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Report on the Use of Raw or Processed Natural Pozzolans in Concrete

Reported by ACI Committee 232



American Concrete Institute®

Report on the Use of Raw or Processed Natural Pozzolans in Concrete

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This report reviews the use of raw or processed natural pozzolans in concrete and provides an overview of the properties of natural pozzolans and their use in the production of hydraulic-cement concrete. Long before the invention of portland cement, natural pozzolans mixed with lime were used to strengthen concrete and mortar. Today, they can be used to enhance the properties of fresh and hardened concrete and may provide economic value in some cases.

Keywords: alkali-silica reaction; diatomaceous earth; lime; pozzolan; pozzolanic activity; strength; sulfate attack.

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CHAPTER 1—INTRODUCTION AND SCOPE

1.1—Introduction

Pozzolans are made up of siliceous or siliceous and aluminous materials that, in finely divided form, will react with calcium hydroxide to form cementitious materials. The term “pozzolan” evolved from the name given to a deposit of volcanic material located near Pozzuoli, Italy. This deposit, originally referred to as pozzolana, consisted of pumice ash, or tuff, comprised of trachyte found near Naples and Segni, Italy. Trachyte is a volcanic rock comprised primarily of feldspar crystals in a matrix of siliceous glass. Pozzolana was formed from an explosive volcanic eruption in 79 AD at Mount Vesuvius, which engulfed Herculaneum, Pompeii, and other towns along the bay of Naples. Chapter 3 provides historical information about the use of pozzolans.

The term “natural pozzolan” encompasses a broad range of materials. A few of these materials are pozzolanic in their natural state. However, most of the materials considered natural pozzolans require some type of processing to render the material pozzolanic. Some may require only drying and grinding/classifying, while others may require heat treatment and grinding to adequately activate the pozzolanic nature of the material. Chapter 4 provides a brief description of the various materials classified as natural pozzolans, which are the focus of this report.

1.2—Scope

This report contains information and recommendations concerning the selection and use of natural pozzolans generally conforming to the requirements of ASTM C618-08. Topics covered include the effect of natural pozzolans on concrete properties, a discussion of quality control and quality assurance practices, and guidance regarding handling and use of natural pozzolans in specific applications.

CHAPTER 2—DEFINITIONS

ACI provides a comprehensive list of definitions through an online resource, “ACI Concrete Terminology,” <http://terminology.concrete.org>.

CHAPTER 3—HISTORICAL USE OF NATURAL POZZOLANS

3.1—Ancient history

Many people associate the use of quarried building stones with the construction of structures by the Greeks, Romans, and other similar ancient civilizations. Concretes and mortars using various cementitious binders, however, were likewise used to some extent during these ancient times. These cementitious binders contained pozzolans of a natural origin, such as volcanic ash, pulverized pumice, and diatomaceous earth. When these pozzolans were combined with burned limestone and mixed with water, the combination would form a cementitious material. There have been several millennia have been used in mortar and concrete for several millennia.

prior to the invention of the portland cement we know today, which was first patented in 1824 (Kosmatka and Wilson 2011). Chapter 3 reviews examples of the important role that natural pozzolans have played in the development of mortars and concrete that has led to the development of today's mortars and concretes.

In ancient times, construction throughout the world used mortar and concrete mixtures consisting of fillers and raw, or heat-treated, lime (Malinowski 1991). One of the oldest examples of a hydraulic binder dates back to approximately 5000 BC. The mixture consisted of lime and diatomaceous earth from the Persian Gulf (Malinowski and Frifelt 1993). The next-oldest reported use was in the Mediterranean region. This pozzolan was produced from the volcanic ash of two volcanic eruptions. The first eruption was recorded sometime between 1600 and 1500 BC on the Aegean Island of Thera—now Santorin, Greece—and the second was recorded in 79 AD at Mt. Vesuvius on the bay of Naples, Italy. Both materials are volcanic ashes or pumicites consisting of approximately 80 percent volcanic glass (pumice and obsidian).

Another example is an ancient water-storage tank with a holding capacity of 785 yd³ (600 m³) that was discovered during archaeological excavations in the 1970s at the ancient city of Camiros on the Island of Rhodes, Greece. This structure, which was built in approximately 600 BC, was used until 300 BC when a new hydraulic system with an underground water tank was constructed. This water tank has remained in very good condition for almost three millennia (Efsthadiadis 1978). Examination of the materials used for this structure revealed that the concrete blocks and mortar used were made out of a mixture of lime, Santorin earth, fine sand (less than 0.08 in. [2 mm]), and siliceous aggregates with sizes ranging between 0.08 and 0.79 in. (2 and 20 mm). Blocks were cast by placing the fresh concrete into wooden sidewall molds. Tests on a 0.79 in. (20 mm) cubic specimen extracted from the structure found the compressive strength to be 1740 psi (12 MPa). Mortars like these were known to have a composition of six parts by volume of Santorin earth, two parts by volume of lime, and one part by volume of fine sand. These mortars were used as the first hydraulic cements in aqueducts, bridges, sewers, and structures of all kinds. Some structures are still standing along the coasts of Italy, Greece, France, Spain, and in harbors of the Mediterranean Sea.

Vitruvius, a Roman engineer who lived in first-century BC, wrote in *The Ten Books On Architecture* that the cements made by the Greeks and the Romans were of superior durability because “neither waves could break, nor water dissolve” the concrete (Vitruvius 1960; Morgan 1914). In describing the building techniques of masonry construction, Vitruvius indicated that the Romans developed superior practices of their own from the techniques of the Etruscans and the Greeks. The Greek masons, who discovered pozzolan-lime mixtures sometime between 700 and 600 BC, later passed their knowledge of concrete to the Romans in 150 BC. During the 600 years of their domination, the

Romans discovered and developed a variety of pozzolans throughout their empire (Kirby et al. 1956).

The Greeks and Romans built many such structures over 2000 years ago. Examples are the Roman aqueducts, sea walls, and marine structures on the islands of the Aegean Sea; in Syros, Piraeus, Nauplion, and other cities; the harbors of Alexandria in Egypt; Fiume, Pola, Spalato, and Zara on the Adriatic Sea; and Constanta (Romania) on the Black Sea. All provide evidence of the durability of pozzolan-lime mortar under conditions of mild weathering exposure.

Roman monuments in many parts of Europe are in use today, standing as a tribute to the performance of pozzolan-lime mortars (Lea 1971). Perhaps one of the most notable buildings of the Roman era is the Pantheon in Rome. Constructed in approximately 125 AD, the Pantheon is still standing and in use today. As reported by Lea (1971), the 20 ft (6.4 m) thick walls are constructed of a tuff and pozzolana concrete. The dome, which spans 142 ft (43.3 m), is constructed of cast concrete that contains pumice and pozzolana, making it possibly the oldest known use of lightweight concrete.

3.2—Modern history

The advent of portland cement, which was developed and patented by Joseph Aspdin in 1824 (Kosmatka and Wilson 2011), did not preclude the use of natural pozzolans. Pozzolans remained an integral part of concrete technology in the years following the invention of modern-day portland cement. Structures such as the Suez Canal in Egypt built in 1860, and the Corinthian Canal built in 1880 to connect northern and southern Greece, used concrete containing natural pozzolans. Natural pozzolan technology continued to evolve throughout the first half of the twentieth century.

The use of natural pozzolans in concrete was investigated in the United States as early as 1908 by Bates et al. (1912). Continuing work demonstrated that concretes containing pozzolanic materials exhibited certain desirable properties such as lower cost, lower temperature rise, improved workability, improved sulfate resistance, and resistance to alkali-silica reactions (Price 1975; Meissner 1950; Mielenz et al. 1950; Davis 1950).

The Los Angeles aqueduct constructed from 1910 to 1912 is an example of the first large-scale use of portland-pozzolan cement that was composed of equal parts of portland cement and a rhyolitic pumicite (Price 1975). In the 1920s and 1930s, natural pozzolans were used as a mineral admixture in concrete for the construction of dams and other structures then being constructed by the Los Angeles County Flood Control District. The California Division of Highways used specially made portland-pozzolan cement in several structures because of its proven resistance to sulfate attack from seawater and its lower heat of hydration (Davis 1950).

According to Mielenz et al. (1950), the United States Bureau of Reclamation (USBR) began an intensive study in 1933 to determine the effect of natural pozzolans on the heat of hydration of concrete and to identify other benefits suitable for mass concrete applications in dam construction. In these studies, more than 200 prospective natural pozzo-

lans were evaluated. The results revealed the positive effect of calcination of natural pozzolans on their properties and performance in concrete. Properties reported were:

- (a) Mineralogical and chemical composition
- (b) Pozzolanic activity, water requirement, and strength
- (c) Control of expansion from alkali-silica reactivity

Mielenz et al. (1950) concluded that calcination of clay minerals was essential to develop satisfactory pozzolanic activity, and the response to heat treatment varied with the type of clay minerals present.

There were some sources of natural pozzolan located in the United States, mainly west of the Mississippi River, that did not require calcining to make them active (Price 1975). Many natural pozzolans were usable in their raw state. If moist, they usually required drying and grinding before use. The best natural pozzolans owed their activity to volcanic glass with a SiO_2 content of 70 to 73 percent, of which 40 to 100 percent of the SiO_2 was in the form of rhyolitic glass.

Studies of natural pozzolans by the USBR in the 1930s and 1940s encouraged their use for controlling heat of hydration and alkali-silica reaction (ASR) of concrete in large dams. Generally, the pozzolanic deposit was in the vicinity of the particular project and the amount required was sufficient to support mining and processing costs. The deposit was usually abandoned at completion of the project.

Siliceous shales of the Monterey Formation in Southern California have been produced commercially and used extensively in the surrounding areas. A portland-pozzolan cement containing 25 percent interground calcined Monterey shale was produced during the 1930s and 1940s (Meissner 1950). The California Division of Highways used this cement in the 1930s in several structures, including the Golden Gate Bridge and the San Francisco-Oakland Bay Bridge. Another portland-pozzolan cement containing 25 percent interground calcined pozzolan was used in 1935 for the construction of the Bonneville Dam Spillway on the lower Columbia River.

From 1940 to 1942, the USBR built the Friant Dam on the San Joaquin River in California with a portland cement-pozzolan combination. The pozzolan was a naturally fine rhyolite pumicite, which was batched separately in the concrete mixer at the rate of 20 percent by mass of cement. This pozzolan was obtained from a deposit along the San Joaquin River near Friant.

Stanton (1917) described the Cretaceous volcanic ash bed on the Great Plains near Linton, ND. At one exposure, 1 mile (1.6 km) southeast of Linton, the thickness of the white bed is 26 ft (8 m) and the rock is very fine-grained and mostly massive, although it contains some thin-bedded layers. A sample examined by G. F. Loughlin (Manz 1961) consisted of 80 percent volcanic glass, 15 percent quartz and feldspar, and 2 to 3 percent biotite. The Linton area ash bed is generally overlain by sand and underlain by shale. Contamination of the ash by this adjacent material is detrimental. If the ash is carefully mined, with no contamination of sand or shale, the volcanic ash need only be dried at 212°F (100°C) and finely ground to comply with ASTM C618-08. Tests were performed in 1961 (Manz 1961) on composite samples of volcanic ash from the Linton deposit. The samples were first

crushed and ground in a ball mill and then calcined in an electric kiln for different times and temperatures. Separate samples were calcined as follows: 15 minutes at 1000°F (538°C) and 15 minutes at 1400°F (760°C), as well as 1 hour at 1400°F (760°C) and 1 hour at 1700°F (927°C). All samples were then reground prior to testing. The results of the heat treatments are shown in Tables 3.2a and 3.2b and the results are compared to those of samples that had been ground but not calcined. Based on these tests, the volcanic ash in the uncalcined state complied with most of the ASTM requirements and the performance was improved when calcined at a temperature above 1400°F (760°C).

During the 1960s and early 1970s, a natural pozzolan was used in nearly all of the concrete in the California State Water Project at the rate of 70 lb/yd³ (42 kg/m³), including the lining of the California Aqueduct (Tuthill 1967; Tuthill and Adams 1972). This was the most extensive use of a natural pozzolan in a project in U.S. history. The performance of this pozzolan exceeded the requirements of ASTM C618-08.

Large deposits of diatomite were discovered decades ago in the coastal ranges of central California and the peninsular ranges of Southern California. The largest reserves of freshwater diatomite are in the northeastern counties of Shasta, Siskiyou, Modoc, and Lassen (Burnett 1991). In 1993, a study was undertaken to appraise a lacustrine deposit located approximately 30 miles (48.3 km) north of Reno, NV, as a source of a natural pozzolan. The deposit is an intermingling of diatomaceous earth and dacite pumicite that was calcined and ground before use in concrete. During the period of 1970 to 1989, this natural pozzolan was used in concrete for the construction of structures, bridges, roadways, the Trans-Canada Highway, the Auburn Dam, and the Los Melones Dam and Power Plant. It was also used in research projects by the California Department of Transportation from January 1987 to August 1991.

An accounting of the history and background on mineral admixtures, along with the use of natural pozzolans (raw and calcined), is provided by Mielenz (1983). The experiences in the use of large quantities of fly ash and natural pozzolans in the western United States by the USBR are reported by Elfert (1974). Table 3.2c lists the types of mineral admixtures used in the construction of some concrete dams built from 1915 to 1964.

High-reactivity metakaolin (HRM) has been known as a pozzolanic material for many decades; however, HRM use in concrete did not receive much attention until the mid-1980s. In the United Kingdom, large-scale trials have been conducted using HRM concretes subjected to aggressive environments (Ashbridge et al. 1996). Their research shows excellent strength development, reduced permeability, and increased chemical resistance. In addition, strength, pozzolanic activity, and cement hydration characteristics have been studied in superplasticized metakaolin concrete (Wild et al. 1996).

In the United States, HRM has been evaluated as a pozzolan in various research studies and in the field. In one air-entrained high-performance concrete, the use of metakaolin-containing concrete provided increased strength

Table 3.2a—Cretaceous volcanic ash from North Dakota calcined for 15 minutes (Manz 1961)

Testing parameters	Samples			ASTM C618-08
Processing temperature	212°F (100°C)	1000°F (538°C)	1400°F (760°C)	—
Specific gravity	2.26	—	2.40	—
Blaine fineness, m ² /kg	977	—	976	—
Mean particle diameter, μm	2.7	—	2.5	—
Amount retained on 45 μm (No. 325) sieve, percent	7.9	—	10.3	34.0 maximum
Strength activity index: with lime at 7 days, psi (MPa), 2 x 4 in. (50 x 100 mm) cylinders	611 (4.2)	685 (4.7)	1030 (7.1)	—
Strength activity index: with lime at 7 days, psi (MPa), 2 in. (50 mm) cubes	670 (4.6)	—	1120 (7.7)	—
Strength activity index: with portland cement, at 28 days, percent of control	64	—	80	75 minimum
Water requirement, percent of control	107	—	108	115 maximum
Soundness: autoclave expansion or contraction, percent	0.32	—	0.26	0.80 maximum
Increase of drying shrinkage of mortar bars at 28 days, difference, in percent over control	—	—	0.025	0.03 maximum

Notes: Conducted by the Northwest Laboratories, Seattle, WA, in 1960. These tests were performed on composite samples of volcanic ash from 20 test holes. The portions from each test hole were taken from 1 to 23 ft and 23 to 30 ft (0.3 to 7 m and 7 to 9 m) levels. The material was crushed, ground in a ball mill, and calcined at 1000 and 1400°F (538 and 760°C) for 15 minutes and then reground before testing.

Table 3.2b—Test results of North Dakota volcanic ash calcined for 1 hour (Manz 1961)

Testing parameters	Samples					Specification
	61-1	61-1	61-1	61-5	61-13	ASTM C618-08
Processed calcinations temperature	212°F (100°C)	1400°F (760°C)	1700°F (927°C)	212°F (100°C)	212°F (100°C)	—
Specific gravity	2.37	2.50	2.39	—	—	—
Amount retained on No. 325 sieve (45 μm), percent	2.9	3.2	—	0.6	—	34 maximum
Strength activity index: with lime at 7 days, psi (MPa), 2 x 4 in. (50 x 100 mm) cylinders	952 (6.6)	1385 (9.5)	1020 (7.0)	1090 (7.5)	1020 (7.0)	—
Strength activity index: with portland cement, at 28 days, percent of control	118	111	—	—	—	75 minimum
Water requirement, percent over control	110	112	114	110	110	115 maximum
Color of sample	Light gray	Light buff	Dark buff	Light gray	Light gray	—

Notes: The materials tested were ground with a muller. Calcining was conducted at 1400 and 1700°F (760 and 927°C) for a period of 1 hour and then reground before testing.

and reduced chloride-ion penetration compared with the portland cement control design. Likewise, the HRM concrete maintained good workability and had an air-void system that produced good resistance to cycles of freezing and thawing and to deicer scaling (Caldarone et al. 1994). Benefits of using HRM in ternary systems with ground slag cement and fly ash have also been reported (Caldarone and Gruber 1995a,b). From 1962 to 1972, approximately 227,300 tons (250,000 metric tons) of calcined kaolinitic clay were used in the construction of four hydroelectric dams in Brazil (Saad et al. 1982). Kaolin clay from Brazil has been used since 1965 as an ingredient in concrete in the construction of large dams at a cost of approximately one-third that of portland cement (Saad et al. 1982). This natural pozzolan is produced by calcining kaolin clay and grinding it to a Blaine fineness of 700 to 900 m²/kg. Because of this high fineness and activity, HRM can be used for cement replacement up to 50 percent by volume, with a 90-day compressive strength

similar to concrete made with portland cement. At Jupia Dam, the use of this natural pozzolan, at 20 to 30 percent of the volume of cement, resulted in lower temperature rise, improved cohesion, and reduction of expansion from ASR (Andriolo 1975). When first used for general concrete construction, the natural pozzolan replaced 30 percent of the portland cement by volume and, when used for structural concrete construction, the rate of replacement was 20 percent. The use of this high-reactivity natural pozzolan in mass concrete construction provided substantial improvements to the concrete properties (Saad et al. 1982).

Calcined kaolinitic clay (with a metakaolin content in the range of 85 to 90 percent) has been extensively used in the midwestern United States since 1993 in the construction of highway pavements, bridge decks, and parking structures. Calcined kaolinitic clay is used specifically to provide for ASR mitigation or impart low permeability to concrete (Barger et al. 1997). This material was commercially available in the United States in the 1990s.

Table 3.2c—Mineral admixtures and structures that used them (Elfert 1974)

Name	Date completed	Type of pozzolan
Arrowrock Dam	1915	Granite
Lahontan Dam	1915	Siliceous silt
Elephant Butte Dam	1916	Sandstone
Friant Dam	1942	Pumicite
Altus Dam	1945	Pumicite
Davis Dam	1950	Calcined opaline shale
Glenn Anne Dam	1953	Calcined oil-impregnated diatomaceous shale
Cachuma Dam	1953	Calcined oil-impregnated diatomaceous shale
Tecolote Tunnel	1957	Calcined oil-impregnated diatomaceous shale
Monticello Dam	1957	Calcined diatomaceous clay
Twitchell Dam	1958	Calcined diatomaceous clay
Flaming George Dam	1963	Calcined montmorillonite shale
Glen Canyon Dam	1964	Pumice

cially available as a site-added pozzolan and interground to produce Type IP blended cement (Barger et al. 2001). In its applications, the calcined kaolinitic clay was used not only in binary systems but also in ternary cementitious systems combined with either Class C or Class F fly ash or silica fume.

A calcined shale was commercially available in the Mid-Atlantic United States from 1996 to 2004 and was used largely in the states of Virginia and Pennsylvania. The calcined shale natural pozzolan was used in the production of ready mixed concrete, concrete pipe and products, and prestressed concrete. During the period, this calcined shale pozzolan was used on various projects, accounting for the production of more than 4 million yd³ (3 million m³) of concrete in the two-state area. Although the calcined shale was used widely in ready mixed concrete, it was found to be particularly well-suited to the use in precast, prestressed concrete because of its early strength development, improvement of the rheological properties, increase in electrical resistance, and stability of the air content (Neal and Ramsburg 2002). Production of the calcined shale pozzolan was ceased in 2004 because of a lack of grinding capacity at the facility where it was manufactured.

CHAPTER 4—NATURAL POZZOLANS: DESCRIPTIONS

Sections 4.1 through 4.6 provide a brief description of various materials that are classified as natural pozzolans and are the focus of this report. Section 4.7 provides descriptions of other materials that do not necessarily meet the definition of a natural pozzolan but that are nonetheless addressed in this document.

4.1—Calcined clay

Calcined clay is a naturally occurring raw material comprised essentially of alumino-silicate minerals. Examples of clay are kaolinite, dickite, halloysite, and illite. The purity of these naturally occurring deposits can vary from relatively pure mineral types (98 percent) to mixtures of multiple mineral types. Because clays are, by definition, very fine-grained materials, they are easily quarried and stockpiled. Stockpiles of kaolinite clay compacted fines often weather and dry and return to the uncompacted state and, therefore, require little or no additional deagglomeration.

The calcining of clay to remove bound water, or dehydroxylation, is typically done in rotary kilns or flash calciners where the clays are heated to a temperature adequate to decompose the clay's crystal structure and render it amorphous. For kaolinite clays, this temperature is usually approximately 1020 to 1380°F (550 to 750°C). Other clay types may require different thermal activation temperatures to optimize the material's pozzolanic reactivity. This process is easily monitored by X-ray diffraction.

Depending on the purity of the clay material, the calcined clay may result in one or more phases present (amorphous and crystalline). Calcined clays have been used as manufactured pozzolans in concrete for many years. In the midwestern United States, calcined kaolinite clays have been documented in the literature (Barger et al. 1997) as containing a mixture of approximately 85 to 90 percent metakaolin, 5 to 10 percent quartz, and residual thermally treated mixed clays of illite and montmorillonite or smectite. Higher purity calcined clays (greater than 95 percent metakaolin), specifically kaolinite, are discussed in 4.4 on metakaolin.

4.2—Calcined shale

The raw material is shale or slate, which consists largely of alumino-silicate clay minerals. In addition, there may be varying amounts of calcite (limestone), quartz, feldspar, and mica. The shale or slate is quarried by conventional means, crushed to a maximum size of 1.5 in. (38 mm), and then calcined (heat-treated) in a rotary kiln. Calcining temperatures vary depending on the source, but are typically in the range of 1800 to 2000°F (980 to 1090°C) with a residence time in the kiln of approximately 45 minutes. This results in a clinker ranging in size from 0.25 to 2 in. (6 to 51 mm) that is air-quenched at the discharge of the kiln. The finished product is achieved by grinding the clinker in a ball mill to a high Blaine fineness of 600 to 800 m²/kg. This will result in a finely divided powder with a median particle size on the order of 5 microns, similar in fineness to Type III portland cement. Calcined shale may have a typical elemental analysis of 50 percent silica, 20 percent alumina, 8 percent iron, and 8 percent calcium.

The alumino-silicate clay minerals, derived from the shale or slate, provide the necessary elements needed for a pozzolanic reaction. Heat treatment alters the crystalline structure of the alumino-silica clay minerals, making them capable of participating in a pozzolanic reaction. The amorphous (noncrystalline) phases of the calcined shale will range from

50 to 75 percent, depending on the particular source and heat-treating process.

The loss on ignition (LOI) of calcined shale may range from 1 to 5 percent. The LOI of calcined shale is not related to the presence of carbon, as is the case with fly ash. The LOI of fly ash is due to the presence of residual carbon particles from the coal combustion process and this carbon can have adverse effects on air entrainment in concrete. The LOI of calcined shale is due to the presence of both residual water molecules bound in the clay mineral structure and residual uncalcined calcite. Therefore, the LOI of calcined shale does not have any adverse effect on air entrainment in concrete.

Reported cases of calcined shale being used as a pozzolan date back to as early as 1932. Calcined shale has been commercially available in the Mid-Atlantic and midwestern United States since the mid-1990s (Neal and Ramsburg 2002).

4.3—Diatomaceous earth

Diatomaceous earth is composed of the siliceous skeletal remains of microscopic aquatic plants called diatoms. The silica is present as an amorphous hydrous silica termed opal. Diatomite is diatomaceous earth sufficiently pure to be mined and occurs as a fine, granular, lightweight, porous aggregate with an appearance similar to chalk. Diatomite is also known as kieselgur in Germany and tripolite in Libya. Tripolite should not be confused with the sedimentary rock tripoli, which is a residual silica resulting from the weathering of chert or siliceous limestone that is generally not opaline. Moler is a diatomaceous earth from Denmark containing volcanic ash and up to 30 percent smectite clay (Christensen et al. 2001). Most diatomite deposits commercially mined in the United States, which are highly pure, are found in California, Nevada, Oregon, and Washington (Founie 2006).

All diatomite has pozzolanic reactivity to varying degrees. Diatomite is a highly reactive pozzolan due to its high content of amorphous silica and its high specific surface area. It has a specific surface area approximately 10 times higher than that of portland cement. Lacustrine, or freshwater deposits of diatomite, appear to have higher pozzolanic reactivity. Diatomite can be calcined and finely ground to achieve optimum pozzolanic reactivity and performance characteristics. The temperature of calcination should be below 1650°F (900°C) to avoid loss of opal through cristobalite crystallization (Christensen et al. 2001).

4.4—Metakaolin

Metakaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is a natural pozzolan produced by heat treating kaolinite clays. Kaolinite has a chemical composition of $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. When it is heat treated, in the temperature range of approximately 1100 to 1650°F (600 to 900°C), the chemically combined water is driven away to form an amorphous aluminosilicate called metakaolin. The calcination temperature will depend on the characteristics of the parent kaolin clay, such as degree of crystallinity and particle size. At higher temperatures, it will recrystallize, resulting in the formation of mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) or spinel

(MgAl_2O_4) and amorphous silica (Murat et al. 1985) that will reduce its pozzolanic reactivity. The reactivity of metakaolin is dependent upon the amount of kaolinite contained in the original clay material. The average particle size of metakaolin varies and can be controlled during processing to change its properties. Metakaolin is typically white in color, has a mean particle size in the range of 2 to 10 μm , and has a bulk density in the range of 18 to 40 lb/ft^3 (290 to 640 kg/m^3).

High-reactivity metakaolin (HRM), as described in AASHTO M321-04, is derived from highly refined kaolinite clay that has been processed to remove impurities prior to calcination. The resulting product has a very high content of silica and alumina (greater than 90 percent). The kaolin used to produce HRM is selectively mined to achieve a desired particle size distribution, morphology, and chemical composition. The crude kaolin is dispersed into a slurry and processed, generally by centrifuge, to remove impurities and produce the desired particle size distribution. Additional processing may include magnetic separation and chemical bleaching. The refined slurry is then spray-dried and calcined at an optimal temperature to achieve the desired level of pozzolanic activity.

Although the use of metakaolin as a pozzolanic mineral admixture has been known for many years, its use has grown rapidly since the mid-1980s. In the United States, metakaolin and HRM are primarily manufactured from deposits of kaolin found in Georgia.

4.5—Opaline shales

Opaline shales are described as cherts, shales, and clays containing substantial quantities of opaline silica and sometimes nearly pure opal (Davis 1950). Opal is a hydrous silica formed both as a low-temperature mineral in sedimentary rocks and as skeletal material by organisms like diatoms and sponges. Opal is composed of spherical silica particles and is largely amorphous. When present in coarse aggregates, opal can lead to deleterious expansion in concrete from an alkali-silica reaction (ASR) between the reactive opal and cement alkalis. When present in a fine particle size <250 μm , however, it is a highly active pozzolan-like glass (Shayan and Xu 2004). Because clay minerals present in shales have to be thermally treated to be activated, opaline shales will generally be activated by calcining. In the United States, opaline shales are found principally in states west of the Mississippi River. The Monterey Formation of California is an example of opaline shale.

Gaize is a pozzolan found in France that is not of volcanic origin but is a porous sedimentary rock consisting mainly of opal. The presence of opal is from organisms like sponges, which build siliceous skeletons. Opal is found in the Ardennes and Meuse Valleys in France and is still used in that region. The material is usually calcined at temperatures of approximately 1620°F (900°C) before it is used as a pozzolan or as a component of portland-pozzolan cement.

4.6—Volcanic materials

The earliest pozzolans used were of volcanic origin. These materials formed as a result of volcanic eruptions. Depending

on their composition, mechanism of formation, or alterations over time, the volcanic materials may be classified or identified by different names. Often, a specific material may be named after the geographic area from which it comes. Other classifications may be more general in nature, related to the material's composition or alterations. Sections 4.6.1 through 4.6.6 provide a description and brief discussion related to the more commonly known volcanic materials.

4.6.1 Pumice, pumicite—During an explosive eruption, volcanic gases dissolve in the liquid portion of magma and expand rapidly to create a foam or froth. Once above ground, the liquid part of the froth quickly solidifies to form glass. Pumice is actually a kind of glass and not a mixture of minerals. It is colorless or light gray and has the general appearance of rock froth. The viscosity of the lava, the quantity of water vapor and gas, and the rate of cooling together determine the fineness of the vesicular substance. Large amounts of gas result in a finer-grained disaggregated variety known as pumicite. The chemical composition is that of rhyolite and granite. Figure 4.6.1 shows the scanning electron microscope (SEM) micrograph of a pumice sample from Guatemala before grinding (Day and Shi 1995). The honeycomb-like structure can be observed with the help of SEM under low magnification. The channels inside the pumice range up to 100 μm in diameter with the majority being less than 20 μm after grinding. Very small, irregular particles without pores form, while some big particles with pores are still observed. Because pumice consists mainly of vitreous phase, ground pumice can be a good pozzolanic material (Day and Shi 1995).

One of the main uses for pumice and pumicite is lightweight aggregate for concrete blocks and assorted building products. Other major applications include abrasives, absorbents, and filter aids. In 2000, the total consumption of pumice and pumicite in the United States for these other uses was 769,000 tons (697,000 metric tons) (Bolen 2000).

4.6.2 Trass—Trass is a natural pozzolan of volcanic origin (Lovewell 1971) that has been well known since ancient Roman times. The material is a trachytic tuff that differs from place to place. One source is found in the Valley of the Rhine River in Germany. Similar tuffs have been used in Bavaria. Generally, the only processing required is to grind the materials to a sufficient fineness.

Rhenish and Bavarian trass, composed primarily of volcanic tuff, is a highly pozzolanic material in an untreated state that can become less reactive if heated. Tuffs containing clay (smectite) and zeolite (phillipsite) can be activated by calcining to 1470°F (800°C) (Liebig and Althaus 1998). In a study of uncalcined Turkish trass composed of rhyolitic to rhyodacitic tuff altered to produce varying amounts of zeolites, the compressive strength of mortars was strongly correlated with the zeolite content. The selective ion-exchange or adsorption properties of the microporous crystalline structure of the zeolite (heulandite-clinoptilolite), or both the ion-exchange and adsorption properties, was found to be more important than glass content for pozzolanic activity (Esenli 1995).

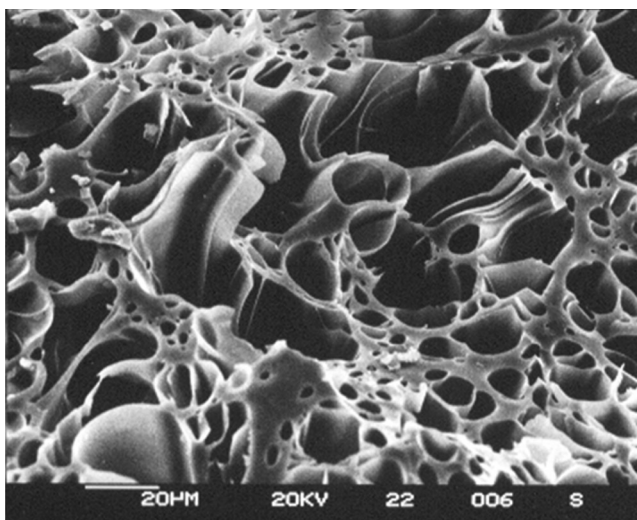


Fig. 4.6.1—Scanning electron microscope micrograph of pumice sample from Guatemala before grinding (Day and Shi 1995).

4.6.3 Santorin earth—Santorin earth is produced from a natural deposit of volcanic ash of dacitic composition on the island of Thera in the Aegean Sea, also known as Santorini. This deposit was formed from approximately 1600 to 1500 BC from a tremendous explosive volcanic eruption (Marinatos 1972).

4.6.4 Tuff—Tuff is a rock composed of greater than 75 percent volcanic ash. Volcanic tuff is essentially solidified volcanic ash, derived from the smaller particles (less than 0.08 in. [2 mm]) in a volcanic deposition. The mineralogical and pozzolanic properties of tuff are similar to the volcanic ash originally deposited, provided that the volcanic ash has not been altered over time. Tuff consists mainly of various amounts of glass and minerals. Depending on the conditions present after deposition, the glass phase can be transformed into secondary mineral phases due to thermodynamic instability. Volcanic ash altered in a moist, acid environment (coal swamp) will form the kaolinite rich rock tonstein. Alteration of ash in mildly alkaline water (marine) results in the smectite rich rock bentonite. In strongly alkaline or saline lakes, ash is altered to zeolite, sometimes with potassium feldspar (Triplehorn and Bohor 1993; Hay 1986).

4.6.5 Volcanic ash—Volcanic ash is formed during explosive eruptions by violent separation of magma, or molten rock, into tiny pieces called pyroclasts and other associated shattering of solid rocks. Explosive eruptions are generated when magma reaches the surface and the volcanic gases dissolved in the molten rock expand and escape, or explode, into the air rapidly. Explosive eruptions also occur when groundwater is heated by magma and abruptly converted to steam. Volcanic ash is composed of fragments of rock, minerals, and glass that are less than 0.08 in. (2 mm) in diameter (LeMaitre 2002; Williams et al. 1982; Day and Shi 1995; Shi 2001). Figure 4.6.5a shows the particle size distribution of two volcanic ashes from Bolivia and Guatemala. Although these two ashes are from different regions, they