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Tech Brief

SUPPLEMENTARY CEMENTITIOUS MATERIALS

Best Practices for Concrete Pavements

INTRODUCTION

The purpose of this tech brief is to describe common supplementary cementitious materials (SCMs), highlight their benefits and drawbacks when used in concrete for highway applications, and discuss recent trends that may affect the use of SCMs during the foreseeable future.

BACKGROUND

State highway agencies (SHAs) and others charged with construction and maintenance of roads and bridges expect one key property from concrete: durability. Meanwhile, service demands placed on concrete structures continue to increase, along with expectations for reduced environmental impact and lower initial and lifecycle costs.

To produce concrete mixtures that satisfy these demands, engineers increasingly turn to SCMs as part of the solution.

HYDRAULIC AND POZZOLANIC ACTIVITY

An SCM is defined by ASTM International as “an inorganic material that contributes to the properties of a cementitious mixture through hydraulic or pozzolanic activity, or both” (ASTM 2015).

Hydraulic activity refers to a property most familiar when discussing hydraulic cement such as ordinary portland cement (OPC). ASTM C125-15a defines hydraulic cement as “a cement that sets and hardens by chemical reaction with water and is capable of doing so under water.” That is, hydraulic cements, including SCMs that have hydraulic properties, react with water to harden, and that hardening process does not require drying.

In the case of OPC, the products formed by the reaction are calcium silicate hydrate (CSH) and calcium hydroxide (CH). The CSH is the desirable product and provides strength; the CH is undesirable, provides little strength, and is a key ingredient in many materials-related distress (MRD) mechanisms (Sutter 2015).

Pozzolanic reactivity refers to the property of a material that needs both water and CH as reactants in order to harden. Again, in the case of OPC-based mixtures, the initial reaction of the cement forms the undesirable CH, but the pozzolan consumes that CH and produces additional CSH. This pozzolanic reaction is the underlying reason why SCMs contribute to durability and can mitigate many MRDs. The most commonly used pozzolan is Class F fly ash.

TYPES OF SCMS

The three individual types of SCMs to discuss are coal fly ash, slag cement, and silica fume. Other materials entering the market include natural pozzolans and alternative SCMs (ASCMs), and these are also discussed briefly in this tech brief.

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Coal Fly Ash

Fly ash is the most common SCM used in concrete. Fly ash is the airborne residue from coal combustion processes and is typically collected from the flue gases by a variety of means including venturi scrubbers, fabric filters, and electrostatic precipitators. These combustion units typically burn pulverized coal as a fuel and, with stable operating conditions and fuel sources, produce a reasonably consistent quality of fly ash. An important characteristic of coal combustion fly ash is the presence of various forms of residual carbon intermixed with the fly ash.

Coal fly ash has been used in concrete since the 1930s with the first results detailing this use published in 1937 (Davis et al. 1937). Currently, more than 53 million tons of pulverized coal combustion fly ash is produced annually in the US, with about 44% beneficially utilized (American Coal Ash Association 2015).

The current single largest source of beneficial fly ash use is for the production of OPC concrete and concrete products, both as a partial cement replacement and as a constituent in blended cements.

Benefits from the use of fly ash include improved workability, decreased heat of hydration, lower-cost concrete, potential increased sulfate resistance and alkali-silica reaction (ASR) mitigation, increased late strength, and decreased shrinkage and permeability (Schlorholtz 2006). However, potential problems exist with fly ash use in concrete, including air-entraining admixture adsorption by residual carbon in the fly ash, ASR-accentuated at pessimism replacement levels, slow initial strength gain, and overall fly ash variability.

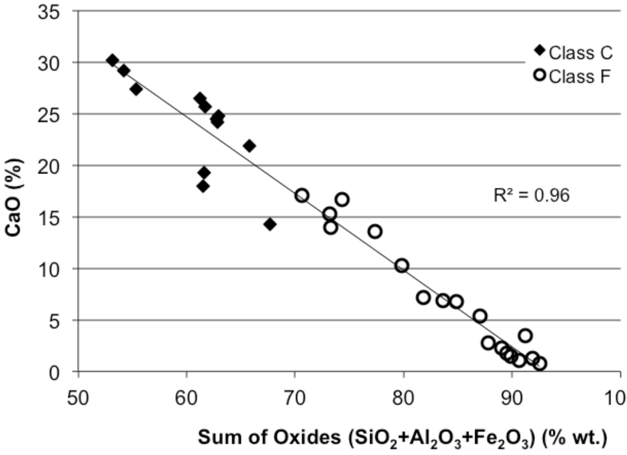
Specification

Depending on physical structure (i.e., crystalline or glassy) and chemical composition, fly ash may be pozzolanic, hydraulic, or exhibit both properties. Although laboratory methods exist to accurately characterize the physical structure, such classifications are not currently practical and fly ash is characterized primarily by its bulk composition.

ASTM C618-15 (AASHTO M 295-11) *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete* classifies fly ash into one of two categories based on the bulk composition. The “sum of the oxides” is used, which is the sum of the silica, alumina, and iron oxides ($SiO_2 + Al_2O_3 + Fe_2O_3$).

The specification defines Class F ash as having a sum of the oxides of 70% or greater, and Class C being 50% or greater. At the extremes of this classification range, Class F ash is pozzolanic and Class C ash is predominantly hydraulic with some pozzolanic properties. Coal ash with a sum of the oxides falling between 50 and 70% will typically exhibit some combination of hydraulic and pozzolanic properties.

This classification approach is widely criticized for being too broad and for not being based on the calcium oxide content (% CaO), which is considered by many to be the more important compositional measure. As shown in Figure 1, a strong relationship exists between the sum of the oxides and CaO content, and either can be used to classify the material into the existing classes used for ASTM C618. However, fly ash properties, such as the ability to mitigate ASR or sulfate attack, are more strongly correlated with CaO content and, therefore, CaO content is commonly considered a better measure of fly ash performance.



Sutter et al. 2013, *NCHRP Report 749: Methods for Evaluating Fly Ash for Use in Highway Concrete*

Figure 1. Relationship between the sum of the oxides and the CaO content for 30 different ashes produced in the US

In Figure 1, the transition between Class C and Class F ash, or between hydraulic and pozzolanic, is approximately 18% CaO ± 4%. Canadian fly ash specifications are based on CaO content and use three classifications: Type F < 8% CaO, Type CI 8-20% CaO, and Type CH >20% CaO (CSA A3000).

In addition to the bulk composition, ASTM C618 and AASHTO M 295 place other limits on fly ash including general compositional restrictions (e.g., SO_3 content, moisture content, and loss on ignition) and some physical properties (e.g., amount retained on the 45 μm sieve strength activity index). Of these latter properties, the strength activity index (SAI) is considered the most problematic with respect to predicting performance.

The SAI test requires that, with a 20% replacement of OPC by fly ash, the tested mortar cubes attain only 75% of the strength of cement-only mortar cubes. It has been demonstrated that inert, non-pozzolanic, non-cementitious materials can meet this requirement (Sutter et al. 2013).

Performance

Because of the wide range of chemical and physical properties observed, different fly ash sources may have vastly different performance characteristics. Table 1 provides a summary of general property changes associated with fly ash substitution for OPC.

Table 1. General changes in concrete mixture properties when Class C or Class F ash is substituted for portland cement in the mixture with comparisons to cement-only mixtures

Property	Class C Replacement	Class F Replacement
Initial Set	Delayed	Delayed
Rate of Strength Gain	Same or higher	Slower
Heat of Hydration	Lower	Significantly lower
Early Strength (3-7 days)	Higher	Lower
Late Strength (28-56 days)	Same or higher	Same or higher
ASR Mitigation?	Only at high replacements	Significant mitigation above pessimism replacement levels

After Kosmatka and Wilson 2011, *Design and Control of Concrete Mixtures: The Guide to Applications, Methods, and Materials*

An important point is that any change in concrete mixture properties not only depends on the specific ash used, but also on the degree of cement replacement.

Even within a given ash class, variations in crystallinity and composition will significantly vary the ash performance. Therefore, fly ash should not be viewed as an “interchangeable part.” If the source of the fly ash changes (i.e., the ash originates from a different power plant) or an existing source changes combustion conditions or fuel source (i.e., coal type), performance of the ash should be verified by testing in concrete.

As mentioned previously, another consideration for fly ash is the amount of unburned carbon in the ash, and also the physical nature of the carbon. The carbon may adsorb the air-entraining admixture (AEA) from the concrete pore water and thereby have a negative impact on the air system of the concrete.

AEAs are long-chain polymers that have a water-loving (hydrophilic) end and a water-hating (hydrophobic) end. As shown in Figure 2, AEA adsorbed on the carbon is not available to stabilize air bubbles.

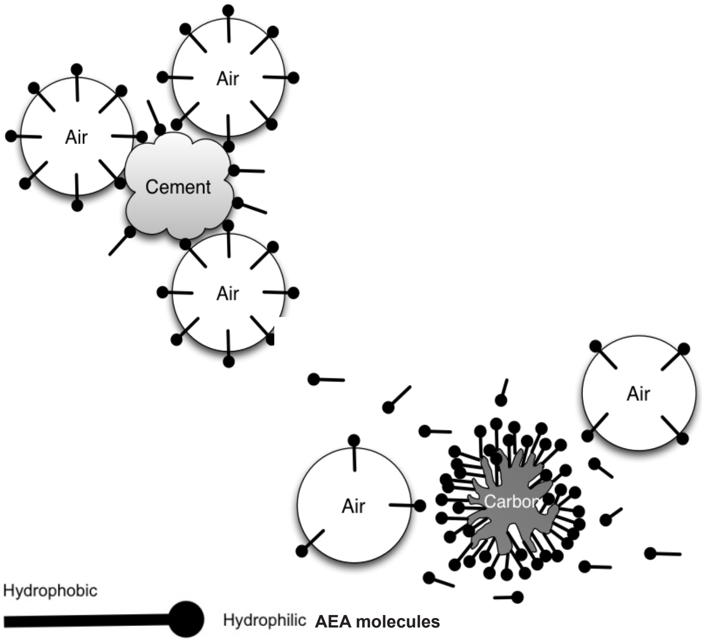


Figure 2. AEA adsorbed on cement and stabilizing air bubbles (top) and AEA adsorbed on carbon unable to stabilize air bubbles (bottom)

The hydrophilic end adheres to the cement grains and the hydrophobic end stabilizes the air bubbles in the mixture. When adsorptive carbon is present, the admixtures are preferentially adsorbed on the carbon and are not available to adsorb on cement and stabilize air, resulting in reduced hardened air content. Significantly increased amounts of AEA may be required in order to achieve a satisfactory air-void system.

The carbon content in fly ash is estimated by the loss on ignition (LOI) test, which determines the total volatile materials, not just carbon. However, the test does not characterize the adsorption capacity of the carbon, which is most important.

Two ashes can have the same LOI content but affect air entrainment very differently. Newly developed tests, such as the foam index test, iodine number test, and direct adsorption isotherm test, provide different approaches to measuring ash adsorption (Sutter et al. 2013). These tests are currently being considered for adoption as standard test methods and have been receiving increased use within the industry.

An emerging issue with respect to carbon is the use of powdered-activated carbon (PAC) as an additive in the coal combustion process to adsorb mercury from flue gases. PAC is highly adsorptive, more so than carbon normally found in fly ash, and a small amount may not significantly affect the LOI value but can drastically affect the ash adsorption properties. As PAC is more commonly included in coal fly ash, the need for adsorption-based tests and specifications will increase.

The most common performance benefit sought from fly ash is for ASR mitigation. A Class F ash, being pozzolanic, is an excellent ASR mitigation tool. Pozzolanic materials consume CH as part of their hydration reaction. The reduction in hydroxyl ions associated with the consumption of CH leads to ASR mitigation.

Because of the variability in ash properties, it is important to verify an ash’s mitigation potential. This is typically accomplished using ASTM C1567 or, in some cases, it may be necessary to perform ASTM C1293.

Class C ashes are not strongly pozzolanic and, therefore, consume less CH and do not mitigate ASR as well as a Class F ash. If a Class C ash is used for mitigation, relatively higher replacement levels are needed (e.g., 35 to 45%).

Slag Cement

Slag cement, previously known as ground-granulated blast-furnace slag (GGBFS), has been used in concrete for well over 100 years (ACI 2011). The first recorded production in the US of blended cement containing both slag and portland cement was in 1896 (ACI 2011).

Slag cement is produced from blast-furnace slag, which results from the reduction of iron ore in a blast furnace to form iron. The iron ore and flux materials are continuously charged in the furnace and the molten iron and slag are periodically and separately tapped off. The molten slag is quenched with water, locking in a predominately glassy structure with a composition very similar to OPC.

Like OPC, slag cement is hydraulic and produces calcium silicate hydrate (CSH) as a hydration product. However, slag cement reacts slower than portland cement; the hydration of portland cement produces CSH and CH and that CH reacts with the slag cement, breaking down the glass phases and causing the material to react with water and form CSH.

Slag cement is not pozzolanic but it does consume CH by binding alkalis in its hydration products. Therefore, although it is a hydraulic cement, it provides the benefits of a pozzolan.

Specification

Slag cement is specified under ASTM C989-15 (AASHTO M 302-15) *Standard Specification for Slag Cement for Use in Concrete and Mortars* (ASTM 2015). The specification is essentially a material-performance specification and classifies the material under three categories: Grade 80, Grade 100, and Grade120.

The numeric portion of the grade classification refers to the relative strength of mortar cubes using the same SAI test included in the fly ash specification with the important exception that, for slag cement, a 25 to 50% replacement of OPC is used.

With this replacement level, based on the average of the last five consecutive samples, slag cement mortar cubes achieving 75% of the 28-day (28-d) strength of cement-only mortar cubes are rated Grade 80, those achieving 95% of the strength ratio are Grade 100, and those achieving 115% of the strength ratio are Grade 120.

It is well known that results of the strength activity test, for both fly ash and slag cement, are strongly affected by the choice of cement used as the reference cement (Sutter et al. 2013). Therefore, ASTM C989 has recently adopted the use of a Cement and Concrete Reference Laboratory (CCRL) reference cement for all SAI testing.

In addition to the strength requirements described, slag cement specifications place limits on the material including general compositional restrictions (e.g., sulfide sulfur) and some physical properties (e.g., amount retained on the 45 μm sieve).

Performance

Slag cement affects the properties of both fresh and hardened concrete. Regarding fresh properties, concrete containing slag cement is consolidated more easily under vibration compared to straight-OPC concrete (ACI 2011). Also, because slag cement is slower to react, setting time can be increased significantly compared to OPC concrete. This latter effect leads to other issues.

Most notably, although curing of any concrete is essential for achieving a quality product, it is even more critical with slag-cement-based concrete. The lower reaction rate, especially at lower temperatures, is often overlooked, and this can lead to durability issues such as scaling. However, the slower reaction rate and associated heat evolution makes slag cement an ideal ingredient for mass concrete placement where control of internal temperatures is critical to achieving durability. Up to 80% replacement of OPC with slag cement is used for mass concrete.

Slag cement is effective at mitigating ASR, but replacement levels higher than 50% of OPC are needed compared to Class F fly ash. The ASR mitigation stems from a number of mechanisms.

First, as previously described, slag cement binds alkalis in its CSH reaction products, thereby reducing one of the key ingredients in ASR. Second, as CH is consumed by the hydration of slag cement, an increased hardened-cement-paste (HCP) density is achieved, resulting in a lower permeability, which improves resistance to ASR and external sulfate attack.

Research has shown that slag performance for mitigating ASR is dependent on a number of factors including the physical and chemical characteristics of the slag cement, the ASR potential of the aggregate, and the alkali content of the portland cement used (Thomas and Innis 1998).

Silica Fume

Silica fume is produced in arc furnaces during the production of silicon alloys. It is an extremely fine (i.e., particle size averaging 0.1 to 0.2 μm in diameter) amorphous silica that is highly pozzolanic.

The first mention of silica fume use in concrete was in a 1946 U.S. patent (ACI 2012a), but the material did not gain wide use until the 1980s. Other amorphous silica products are available (e.g., fumed silica, precipitated silica, colloidal silica) and, although these materials may provide benefits when included in a concrete mixture, they should not be assumed to be equal to silica fume and performance of these materials should be verified through concrete testing.

As stated, silica fume is pozzolanic and provides no hydraulic properties. However, it is highly pozzolanic and very effective when used as a blended ingredient with OPC. Because it has a very fine particle size, silica fume results in an increased water demand, leading to the use of high-range water reducers (HRWRs) to maintain or decrease the water-to-cementitious (w/cm) ratio of the mixture.

Specification

Silica fume is specified under ASTM C1240 *Standard Specification for Silica Fume Used in Cementitious Mixtures*. Regarding chemical classification, the specification places a limit on SiO_2 content of 85% (minimum), along with limits on moisture content and LOI. For physical requirements, there is a limit on the amount retained on a 45 μm sieve and a requirement for the accelerated pozzolanic strength activity index of 105% of control (minimum) at 7 days using a 10% replacement of OPC with silica fume.

The accelerated pozzolanic strength activity index differs from the SAI test in two ways. First, the test requires a constant flow and that the w/cm ratio be maintained between the test and the control samples. To achieve that goal, use of an HRWR is permitted. Second, after 24 hours of moist curing at room temperature, the test samples are further cured at 65º C (150º F) for an additional 6 days, thereby accelerating the pozzolanic reaction.

Performance

Silica fume accelerates the hydration of OPC by providing nucleation sites for the formation of OPC hydration products. This is generally accompanied by an increased heat of hydration, particularly at early ages. Because of its fine particle size, silica fume improves the packing density of the solids and leads to a higher density HCP.

Another important factor that leads to increased concrete strength and durability is that silica fume is able to pack around aggregate particles effectively, consume CH at the aggregate-paste interfacial zone, and greatly improve the strength and impermeability of the interfacial transition zone.

Silica fume is a very effective pozzolan and, when combined with the significant decrease in permeability provided, silica fume is very effective at mitigating ASR and sulfate attack.

Regarding ASR, it is very important to achieve good dispersion of the silica fume in the concrete mixture. Clumps of silica fume can act like an expansive aggregate and actually contribute to ASR.

Unlike fly ash or slag cement, which are typically less than or equal to OPC in cost, silica fume is more expensive, limiting its use to a few key areas. However, when low permeability, ASR and sulfate attack mitigation, or high strength is required, silica fume may be considered. In fact, silica fume is widely used in bridge-deck mixtures, where all of the above properties are desired.

Silica fume is also becoming more common in blended products, particularly ternary mixtures, which are discussed in a following section.

NATURAL POZZOLANS AND ALTERNATIVE SCMS

With issues of availability for other SCMs, natural pozzolans and ASCMs are attracting interest within the industry. Natural pozzolans have been used in varying degrees for many years, arguably dating back to Roman times.

One of the first large-scale construction projects that used natural pozzolans was the Los Angeles aqueduct, constructed from 1910 to 1912 (ACI 2012b). Numerous other large projects have been constructed using natural pozzolans.

Some natural pozzolans can be used as removed from the ground, but most require some sort of processing such as drying, calcining, or grinding. Examples of natural pozzolans include some diatomaceous earths, opaline cherts and shales, tuffs and volcanic ashes, pumicite, and various calcined clays and shales. Natural pozzolans are specified under ASTM C618 (AASHTO M 295).

When considering the use of natural pozzolans, concrete testing should be performed as the pozzolanic properties can vary significantly from other materials such as fly ash.

Alternative SCMs are defined as inorganic materials that react, pozzolanically or hydraulically, and beneficially contribute to the strength, durability, workability, or other characteristics of concrete, and do not meet ASTM specifications C618, C989, and C1240 (ASTM 2011). Examples include some slags or fly ash from co-combustion processes such as coal with biomass.

These materials have been used in limited applications, but, in some markets, ASCMs could offer an alternative to conventional SCMs. ASTM C1709 *Standard Guide for Evaluation of Alternative Supplementary Cementitious Materials (ASCM) for Use in Concrete* (ASTM 2011) was developed to provide a clear methodology for evaluating these materials, and it is recommended that the protocol be followed when evaluating these materials for use in highway construction.

TERNARY MIXTURES

Ternary mixtures are concrete mixtures that contain OPC and two other materials in the binder fraction. The binder materials may be combined at the batch plant, or obtained as a pre-blended product.

In general, ternary mixtures perform in a manner that can be predicted by knowing the characteristics of the individual ingredients.

A benefit of ternary mixtures is that negative properties of a one SCM can be offset by positive properties of another. Overall, the combined use of SCMs in this manner allows for reduction of the OPC content, which leads to performance, economic, and environmental benefits. Table 2 shows some key properties of concrete and how those properties are affected by SCMs.

Table 2. Properties of concrete mixtures and the general effect of each SCM type on that property

Property	Class C Ash	Class F Ash	Slag Cement	Silica Fume
Initial Set Time	+	+	+	–
Strength Gain (early)	+	–	–	+
Strength Gain (late)	0	+	+	< >
Setting Time	+	+	+	–
Heat of Hydration	–	–	–	+
Plastic Shrinkage Cracking	< >	< >	< >	+
Permeability	–	–	–	–
ASR Mitigation	< > or 0	+	< > or +	+
Sulfate Attack Mitigation	0	+	< > or +	+

+ indicates increase, – indicates decrease, 0 indicates no change, and < > indicates the effect varies depending upon the characteristics of the SCM or the replacement level

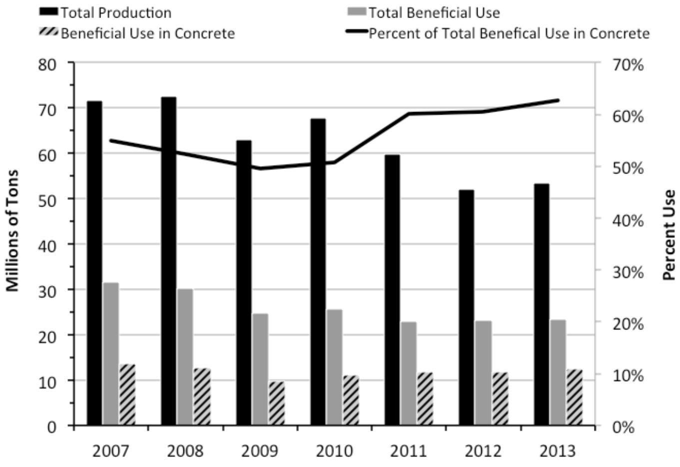
After Kosmatka and Wilson 2011, *Design and Control of Concrete Mixtures: The Guide to Applications, Methods, and Materials*

Based on these general observations, ternary combinations can be envisioned that result in overall better performance.

TRENDS

A few general trends are worth noting. First, the use of SCMs is increasing overall. This is due to a number of factors including lower initial cost and improved concrete durability. Regarding the latter, there is an increasing recognition that blended cements (i.e., ASTM C595 or AASHTO M 240) and ternary blends can significantly improve durability. There is also an increasing need for SCMs to mitigate ASR as the availability of high-quality aggregates decreases.

For SCMs, the largest single concern is fly ash availability. The issue with fly ash can be seen in Figure 3.



American Coal Ash Association Inc. 2015

Figure 3. Trends in fly ash production and beneficial use

From 2007 through 2013, the total production of fly ash decreased by approximately 25%; however, the amount of fly ash used in production of cement and concrete continued to be used at a rate of 10 to 12 million tons (9 to 11 million metric tons) per year. At the same time, total beneficial use of fly ash over this period decreased significantly, with the result that, in 2013, beneficial use of fly ash in concrete was 63% of the total beneficial use of fly ash.

A significant amount of ash is still unused, but much of that ash is either unsuitable for use in concrete without post-combustion processing or the material is generated at locations that are a significant distance from the point of use. In some cases, the availability of transportation limits the ability to get usable ash to market. The net result is that some shortages of ash have been reported.

Recovered fly ash landfills or impoundments could become an increasing share of the total fly ash supply over the next few years. The recovered ash would need to be processed to remove LOI or contaminant materials, which would impact the material cost. When processed, the ash would need to meet the chemical and physical specifications of ASTM C618. However, the concrete industry has limited experience with such materials and the performance of recovered ash will need to be established through field experience.

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