

Supplementary Cementitious Materials

Part I: Pozzolanic SCMs

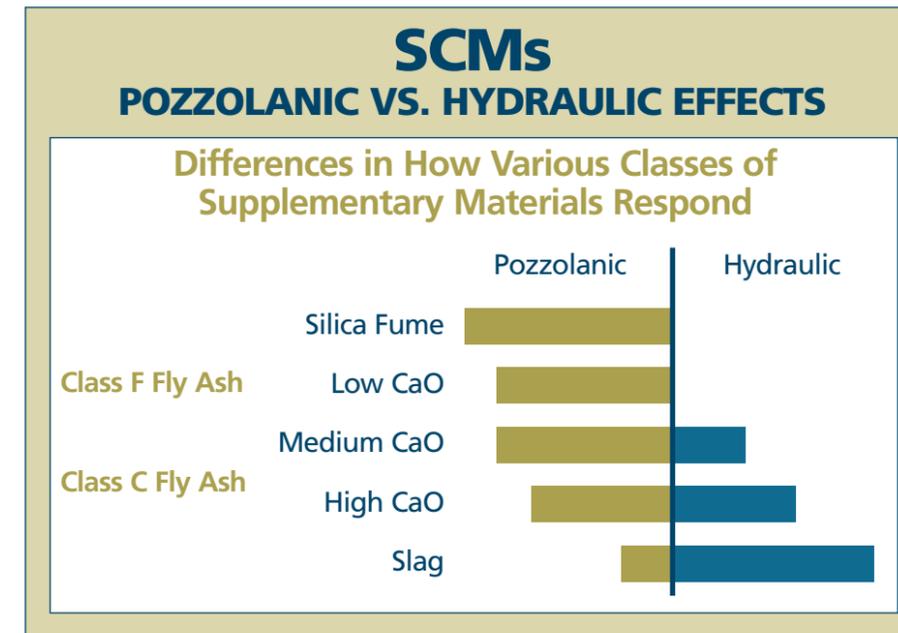
What are SCMs and how can you use them to your advantage?

BY ADAM D. NEUWALD

This is the first of a two-part series covering Supplementary Cementitious Materials. We begin with a discussion on pozzolanic SCMs. Part 2, which will focus on hydraulic SCMs, will appear in the January/February 2005 issue of *MC Magazine*.

Concrete is by far the most widely used construction material because of its low cost, availability of raw materials, strength, durability and, most importantly, versatility. Worldwide, more than one ton of concrete is produced every year for each person on the planet; looking at North America alone, this number jumps to roughly 2.5 tons produced per person per year.

The key to concrete's success is its versatility and no other sector of the construction industry utilizes this attribute more than the manufactured concrete products industry. Concrete can be designed to withstand the harshest environments while taking on the most inspirational forms. Engineers are continually pushing the limits with the help of innovative chemical admixtures and supplementary cementitious materials



(SCMs). Supplementary cementitious materials are often incorporated in the concrete mix to reduce cement contents, improve workability, increase strength and enhance durability.

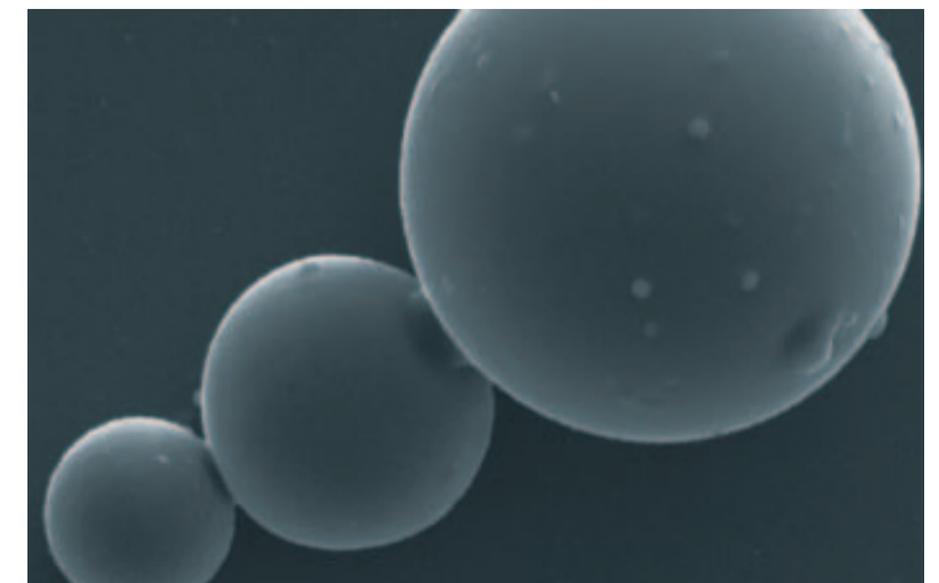
Background

The use of SCMs dates back to the ancient Greeks who incorporated volcanic ash with hydraulic lime to create a cementitious mortar. The Greeks passed this knowledge on to the Romans, who constructed such engineering marvels as the Roman aqueducts and the Coliseum, which still stand today. Early SCMs consisted of natural, readily available materials such as volcanic ash or diatomaceous earth.

More recently, strict air-pollution controls and regulations have produced an abundance of industrial byproducts that can be used as supplementary cementitious materials such as fly ash, silica fume and blast furnace slag. The use of such byproducts in concrete construction not only prevents these products from being land-filled but also enhances the properties of concrete in the fresh and hydrated states.

SCMs can be divided into two categories based on their type of reaction:

hydraulic or pozzolanic. Hydraulic materials react directly with water to form cementitious compounds, while pozzolanic materials chemically react with calcium hydroxide (CH), a soluble reaction product, in the presence of moisture to form compounds possessing cementing properties. Part 1 of this article focuses specifically on pozzolanic SCMs. Part 2 will address hydraulic SCMs, blended SCMs for enhanced performance and a summary of SCMs and



their influence on the fresh and hydrated properties of concrete.

The word "pozzolan" was actually derived from a large deposit of Mt. Vesuvius volcanic ash located near the town of Pozzuoli, Italy. Pozzolanic SCMs can be used either as an addition to the cement or as a replacement for a portion of the cement. Most often an SCM will be used to replace a portion of the cement content for economical or property-enhancement reasons. Here is a brief overview of some of the more common pozzolans used in the manufactured concrete products industry.

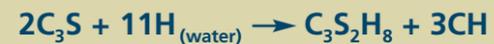
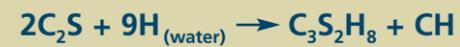
Silica fume

Silica fume is an industrial byproduct of high-purity quartz with coal or coke and wood chips in an electric arc furnace during the production of silicon metal or ferrosilicon alloys. Silica is removed from exhaust gases as it cools and condenses into ultrafine droplets of silica glass. Silica fume has a high content of amorphous silicon dioxide (92 percent to 94 percent SiO₂), is spherical in shape and is extremely small, having an average diameter of about one-tenth of a micron (0.1 μm). An average silica particle is roughly one one-hundredth the size of a cement grain.

Cement Hydration and Pozzolans

Hydration is the result of a chemical reaction that occurs between water and the chemical compounds present in portland cement. Portland cement is predominately composed of two calcium silicates which account for 70 percent to 80 percent of the cement. The two calcium silicates are dicalcium silicate (C_2S) and tricalcium silicate (C_3S). The other compounds present in portland cement are tricalcium aluminate (C_3A), tetracalcium aluminoferrite (C_4AF) and gypsum. For the sake of simplicity this discussion focuses only on the reaction between the calcium silicates and water.

The reaction of dicalcium silicate and tricalcium silicate with water (abbreviated as "H") produces calcium silicate hydrate (C-S-H) and calcium hydroxide (CH), as illustrated in the following chemical equations.



C-S-H accounts for more than half the volume of the hydrated cement paste while CH accounts for about 25% of the paste volume. The remainder of hydrated portland cement is predominantly composed of Calcium Sulfoaluminates (ettringite) and capillary pores.

C-S-H is a poorly crystalline material with a variable composition that forms extremely small particles less than 1.0 μm in size. C-S-H is the main cementitious compound, or glue, that gives concrete its inherent strength. The structure of C-S-H becomes much more stable and resistant to subsequent environmental changes upon prolonged moist curing or curing at elevated temperatures. Calcium hydroxide, on the other hand, is a well-crystallized material with a fixed composition. CH contributes somewhat to concrete's inherent strength because it will form large crystals inside voids, thereby reducing porosity. However, CH is a soluble compound, meaning it will move throughout the pore system in the presence of water, making it extremely vulnerable to chemical attack.

All you really need to remember is that C-S-H is a superior reaction product because it creates a denser microstructure that increases strength, reduces the permeability of the concrete and improves its resistance to chemical attack. The formation of CH, on the other hand, increases the concrete's porosity and is susceptible to sulfate attack. The pozzolanic reaction converts the soluble CH to C-S-H, increasing the overall strength and durability of the concrete.

Silica fume can be used as an addition to cement, but is usually used as a 5 percent to 10 percent replacement by mass for cement. Silica fume is typically more expensive than cement and is considered a property-enhancing material. Silica fume is regularly used in high-strength concrete applications or in concrete products that will be subjected to abrasive or corrosive environments such as coastal applications,

bridge decks or water conveyance structures.

Silica fume is available in a variety of forms. As-produced silica fume is extremely fine and can be delivered in bags or in bulk. The fineness of this material and the ease with which it becomes airborne may create handling problems that raise health concerns, which is why many precasters prefer to use densified or slurried silica fume.

Silica fume is densified by placing the material into a silo and blowing compressed air in from the bottom. The particles then begin to tumble and stick together. Densified silica is available in bags or bulk and mixing times may need to be increased to ensure that the particles adequately break down during the mixing process.

Slurried silica is a water-based material containing roughly 42 percent to 60 percent by mass of silica fume. Most slurries contain a high-range water-reducing admixture (HRWRA) to offset the increased water demand associated with its use. Some silica fume is pelletized for landfill purposes and should not be used in concrete.

Silica fume improves the strength and durability of concrete by creating a denser cement matrix when compared to conventional concrete. Research has found that when silica fume is used at a 15 percent replacement level, there are roughly 2 million silica fume particles for each grain of cement present. This ultimately reduces the porosity of the hydrated cement matrix through improved particle packing. Silica fume fills the voids between cement particles just as cement fills the voids between sand and sand fills the voids between coarse aggregate.

Silica fume also modifies the paste structure around aggregates and other embedded items. This critical region is known as the interfacial transition zone (ITZ) and in conventional concrete is characterized by a massive calcium hydroxide layer laden with voids creating a weak link between the paste and aggregates. Due to their small size, silica fume particles pack around the aggregate more efficiently, reducing porosity, modifying the paste structure and preventing bleeding. Many researchers believe this mechanism gives silica fume concrete its increased strength gain when compared to conventional concrete.

Silica fume is a pozzolan and will consume roughly 50 percent of the cal-

cium hydroxide present within the first 28 days when used at a 10 percent replacement level under normal curing conditions. The pozzolanic reaction is extremely sensitive to temperature and will be greatly accelerated by steam curing and other accelerated curing methods making it possible to achieve much higher early strengths. Due to its extremely small size and high surface area (20,000 m²/kg), silica fume minimizes bleeding, which may lead to plastic shrinkage cracking. Moist curing should begin as soon as possible to prevent this from occurring.

At replacement levels of only 2 percent to 3 percent silica fume may actually reduce the water demand, otherwise the water demand of silica fume concrete is substantially higher because of its extremely high surface area. It is best to use a dispersing agent such as a HRWRA when using silica fume to overcome surface forces, ensuring adequate particle dispersion. Silica fume concrete may be slightly darker in color and has been reported as being "sticky" during finishing.

As previously mentioned, silica fume is a property-enhancing material and can be used to meet durability requirements in project specifications. Precasters often incorporate silica fume in parking garage products; marine structures such as sea walls, docks and pilings, and coastal bridges; and high-



strength mix designs for such products as precast concrete bank vaults. Silica fume also can be used to increase the compressive strength of lightweight concrete as well as conventional concrete, making it possible to reduce the wall thickness or other dimensions of a product to overcome transportation limitations.

Fly Ash

Fly ash is by far the most widely used supplementary cementitious material in the manufactured concrete products industry because of its low cost (about half that of cement), availability and property-enhancing characteristics. Fly ash is a byproduct of the combustion of ground coal for use in electric power plants. It is a fine residue of mineral impurities that melt and recrystallize within the air stream moving through the combustion boiler. The material is then collected from exhaust gases using electrostatic precipitators or filters. According to the American Coal Ash Association, roughly 12.5 million tons of fly ash were used in the production of con-

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For Further Review...

To learn more about SCMs, check out these standards.

ACI Documents

ACI 211.1, "Standard Practice for Selecting Proportions for Normal, Heavyweight and Mass Concrete"

ACI 232.1, "Use of Raw or Processed Natural Pozzolans in Concrete"

ACI 232.2, "Use of Fly Ash in Concrete"

ACI 234, "Guide for the Use of Silica Fume in Concrete"

ASTM Documents

ASTM C 618, "Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolans for Use in Concrete"

ASTM C 1240, "Standard Specification for Silica Fume Used in Cementitious Mixtures"

crete in the United States during 2002.

Fly ash was first used in large-mass concrete structures such as dams to reduce cost and minimize the heat of hydration. Additional research revealed property-enhancing benefits of fly ash, including resistance to certain harmful chemicals, sulfate attack and alkali silica reaction (ASR). The oil crisis during the 1970s also led to the construction of additional coal-burning power plants throughout the United States creating

an abundance of fly ash.

Fly ash is a variable material and its composition is determined by the chemical composition of the coal used by the power plant. There are two basic forms of fly ash characterized by the percentage of compounds present in the material. The four main constituents are silicon dioxide (SiO₂), aluminum oxide (Al₂O₃), iron oxide (Fe₂O₃) and calcium oxide (CaO). ASTM C 618 classifies fly ash based on the sum of the first three constituents (SiO₂, Al₂O₃, Fe₂O₃). When this sum exceeds 70 percent the Class F designation is given to the material while their sum must exceed only 50 percent to be classified as a Class C fly ash. Class C fly ashes also contain higher levels of calcium oxide usually exceeding 20 percent. Class F fly ashes are pozzolanic in nature while Class C fly ashes react both pozzolanicly and hydraulically and will be covered in Part II of this article.

Class F fly ashes have lower calcium contents and are typically derived from higher-ranked coals containing clayey mineral impurities. These coals are typically found east of the Mississippi River. The principal reaction product of Class F fly ash is suggested to be more gel-like and denser than that from portland cement hydration. Class F fly ashes react more slowly than portland cement, compromising the initial

strength gain of the fly ash concrete. Longer set times can be expected as the quantity of fly ash increases, therefore finishing operations may need to be delayed. When using fly ash in the manufactured concrete products industry, accelerated curing methods and extended moisture curing should be used to initiate the pozzolanic reaction and improve initial strength gain.

Fly ash is spherical in shape and greatly improves the workability of fresh concrete by acting like small ball bearings during the mixing and placing process. Typically the amount of water can be reduced by 2 percent to 3 percent for every 10 percent of fly ash used to replace cement. Depending on how fine the fly ash and the content of unburnt carbon, the water content can usually be reduced by about 6 percent to 10 percent with a 25 percent cement replacement.

Unfortunately, fly ash has an adverse effect on maintaining a stable air-void system, especially for higher carbon content Class F fly ashes. The carbon content of fly ash is often given by the Loss on Ignition Value (LOI) shown on the material certification report. This value is obtained by drying the sample of ash and then massing it. The sample is then ignited at 750 C in a muffle furnace. The loss in weight represents the quantity of unburnt carbon present in the material and is often a good indication of how it will affect the air content of the concrete. Trial batches should always be cast prior to using a new material. The air content of the concrete should be measured regularly when using a fly ash with a LOI value greater than 3 percent.

Either type of fly ash can be used as a cement replacement to reduce production costs. Class F fly ashes have also been found to improve sulfate resistance better than Class C fly ashes. However, some ashes with high alumina contents are not as effective in improving sulfate resistance. The following equation developed by the

Bureau of Reclamation can be used to assess the suitability of a fly ash for improving sulfate resistance. Resistance factors (R) below 2.0 have been found to limit linear sulfate expansion to about 0.1 percent after three years of exposure. Typically the lower the resistance factor the better the sulfate resistance.

$$R = (\text{CaO} - 5) / \text{Fe}_2\text{O}_3$$

Raw and processed natural pozzolans

As mentioned earlier, the ancient Greeks and Romans used a combination of lime and volcanic ash to make a cementitious mortar to construct many of the impressive monuments which still stand today. The earliest known use of a pozzolan actually dates back to about 4500 BC. It consisted of a mixture of lime and diatomaceous earth from the Persian Gulf. ACI defines natural pozzolans as "either a raw or calcined natural material that has pozzolanic properties." Calcining is the process of altering the composition or physical state by heating a material below the temperature of fusion. Sources of natural pozzolans that do not require calcining to increase their reactivity are typically located west of the Mississippi River. The price and availability of raw or processed natural pozzolans is dependent on the location of such materials.

Research has indicated that most natural pozzolans produce



hardened concrete properties similar to industrial byproduct pozzolans. Some investigators have even reported that natural pozzolans are more effective in controlling alkali silica reaction than fly ash. More reactive pozzolans such as metakaolin and rice husk ash are often used in the same manner and proportions as silica fume.

Metakaolin is a calcined or "thermally activated" clay and is produced with high purity kaolin-containing clay that is purified by water processing prior to low temperature thermal activation between 600 and 900 C. The material is then

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the performance of the concrete.

Trial batches should always be utilized when changing a mix design and proportions should be calculated in accordance with ACI 211.1, "Standard Practice for Selecting Proportions for Normal, Heavyweight and Mass Concrete." Trial batches also allow production personnel time to become familiar with the new material's behavior. Highly reactive pozzolans such as silica fume, metakaolin and rice husk ash may actually increase initial strength gain, thereby reducing set times. Conversely, less reactive pozzolans like fly ash may delay the strength gain, possibly requiring accelerated curing methods to achieve desired stripping strengths.

The pozzolans mentioned above are available in bulk quantities as well as smaller bags for limited-use applications. You should use the material's bulk density when ordering and be sure your supplier has a sound quality control program in place. Pozzolans may be delivered and stored in the same manner as cement. Take appropriate precautions to prevent cross-contamination should be taken, such as color coding silos or feed lines. Cement should always be batched first followed by the SCM. Pozzolans tend to flow fairly easily, so consider installing a positive shut-off valve to prevent additional material from flowing through the slide or screw once the device is stopped.

Generally speaking, most pozzolans will improve the workability and cohesion of the mix due to improved particle packing. ACI even suggests that this may increase the life of dry-cast equipment. Because of differences in specific gravities, a mix containing a pozzolan as a cement replacement by mass will typically produce a higher yield. The yield of the concrete mix should be adjusted using the specific gravities of the actual materials used.

Pozzolans often have a variable chemical composition which may adversely react with different chemical admixtures. High-carbon content pozzolans typically require an increased dosage rate of air-entraining admixtures to achieve a stable air-void system. Always check the compatibility of your admixtures with the SCM.

One final precaution to consider is the safety of your production personnel. The fine nature of many of these materials may cause a considerable amount of them to become airborne. Materials such as silica fume present a potential health concern which OSHA has recently taken an interest in. Employees handling or working around airborne silica should always wear proper personal protection equipment (PPE) such as respirators and safety glasses.

Part II of this article will cover hydraulic supplementary cementitious materials, blended SCMs as well as a comprehensive review of all SCMs and their property-enhancing characteristics. In the meantime, consult the literature listed in the sidebar "For Further Review ..." to learn more about SCMs. **mc**

ground to a very high fineness (0.5 to 20 μ m) and marketed as high-reactivity metakaolin. Research has shown that calcium hydroxide produced during cement hydration will be completely consumed when high-reactivity metakaolin is used at a 20 percent replacement level. Metakaolin will increase the concrete's strength, reduce permeability and improve workability when a water reducing agent is used. Metakaolin is white in color and ideal for use in architectural concrete.

Rice husk ash (RHA) is a natural byproduct from the processing of paddy rice. The husks, which are approximately 50 percent cellulose, 30 percent lignin and 20 percent silica, are incinerated by controlled combustion leaving behind an ash that predominantly consists of amorphous silica. Rice husk ash is highly pozzolanic due to its extremely high surface area (50,000 to 100,000 m^2/kg). Research has shown that higher compressive strengths, decreased permeability, resistance to sulfate and acid attack, and resistance to chloride penetration can all be expected when a high-quality RHA is used in amounts of 5 percent to 15 percent by mass of cement.

Incorporating pozzolans into a mix design

The choice to use natural and/or industrial byproduct pozzolans is based on availability and economics. If your plant is located near a natural deposit or a source of industrial pozzolans, then the material may be fairly inexpensive and can be used to replace a portion of your cement while improving