Silica Fume Association 2004). Densified silica fume is in an agglomerated form created by aerating the as-produced material and creating an electrostatic charge between the particles. Bulk tankers can transport densified silica fume to concrete batch plants. Unless densified, silica fume is difficult to intermix to form blended cement or to use with portland cement to make concrete, because it tends to float on the surface of the mixture (H.G. van Oss, personal communication). Bulk tankers transport silica fume slurry to storage tanks at construction sites. Often another level of regional supplier repackages the material for the end user in their area. Silica fume is a value-added product in the United States for making high-compressive-strength concrete used in high-rise buildings, parking structures, bridge decks, and girders. In Canada and Europe, silica fume is more often interground with portland cement to create blended cements with high compressive strength, and the cost of the material is much less in this form (Kuennen 1996). Other uses of silica fume include shotcrete mixtures, grouts, concrete blocks, and bricks.

#### **Ground, Granulated Blast Furnace Slag**

The iron-making process creates slag during a high-temperature reaction with carbon-reducing agents and fluxes. The impurities of the iron oxide ores and fluxing agents combine to form a liquid silicate melt, called slag, that floats on top of the liquid crude iron. The slag is removed or tapped from the blast furnaces separately. There are several methods of cooling the slag, but quickly quenching the slag in water creates sand-sized particles of glass, granulated blast furnace slag (GBFS; Figure 4), and grinding of this granulated slag increases the surface area and the reactivity of the GGBFS product.

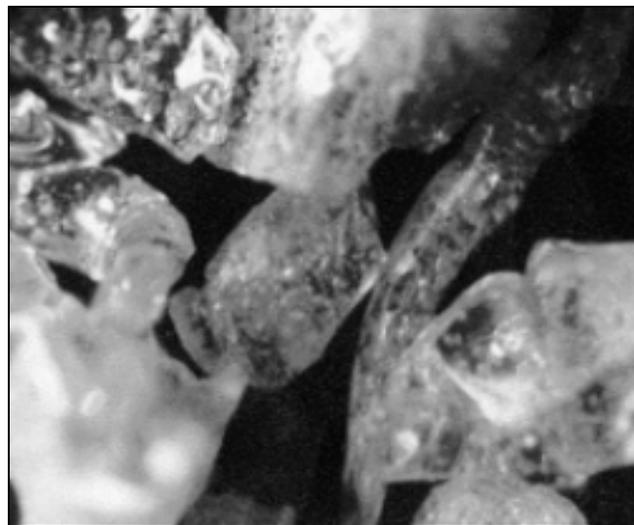
**Raw Materials and Processing.** The amount of slag produced from a blast furnace is dependent on the chemistry of the raw material, and the grade of the iron ore is the major factor. Ore feed of 60%–66% grade iron in a blast furnace will yield about 0.25 to 0.3 t of blast furnace slag per ton of crude iron produced (van Oss 2003b). Lower grades of ore will yield greater amounts of slag. Blast furnace slags are typically composed of  $\text{SiO}_2$  (33%–36%),  $\text{CaO}$  (calcium oxide, 37%–40%),  $\text{Al}_2\text{O}_3$  (aluminum oxide, 7%–9%),  $\text{Fe}_2\text{O}_3$  (iron oxide, 1%–10%), and  $\text{MgO}$  (periclase 10%–11%). Of the by-products, the chemical composition of slag is closest to that of portland cement; however, slag has a higher silica and lower calcium content (Lohtia and Joshi 1995).

The quenching or cooling process for the slag determines whether the material will be reactive. To form GBFS, the slag is removed from the furnace and rapidly quenched with water in a granulator. The result is glassy granules (Figure 5) that are then dried and ground or interground with portland cement to create blended cement, or the GGBFS is marketed as a mineral admixture for concrete. GGBFS is a hydraulic cement admixture that works with portland cement to create high-strength concrete (Slag Cement Association 2003). Quickly cooled slag using water or steam to



Courtesy of Silica Fume Association.

**Figure 3.** Silica fume powder after collection and processing



Courtesy of Slag Cement Association.

**Figure 4.** Microscopic view of GBFS



Courtesy of Slag Cement Association.

**Figure 5.** Unground GBFS

**Table 6. Physical and chemical requirements for GGBFS from ASTM C989-99**

Physical Requirements		
Fineness: Amount retained when wet screened on a 45- $\mu\text{m}$ (325) sieve, maximum		20%
Air content of slag mortar, maximum		12%
Slag activity index,* minimum	Average of Five Consecutive Samples, %	Any Individual Sample, %
7-day index:		
Grade 80	NV†	NV
Grade 100	75	70
Grade 120	95	90
28-day index:		
Grade 80	75	70
Grade 100	95	90
Grade 120	115	110
Chemical Requirements		
Sulfide sulfur (S), maximum		2.5%
Sulfate ion reported as $\text{SO}_3$ , maximum		4.0%

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\* Slag activity is evaluated by determining the compressive strength of both portland cement mortars and corresponding mortars made with the same mass of 50–50 combinations of slag and portland cement. Slag activity index is the strength activity index (SAI) determination of slag.

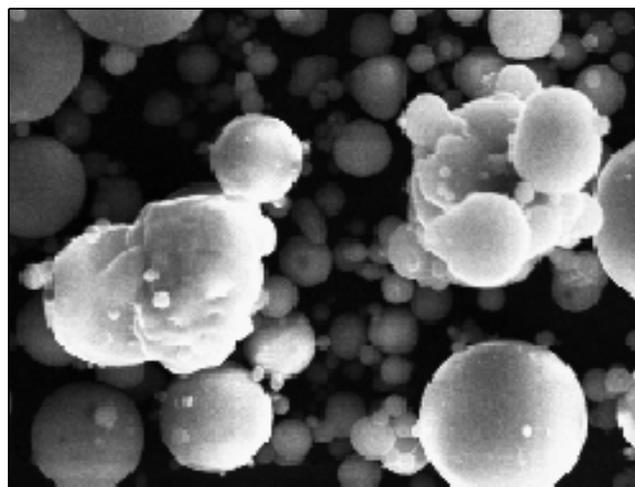
† NV = no value given.

form pelletized slag can be interground with portland cement but is often used as a lightweight aggregate.

**Specifications.** ASTM C989-99 (2003d) classifies GGBFS into three grades based on the slag activity index. This index measures the compressive strength of the mortar prepared in accordance with test method ASTM C109 (2003e). Test mortars containing an equal weight of blast furnace slag to portland cement are compared to standard portland cement mortars. The slag activity index is measured after the mortar has set 7 days and again at 28 days. Measurements are taken on the average of five consecutive samples and individual samples (Table 6). Slag activity index grades are based on minimum percentages; most GGBFS marketed in the United States is 120 grade that has a 95% minimum slag activity index for 7 days and 115% for 28 days. ASTM C595-03 (2003f) states the specifications for using GGBFS in blended hydraulic cement.

**Finished Product Uses.** Iron-producing companies contract with a processing business to handle the slag. The processor crushes or grinds the slag to meet market specifications, using screens and magnetic separators to recover any metal. GGBFS is a value-added product selling for about \$60/t that can be shipped greater distances. GGBFS can replace from 25% to 50% of portland cement in concrete (Slag Cement Association 2002) and is used in manufactured products such as block, segmental retaining wall units, and pavers. Mixed with hydrated lime, GGBFS can be used in flowable backfills. Specialized concretes can use a combination of GGBFS, fly ash, and silica fume. GGBFS is valued as an admixture in cement for its light color, resulting in a very light colored concrete. Adding GGBFS to a cement mixture gives the concrete greater resistance to sulfate and alkali-silica attack, increased workability while pouring concrete, and durability of the finished product.

**Finished Product Marketing.** GGBFS production and sales are limited to the eastern United States, near iron and steel manu-



**Figure 6. Secondary electron image of fly ash with glass spheres and masses. End product from Salt River Minerals Group, Cholla Generating Station, Arizona. Field of view = 42  $\mu\text{m}$ .**

facturers or near ports where they can receive imported material to grind and market. More than a dozen grinding plants are operating, and the number of blast furnaces in the United States is on the decline. Using existing slag piles, however, is an economical way to remove these piles from the landscape if the material meets specifications (van Oss 2004). If weathered, the slag may not be acceptable for use as a mineral admixture to concrete but can be used as a fine-grained aggregate in cement.

### Fly Ash

Fly ash is the major coal combustion by-product of electrical generation from coal-burning power plants. The amount of coal combustion by-product produced at each power plant varies, depending on the type of burners and precipitators, and the percentage of ash in the coal source. The ratio of fly ash to bottom ash produced by coal combustion depends on the type of burner and the type of boiler. Electrical or mechanical precipitators collect fly ash from the flue-gas stream coming from the combustion chamber. This material is glassy, predominantly spherical, and less than 45  $\mu\text{m}$  in size (Figure 6).

**Raw Materials and Processing.** Ash in coal consists of minerals and rock particles deposited in the peat swamp or introduced authigenically during the coalification process. Most (95%) of the mineral matter present is clay, pyrite, and calcite. Clay minerals constitute from 60% to 80% of the total mineral content of coal. The types of clay minerals depend on the chemical conditions of the depositional environment. Clays can be detrital in origin or be secondary precipitates from aqueous solutions. Kaolinite is the dominant clay mineral in coals developed in freshwater environments. Illite is dominant in coals overlying marine sediments, developing in moderately alkaline environments. Clays may be finely dispersed in the coal or concentrated in layers, such as tonsteins developed from volcanic ash layers. The mining process also introduces minerals by mining small partings within a seam or from roof or floor material. This dilution adds to the total content of noncombustible material in the coal that ultimately becomes part of the ash by-product.

Coal for electricity generation is finely crushed, typically in ball or roll mills, and air-fed into a 1,037°–1,482°C combustion chamber where the carbon immediately ignites. During coal combustion, the volatile matter vaporizes and carbon burns to heat the

boiler tubes. The inorganic material such as clays, quartz, and feldspar becomes molten and remains in the combustion chamber as slag on the boiler tubes, is carried away by the flue-gas stream as fly ash, or falls through to the bottom of the boiler as bottom ash. The molten material solidifies in the flue-gas stream leaving the combustion chamber, giving approximately 60% of the fly ash particles a spherical shape.

Air pollution control devices, commonly electrostatic precipitators (ESPs), collect the coarse fly ash (>44  $\mu\text{m}$ ) first. The finer material is collected later along the air-stream path. ESPs have an overall efficiency of 99%+ (Helmuth 1987). Mechanical precipitators are typically baghouses, cyclones, or venturi scrubbers. Baghouses use fabric filter-tubes or envelopes for capturing fly ash from the flue gas. Baghouses are very efficient for all size ranges (0–44  $\mu\text{m}$ ), with an overall efficiency of 99%+ (Helmuth 1987). Several hoppers collect the fly ash particles by size along the length of the ESPs. The captured fly ash can be sent through an air classifier system to ensure consistent grain size.

Depending on the sulfur content of the coal, flue-gas desulfurization (FGD) is necessary to remove sulfur dioxide ( $\text{SO}_2$ ) to meet the 1990 Clean Air Act Amendment standards. Dry scrubbers inject a very fine mist of lime into the unfiltered exhaust gas. The small amount of water used for injection evaporates in the hot exhaust, leaving calcium sulfate ( $\text{CaSO}_4$ ), which is removed with the fly ash. Dry scrubbing creates a fly ash high in sulfur trioxide ( $\text{SO}_3$ ) that is not marketable for most fly ash applications and is disposed of in ponds. Wet scrubbers spray the filtered exhaust gas with a solution of lime, limestone, quicklime, or soda ash as a reactant with  $\text{SO}_2$ . In the wet scrubber process, the fly ash is captured before the lime solution is added; therefore it has the potential for being marketed as a pozzolan. Saleable fly ash is loaded into pneumatic containers, either truck or rail, and the remaining fly ash goes to disposal ponds.

**Specifications.** ASTM C618-03 (2003b) defines fly ash as finely divided residue that results from the combustion of ground or powdered coal and is transported by flue gases. This definition does not include residue from burning municipal garbage or other refuse with coal, injection of lime directly into the boiler for sulfur removal, or “incinerator ash,” the result of burning industrial or municipal garbage in incinerators.

ASTM C311-02 (2003a) includes chemical analyses and physical methods for testing fly ash used as a mineral admixture in portland cement concrete, and ASTM C618-03 (2003b) outlines the physical and chemical requirements (Table 7). ASTM C618-03 has optional requirements that apply to air entrainment, effectiveness of alkali silica reaction, and sulfate resistance. For use in concrete, state departments of transportation, the Bureau of Reclamation, and the Army Corps of Engineers may have further requirements; Canada and Europe have other standards for fly ash.

In the United States, ASTM C618-03 (2003b) classifies fly ash into two categories (Class C and F) as an artificial pozzolan for use as a mineral admixture in portland cement concrete and Class N for all natural pozzolans (Table 7). Class C normally results from burning sub-bituminous coal or lignite and Class F from burning bituminous coals; however, there are exceptions to this generalization. As an example, lignite and sub-bituminous coal can produce either a Class F or a Class C fly ash. The type of fly ash depends on the depositional environment of the peat swamps from which the coal developed. Classes C and F fly ash differ significantly based on total  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  content; Class F has a minimum of 70% and Class C has a minimum of 50%. Fly ash not fitting within these two classes may be well suited for other applications such as soil and waste stabilization but cannot be used in concrete or port-

**Table 7. Summary of chemical and physical requirements for fly ash and natural pozzolans defined in ASTM C618-03**

	Class N	Class F	Class C
<b>Chemical Requirements</b>			
( $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ ), minimum %	70.0	70.0	50.0
$\text{SO}_3$ , maximum %	4.0	5.0	5.0
Moisture content, maximum %	3.0	3.0	3.0
LOI, maximum %	10.0	6.0	6.0
Optional chemical requirements:			
Available alkalis, as $\text{Na}_2\text{O}$ , maximum %	1.5	1.5	1.5
<b>Physical Requirements</b>			
Fineness: Amount retained when wet-sieved on 45- $\mu\text{m}$ (325) sieve, maximum %	34	34	34
SAI: <sup>*</sup>			
With portland cement at 7 days, minimum % of control	75	75	75
With portland cement at 28 days, minimum % of control	77	75	75
Water requirement, maximum % of control	115	105	105
Soundness: Autoclave expansion or contraction, maximum %	0.8	0.8	0.8
Uniformity: <sup>†</sup>			
Density, maximum variation from average %	5	5	5
Percent retained on 325 sieve, maximum variation, percentage points from average	5	5	5

Adapted, with permission, from the *Annual Book of ASTM Standards*, copyright ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

<sup>\*</sup> The SAI comes from a control mixture of portland cement mortar and a test mixture of portland cement and test sample in accordance with ASTM C311-02 (2003a). SAI with portland cement is a measure of reactivity with a given cement and can vary as to the source of both the fly ash or natural pozzolan and the cement.

<sup>†</sup> The density and fineness of individual samples must not vary from the average established by the 10 preceding tests, or by all preceding tests if the number is less than 10.

land cement. The intent of these minimum requirements is to ensure that sufficient potentially reactive material is present.

Class F fly ash with less than 10%  $\text{CaO}$  is considered low calcium and is not self-hardening but exhibits pozzolanic properties. Often this type contains >3% LOI. Quartz, mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), and hematite are major crystalline phases identified in North American Class F fly ash (Lohtia and Joshi 1995).

Class C fly ash containing more than 10%  $\text{CaO}$  is classified as high calcium and is cementitious. Class C fly ash typically is derived from sub-bituminous coal and some North Dakota and Gulf Coast lignite. Commonly, the higher the  $\text{CaO}$  content, the greater the degree of self-hardening. Class C often has a very low LOI of less than 1%. Crystalline phases of the Class C fly ash often include anhydrite, tricalcium aluminate ( $\text{Ca}_3\text{Al}_2\text{O}_6$  or  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ ), lime, quartz,  $\text{MgO}$ , mullite, merwinite ( $\text{Ca}_3\text{Mg}(\text{Si}_2\text{O}_8)$ ), and ferrite (Lohtia and Joshi 1995).

Physical characteristics of fly ash and natural pozzolans include size, morphology, fineness, and specific gravity. Fineness is determined by the percentage of the ash retained on a 45- $\mu\text{m}$  (325-mesh) sieve. ASTM C618-03 (2003b) requires that no more than 34% of the fly ash be retained on a 325-mesh screen. Particle-size distribution can be quite variable, depending on the collection method and size,

and can differ within coal from the same mine. The coarser material tends to be less reactive as a pozzolan.

Specific gravity of fly ash is related to chemical composition, color, and shape of the particles. The inconsistency of coal and its minerals makes this quite variable. Specific gravity is increased by opaque spherical magnetite or hematite particles if they are present in sufficient quantity. These materials, along with unburned carbon (% LOI), affect the color of the fly ash. Greater amounts of quartz and mullite decrease the specific gravity. Grinding fly ash may release some volatiles trapped inside the spheres, increasing the specific gravity. Fly ash with a large fraction of low-density particles is more reactive than fly ash with higher density particles, which have iron impurities. Pozzolanic reactivity depends on the amount of low-specific-gravity glass present.

**Finished Product Uses.** Concrete is a major use of fly ash. Class F fly ash is used to prevent alkali-silica reaction (ASR) in concrete and is preferred in many southwestern states where the aggregate tends to have reactive material. Light-colored concrete is desirable in some markets, particularly California. A low percentage of LOI results in a light-colored fly ash. LOI percentage can also be a factor in using fly ash in air-entrainment admixtures to counteract freeze-thaw cracking. The type and amount of unburned carbon material can be detrimental to these admixtures. Adding fly ash to a concrete mixture at 15%–25% by weight is common practice. Fly ash works as a fine-grained aggregate in concrete. Processing coal fly ash into pellets through a sintering process allows some systems to use any of the unburned carbon remaining in the fly ash for heat generation.

Fly ash, particularly high-calcium fly ash, combined with lime improves soils for roadway construction. Fly ash can be mixed with recycled pavement to create a new base course, reducing the need for additional aggregate. Roller-compacted concrete (RCC), a very stiff concrete rolled out with asphalt paving equipment, requires large amounts of fine aggregate that can be satisfied with fly ash. Fly ash's pozzolanic properties increase the strength of RCC, lowering the cost. Because RCC is often used in large structures such as dams, lowering the heat of hydration by adding fly ash is very important to minimize cracking. The use of fly ash for these large pours has greatly diminished the demand for Type IV portland cement.

Backfill is low-strength concrete used for infilling trenches. For this use, fly ash is mixed with water and small amounts of sand and portland cement, if necessary. Using Class C fly ash may require less portland cement to form a competent backfill. Fly ash backfill is gaining popularity because it can be poured in place and is less time-consuming than conventional backfilling with compacted soil (Bryggman and Nallick 1993).

**Finished Product Marketing.** Marketing of fly ash is similar to that of most industrial minerals; quality, consistency, and class of fly ash are very important in determining usage and market area. FGD gypsum contamination by the type of scrubber system installed at a power plant restricts a significant amount of fly ash from use. LOI content can limit usage because unburned carbons are detrimental to concrete or color characteristics. Transportation infrastructure is important, and pneumatic or bottom-dump truck transport is preferred except when large quantities can be shipped by rail and sold to distant markets. Storage facilities at different locations in the market area increase sales but are economically feasible only if the quality of the product is in demand. Fly ash can behave like a specialty mineral in that if the fly ash is of superior quality, distance from market is less of a factor.

Most electrical utilities contract with ash marketers to handle and sell their fly ash as a pozzolanic admixture if it is suitable for concrete. There are more than 40 commercial ash-marketing firms

throughout the United States. Most utilities also employ an ash market specialist to monitor ash quality, use, or disposal and to interface with the ash marketers under contract with the utility (U.S. Department of Transportation 2004). A few utilities have dedicated in-house ash-marketing programs. Ash marketers supply the product to concrete or cement marketers in bulk. Many ash marketers are divisions of concrete companies. In Europe and Asia, fly ash is more often blended into portland cements; in the United States, fly ash typically is sold as an admixture to the concrete (Table 2).

Ash marketers have load-out facilities and testing facilities at the generating station. They sample and test the fly ash coming from each unit to ensure consistency of the % LOI, fineness, and color (brightness) of the product. Some marketers also air-classify the fly ash they receive from the power plants to maintain consistency of particle size in their product. Marketers also maintain storage facilities in their market areas to absorb excess fly ash production and to maintain a steady flow of material to their customers on short notice. In the United States, fly ash production is greater during certain months of the year when the electricity usage is high, such as summer months in the south and winter months in the north. These times may not coincide with the peak usage times of fly ash, so if the fly ash is highly marketable, storage units are feasible.

**Use-Specific Transportation.** Concrete, concrete products, and grout are the principal products using fly ash (ACAA 2004a). Fly ash, like many of the other mineral admixtures to concrete, is shipped in pneumatic tanks, bottom-dump trucks, or pneumatic railcars. Many fly ash marketers use trucks as their main mode of transportation if the plant is close to their markets, or if they do not have rail load-out facilities. Where the marketer does not sell large enough quantities of fly ash, rail transport may not be economically feasible. If sales are significant, fly ash is stored dry in silos in population centers to provide an on-demand source of material.

Although today's fly ash marketers analyze the fly ash coming from the collectors on a regular basis to keep their product consistent and maintain quality, this was not always the case, and some concrete producers are still skeptical about using fly ash in their product. Ensuring the quality of fly ash is critical to the growth of the industry, especially in portland cement application (Schwartz 2003). Environmental concerns about concentrations of trace elements in the ash and the possible leaching of these elements also act as market barriers. These concerns are more of an issue in other uses of fly ash, such as structural fill, than in concrete where the fly ash is locked into the concrete matrix. Many of the trace elements have very low solubility in the ash (glass) matrix (D. Pflughoeff-Hassett, personal communication). Using fly ash in cementitious material can reduce the solubility of potentially toxic elements by both chemical and physical mechanisms and can prevent them from leaching into groundwater (Bryggman and Nallick 1993).

### Rice Hull Ash

Rice is a primary staple crop in the world, and rice milling produces more than 100 Mt of hulls annually (King 2000). The common practice of burning rice hulls in the field creates a pollution problem. The combustion of hulls to produce energy or burning hulls to complete the milling process creates ash. Collecting and grinding this ash creates a product similar to silica fume. The cost of installing an electric power plant in the United States using rice hulls as fuel is about \$1 million/MW of electric power capacity and requires 1.5–2 t of hulls per MW-hr. In California, 20–25 MWe facilities use rice hulls as a fuel source in the milling process (TropRice 2003). California and Louisiana have rice hull power plants near rice-producing areas. Rice hull ash has the greatest

**Table 8. Effects of pozzolans and SCMs on the performance of concrete**

Property	Silica Fume	GGBFS	Fly Ash (Class C and Class F)	Calcined Clay, Shale	Diatomite	Rice Hull Ash
Water demand	Depends on mixture	Decreases	Generally decreases; with higher % LOI and coarse (>45 $\mu\text{m}$ ) particles, increases	Increases	Increases because of microporosity	Increases
Workability	Decreases, becomes sticky	Improves	Improves	Improves	Unknown	Improves
Flow of pour	Decreases	Increases	Increases	Unknown	Unknown	Unknown
Compressive strength	High compressive strength attained in same time as portland cement	Lower during first 3–7 days. By 28 days, meets or exceeds strength of portland cement.	Increases slower than normal; with time (+60 days), exceeds strength of portland cement.	Increases with time, slower than portland cement	Increases with time, slower than portland cement	Moderately high, greater than portland cement
Durability	Increases	Increases	Increases	Increases	Increases	Increases
Heat of hydration	Accelerates temperature rise in first 72 hours	Lower	Lower, except in high-calcium fly ash	Lower	Lower	Same as portland cement
Air-entrainment agent	Increases demand	Increase demand	Higher % LOI, greater demand	Unknown	Unknown	Increases demand
ASR resistance	Increases	Increases	Increases	Increases	Increases	Increases
Sulfate resistance	Increases because of refined pore structure	Increases	Increases with Class F fly ash	Increases	Increases	Increases
Bleeding of hydrated lime, $\text{Ca(OH)}_2$	Lower than normal; increases potential for cracking	Generally lower	Generally lower	Lower than portland cement	Lower than portland cement	Negligible difference

Adapted from Malhotra and Mehta 1996; Lohtia and Joshi 1995.

potential in major rice-producing countries such as China and India. The market for rice hull ash has not developed in the United States to the point of having specific marketers of the product.

### ADVANTAGES OF POZZOLANS AND SCMS

Mineral admixtures have many advantages in portland cement applications where they can improve the properties of concrete. Their pozzolanic or cementitious nature adds a component by replacing part of the portland cement in concrete, in general reducing cost. Offsetting the use of portland cement by using mineral admixtures can save energy and lower  $\text{CO}_2$  emissions from cement plants.

The chemical and physical properties of the different mineral admixtures (Table 1) when added to concrete determine what properties of the concrete are enhanced. Table 8 lists the effects of these admixtures on the performance and other attributes of concrete. Characteristics of concrete influenced by adding pozzolans or SCMs are discussed in the following paragraphs.

The very fine particle size of many of the mineral admixtures can be advantageous when the aggregate is deficient in sand-sized material (Lohtia and Jodhi 1995). The admixtures act as filler and are part of the cement paste, reducing the total surface area to be coated with cementitious material. Adding fine (1–20  $\mu\text{m}$ ), spherical particles such as fly ash can also refine the pore structure in the concrete, which reduces the amount of water needed to produce a concrete of certain consistency. Conversely, the angular shape and microporosity of some natural pozzolans increase the water demand in the concrete mixture. The percentage of LOI can also affect the amount of water needed to create the needed consistency of the concrete.

Workability is the homogeneity and ease with which concrete can be mixed, transported, compacted, and finished (Ramachandran

and Feldman 1995). The spherical shape of the fly ash, in particular, acts like ball bearings and increases workability of the concrete, decreasing the need for aggregate fines. Calcined shale and clay also improve the workability of a concrete pour; silica fume, however, actually decreases workability because of its highly reactive nature.

Strength and durability of concrete are improved by the fine-grained nature of mineral admixtures, which decreases the porosity of the concrete (Lohtia and Joshi 1995). Formation of cementitious compounds by pozzolanic reaction causes pore refinement and reduces microcracking in the transition zone between the concrete and aggregate. This significantly improves the strength and durability of the concrete. Because of retarded heat of hydration, adding fly ash, GGBFS, or natural pozzolan to concrete lowers the early strength. Strength increases over time and eventually meets, and can exceed, the strength of concrete made with portland cement alone. Silica fume is highly reactive, and concrete made with silica fume attains high compressive strength in the same time as portland cement concrete and exceeds the norm in 3 days (Lohtia and Joshi 1995).

Heat of hydration is an exothermic reaction during hydration of portland cement. Pozzolanic reactions occur after cement hydration begins when  $\text{Ca(OH)}_2$  becomes available. Replacing a portion of the portland cement with fly ash or most natural pozzolans retards rate of hydration and manifests pozzolanic reactions late in the aging process of the concrete. As a rule of thumb, the percent reduction in heat liberation at 7–28 days is about one half the percentage of mineral admixture substitution for portland cement. Conversely, silica fume is highly reactive and accelerates the temperature rise in the first 72 hours (Lohtia and Joshi 1995). Heat of hydration is slower for GGBFS than for portland cement, and the hydration products tend to be more gel-like than portland cement, filling voids and increasing the ultimate strength of the concrete. Reduced heat of hydration is particularly important in

massive structures where the temperature increase becomes significant and can lead to cracking because of thermal stresses induced in hardened portions of the concrete mass.

Using air-entrainment admixtures (AEAs) in cement or concrete enhances the freeze-thaw resistance by increasing the void content of the concrete. The addition of most mineral admixtures increases the demand for AEA. Class C fly ash (high calcium) generally requires less AEA than Class F. The key factor is the % LOI, which appears to increase the need for AEA. This increased demand can influence the amount of water used in the mixture, depending on the type and amount of admixture added.

The presence of reactive material in the aggregate, such as opal, chalcedony, siliceous shale, and schist, causes ASRs in concrete. ASR occurs when silicate minerals react with alkali metal ions (as  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ ) in portland cement paste, forming a gel. With moisture, the gel can swell and expand and crack the concrete around the individual aggregate particles, causing pop-outs. Most mineral admixtures are effective in controlling ASRs. The available alkali in the mix is reduced by the amount of admixture added, as long as this material itself does not contain soluble alkalis. The size of the particles (0–45  $\mu\text{m}$ ) improves the packing of cementitious materials and reduces the permeability of the concrete because of the pozzolanic action. This reduces the ion migration and available external moisture in the concrete, increasing the resistance to ASR. The smaller particles of the pozzolans are preferentially attacked by alkaline solutions (sacrificial silica), forming a calcium-silicate hydrate (C-S-H) that is more stable than the silica gel and protects the aggregate from ASR attack. Some high-calcium fly ash (Class C) containing large amounts of soluble alkali sulfates increases the alkali-silica reactivity. For this reason, Class F fly ash is preferred to counteract ASR. Natural pozzolans, silica fume, and GGBFS are also effective in dealing with alkali-silica reactivity.

Concrete in certain applications must resist chemical attack by seawater, sulfate-bearing groundwater, or leaching by acidic waters. Sulfates such as gypsum react with hydration products of the tricalcium aluminate ( $\text{C}_3\text{A}$ ) phase of portland cement to form ettringite. This formation of ettringite can cause swelling and internal cracking, which ultimately weakens the concrete. Adding mineral admixtures improves the resistance of the concrete to these chemical attacks through lowering the amount of  $\text{C}_3\text{A}$  by reducing the percentage of portland cement. The pozzolanic reactions of the mineral admixtures help decrease the permeability of the concrete, making it harder for harmful chemicals to penetrate the concrete.

### GOVERNMENT, ENVIRONMENT, AND HEALTH CONSIDERATIONS

The biggest challenges for natural pozzolans are environmental concerns of  $\text{CO}_2$  reduction and conservation of natural resources. Mining the natural pozzolans also requires energy, and often the raw materials then undergo drying, grinding, and calcining, which uses significant energy and produces some  $\text{CO}_2$ . Using industrial by-products recycles materials and reduces the depletion of natural resources. Although these by-products were created through industrial processes requiring energy that creates  $\text{CO}_2$  emissions, little or no additional energy is needed to create a usable product, making by-products very attractive to the portland cement industries, competing directly with many of the natural pozzolans. As an example,  $\text{CO}_2$  emission savings for fly ash are almost a 1:1 exchange by weight (B. Kepford, personal communication).

Challenges lie ahead in the utilization of fly ash. The 1990 Clean Air Act Amendments requires power plants to reduce nitrogen oxide ( $\text{NO}_x$ ) emissions. Lowering  $\text{NO}_x$  emissions generally restricts oxygen during the combustion process, resulting in more

unburned carbon (% LOI) in the fly ash. Unless the fly ash goes through a washing process to remove the carbon, the fly ash is unsuitable for use in concrete, its largest market. Some  $\text{NO}_x$  removal systems leave residual ammonia on the fly ash. Depending on the type of coal, the amount of ammonia adsorbed can differ. Although the ammonia does not have a detrimental effect on the performance of fly ash in concrete, ammonia fumes liberated in the concrete mix can be objectionable under certain working conditions (EPA 2003b). There is some concern of health problems related to the direct inhalation of fly ash (EPRI 1998). Because fly ash particles are spherical, they may be less likely to lodge in lung tissue than angular particles from other sources. Very small particles (<10  $\mu\text{m}$ ), however, can go deep into the lungs. Coal ash does contain small amounts of other materials, and there is the potential for irritation and inflammation of lung tissue. Personnel working in the ash collection process, as ash haulers and silo operators, have the greatest potential for inhaling this material. An Electric Power Research Institute technical report (1993) concluded that routine operating activities did not produce hazardous exposure.

On the positive side, the use of fly ash reduces greenhouse gases; for every ton of coal ash used, there is a 0.89-t reduction (this can vary) of greenhouse gas (Schwartz 2003) created in the production of portland cement. Using fly ash in concrete or in blended cement reduces land disposal requirements and reduces the use of raw materials in creating portland cement clinker.

Silica fume is a very fine-grained material and should be treated as any other respirable dust. Although silica fume is amorphous silica, some small amounts of crystalline silica are present below measurable limits. The presence of any quartz requires warnings on the material data safety sheets for silica fume.

### TRENDS AND OPPORTUNITIES

Portland cement and concrete are major growth industries, and in the past 10 years, more portland cement manufacturers have realized the benefits of using pozzolans and SCMs in their product. Pozzolans and SCMs add durability to the concrete, extending the life cycle of a project. Another industry trend is the increased use of by-products over calcined clay and shale. As part of implementing sustainable development, conservation of natural resources has added to the desirability of using SCMs derived from industrial by-products. Production of blended cement containing natural pozzolans decreased from 192,000 t in 2001 to 187,000 t in 2002 in the United States. Fly ash is the leading by-product used in part because of the large volume produced—more than any of the other by-products—and its lower cost. Silica fume is a high-value product and only has certain applications. GGBFS use is limited in the United States by the decline in production from blast furnaces; sales of GGBFS have grown, however, and the need for GGBFS is being met by importing material. Fly ash use in clinker and blended cement has increased over the past several years in the United States, and clinker's predominant use is as a partial substitute for portland cement. The U.S. cement industry's 2003 consumption of fly ash for clinker was 2,250 kt and 39 kt for blended cement (van Oss 2003a). The concrete industry consumes a significantly larger volume of fly ash (11.1 Mt) as a substitute for portland cement in concrete (ACAA 2004b). Primary consumption of GGBFS is for blended cement, which has decreased from 369 kt to 333 kt for 2002 and 2003, respectively (van Oss 2003a). van Oss hypothesizes that this decrease is because of "lower sales volumes of slag-rich blends of concrete" or decreased use of slag as a grinding aid to make Type 1 portland cement.

The demand for cement worldwide is projected to rise 4.1% through 2006, with China as the largest market. Other developing

countries in Asia/Pacific, Latin America, and Eastern Europe are expected to have greater demands for cement as well (*Mining Engineering* 2002). Along with this growth, the demand for blended cements and pozzolanic materials will increase. Blended cements are attractive because of the potential to lower carbon emissions by partial replacement of cement clinker with industrial by-products and the superior performance of blended cements in certain applications. Barriers to greater usage of blended cements depend on availability, transportation costs, building code standards, and other legislative requirements (Worrell et al. 2001). Potential for CO<sub>2</sub> reduction varies by country, depending on current use of blended cements and the availability of blended materials. As an example, China's use of coal for power generation and significant iron production make it a candidate for using blended cements. Currently, China uses primarily portland cement. By using blended cements, China could significantly reduce its carbon emissions from clinker production (Worrell et al. 2001).

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