Opportunities from Alternative Cementitious Materials

An Accelerated Technology Implementation Team works toward enhancing twenty-first century concrete construction by encouraging new, more sustainable cements

by James K. Hicks, Michael A. Caldarone, and Eric Bescher

A major impetus for change in cement technology stems from the concrete industry's sustainability goals and the associated demand for reductions in the collective environmental impacts of the production of concrete. These impacts include immediate effects such as greenhouse gas (GHG) emissions, extraction of virgin materials (including water), and energy consumption,[1] and they can be compounded by premature repair or replacement as the result of inadequate durability. Alternative cementitious materials (ACMs) have the potential to provide major reductions in these impacts.

ACM concretes can be produced with significantly lower GHG emissions and energy consumption than mixtures comprising portland cement. In some cases, the amount of water required in the concrete mixture is also significantly lower. Further, ACM concretes can exhibit improved durability—exemplified by reduced permeability, greater resistance to freezing and thawing, and enhanced resistance to high temperatures and chemicals[2]—resulting in increased service life.

Purpose and Driving Forces

Because traditional construction materials are well understood and established in existing codes, specifications, and test methods, there is a natural, cultural resistance to the introduction of new materials. Although most ACMs are now permitted in building codes, including ACI 318-14,[3] and are included in two ASTM standards: ASTM C1157/C1157M, "Standard Performance Specification for Hydraulic Cement," and ASTM C1600/C1600M, "Standard Specification for Rapid Hardening Hydraulic Cement," resistance is still evident in the common use of prescriptive specifications calling for portland cement concrete. The more widespread use of performance specifications based on an owner's requirements could allow more extensive application of ACM concrete.

The Strategic Development Council's Accelerated Technology Implementation (ATI) Team on ACMs is working to help the industry develop usable specification and design information to facilitate safe and reliable use of ACMs and thereby achieve inherent reductions in energy consumption and GHG

Impetus for Change

ACI's Strategic Development Council (SDC) helps to identify and facilitate the application of Industry Critical Technologies (ICTs) throughout the concrete industry. ICTs include tools, materials, and procedures that SDC's Technology Management Committee has determined as having high potentials for positively affecting concrete industry competitiveness and enhancing the sustainability and/or quality features of concrete.

ICTs have strong and broad support from SDC members, from among whom a champion is identified. The champion, together with other interested SDC members, forms an Accelerated Technology Implementation (ATI) team to identify those barriers that are restraining or obstructing the timely acceptance of the ICT within the construction industry at large. The ATI team develops strategies and tactics to remove the identified barriers, and these often include interacting with Standards Developing Organizations such as ACI.

The ATI Team on Alternative Cementitious Materials (ACMs) is developing a state-of-the-art report on ACMs, providing current information regarding binders other than portland cement. The ATI Team's goals include establishing a guideline or practice within ACI, thereby encouraging concrete industry practitioners to specify, formulate, and use ACMs to produce highly sustainable concrete mixtures with enhanced durability and increased service life.

emissions, as well as other environmental benefits. As part of that work, the ATI Team has developed a state-of-the-art report (SOAR) on ACMs.

The central reason for the development of a SOAR and associated guide was to enhance the industry's understanding of ACMs, with the intended result of overcoming the resistance to using ACMs in place of portland cement in concrete. This article provides a summary of the materials covered in the SOAR.

ACM Concrete Systems

ACM concretes include concretes in which the cementitious phase contains no portland cement. ACM concretes generally can be produced and placed using methods and equipment applicable to standard concrete. They also have performance characteristics that are similar to or better than those for standard concrete.[4]

ACM concrete can contain geopolymers, activated glassy cements, hydraulic fly ash cements, activated slag cements, calcium aluminate cements, calcium sulfoaluminate cements, magnesia-based cements, or CO_2-cured cements. While geopolymers, activated glassy cement, and hydraulic fly ash cements can comprise fly ash, they have distinctive differences. Geopolymers are typically produced from low calcium content fly ash and are activated by alkali hydroxides, sodium silicate, or both with water. Activated glassy cement is typically produced from high-calcium fly ash and is activated with a high-pH activator coupled with an organic acid and water. Finally, hydraulic fly ash cement is typically produced from high-calcium fly ash and activated with a pH-neutral activator coupled with a retarder and water.

Geopolymers

Over the past 30 years, scientists have pursued various methods to produce fly-ash-based cements known as geopolymers. The fly ashes typically have low calcium content and are activated by alkali hydroxides, sodium silicate, or both in water. Geopolymers reportedly attain strength through polymeric silicon-oxygen-aluminum framework structures.[5] Typically, concrete made with geopolymer cement loses plasticity within a few minutes after mixing and also requires elevated curing temperatures of 60 to 150°C (140 to 302°F) for the initial few days.[6] As a result, geopolymer cement concrete has had limited acceptance in the construction industry. However, at least one geopolymer concrete, based on the chemical activation of a mixture of slag cement and fly ash, has been successfully used for airport and building construction.[7]

Activated glassy cements

Activated glassy cements are made of either natural materials such as clays or industrial by-products such as fly ash and slag cement. The glassy components are typically aluminosilicates. When combined with water and a functional addition that meets ASTM C688, "Standard Specification for Functional Additions for Use in Hydraulic Cements," these materials form hydraulic cement per ASTM C1157/C1157M. The functional additions typically raise the pH, thus increasing the reactivity of the glassy phases. As the concentration of alumina and silicate species approach saturation in the pore fluid, an amorphous to semicrystalline inorganic polymer is formed that, in some cases, may be similar to a geopolymer.[6]

Hydraulic fly ash cements

A more recent glassy cement system comprises Class C and Class F fly ash with a proprietary, non-alkali activator.[8] The hydration product is mainly composed of a calcium-alumino-silicate-hydrate that forms the binder phase. This is in contrast to the calcium-silicate-hydrate (CSH) gel that is the primary binding phase of portland cement concretes.[9]

Depending on the curing conditions and the concentration of the activator, hydraulic fly ash cement can exhibit a wide variety of beneficial properties including high compressive strength, low creep and drying shrinkage, good acid resistance, and good fire resistance. Also, the system will not promote deleterious expansion associated with alkali-silica reaction. The spherical shape of fly ash particles is beneficial for reducing water demand and for maximizing particle packing to reduce porosity.[10]

Activated slag cements

An activated slag cement concrete is one in which the binder phase is made of ground-granulated blast-furnace slag (GGBFS), water, and an activator that triggers the chemical reactions involving dissolution of slag cement and polymerization of calcium-silicate and aluminum-silicate phases that serve as the binder. Although slag cement can self-activate, external activators are needed to enhance reaction rates and form stronger products. Sufficient alkali content is also necessary for the development of significant strength. Because slag cement is deficient in alkalis, these have to be supplied externally.

Alkali-activated slag cement displays very good strength[11] and durability,[12] and it exhibits a variety of other potentially valuable characteristics, such as fire resistance and resistance to damage associated with contact with waste water.

Calcium aluminate cements

Calcium aluminate cements (CACs) are a special class of cement containing primarily aluminates and calcium. Small amounts of ferrite and silica are also typically present. CACs were developed in the early 1900s to resist sulfate attack. CACs are inherently rapid hardening and can be rapid setting. The setting time is adjustable with appropriate chemical admixtures. These cements are often used in repairs, rehabilitation, and construction of concrete flatwork (for example, sidewalks and overlays). The rapid hardening properties, resistance to sulfate attack, and abrasion resistance (as well as being a material that does not promote alkali-aggregate reaction) make these cements desirable in a wide range of special applications. The manufacturing process for CACs generates significantly less CO_2 than portland cement production—roughly on the order of 50%. However, slightly more grinding energy is required than for portland cement due to the increased strength of the clinker.[13]

Several building collapses in the 1970s were attributed to CAC conversion, a process in which metastable phases of the CAC hydration products convert to more stable hydration products with smaller crystalline structure. Conversion results in an increase in the porosity of the overall matrix, and the strength decreases by as much as 50%. Many structural codes subsequently banned the use of this material. Since this time, intensive research has provided a greater understanding of CAC chemistry and behavior, allowing the development of concrete mixtures with reduced conversion rates.

Calcium sulfoaluminate cements

Calcium sulfoaluminate (CSA) cements are a type of rapid-setting or shrinkage-compensating cement that first came to prominence in the 1970s. They are receiving increasing examination from the cement industry and researchers as a lower-energy, lower-CO_2 alternative to portland cement. Such cements contain as a primary phase ye'elimite—$(CaO)_4(Al_2O_3)_3SO_3$ or $C_4A_3\overline{S}$ in cement chemistry notation—which was used by Alexander Klein in the 1960s as an expansive additive to portland cement and is sometimes called Klein's compound or salt.[14] These cements are defined within the $CaO–Al_2O_3–SiO_2–Fe_2O_3–SO_3$ compositional system.

To date, studies on the durability of CSA cements have been promising. In addition to their beneficial setting and shrinkage properties, long-term strength and durability have been shown to exceed those properties for portland cement. These cements have seen widespread and high-volume use as bridge decks, airport runways, and pavement patching materials, where rapid setting is required.

Significant environmental advantages are associated with CSA cements. Less limestone is required in the production of the calcium sulfoaluminate clinker needed for CSA, so its production generates less CO_2 per unit of raw material than portland cement. The calcining of the raw materials for clinker formation also occurs at temperatures of 1160 to 1200°C (2120 to 2190°F), much lower than those used for firing portland cement clinker (1450°C [2640°F]).

Magnesia cements

Magnesia cements are a range of cements based on magnesium oxide (MgO) as the key reactive ingredient. The first type of magnesia cement—magnesium oxychloride—was developed by Stanislas Sorel in 1867 and is now referred to as Sorel or magnesite.[15]

With varying levels of success, a variety of other magnesia cements have been developed based on permutations of MgO as the binding phase. Magnesium oxysulfate cements have similar properties to magnesium oxychloride cements. Poor weathering resistance is the main drawback for this type of cement.

Magnesium phosphate cements are characterized by very high early strength and rapid setting—properties that make these cements useful as a rapid patching mortar. Unlike magnesium oxychloride and oxysulfate cements, magnesium phosphate cements have good resistance to water and freezing-and-thawing cycles. A major drawback, however, is the cost of the cement (due to the high cost of phosphate), which limits applications to niche areas.

CO_2-cured cement

CO_2-cured cement is composed primarily of low-lime calcium silicate phases such as wollastonite/pseudowollastonite ($CaO \cdot SiO_2$) and rankinite ($3CaO \cdot 2SiO_2$) in contrast to the high-lime alite ($3CaO \cdot SiO_2$), belite ($2CaO \cdot SiO_2$), tricalcium aluminate ($3CaO \cdot Al_2O_3$), tetracalcium aluminum ferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$), and gypsum ($CaSO_4 \cdot 2H_2O$) phases present in portland cement. CO_2-cured cement is made from the same raw materials as portland cement and existing portland cement plants can be used without modification for its manufacture. However, the clinker of CO_2-cured cement is produced at a temperature of about 1200°C (2190°F)—about 250°C (450°F) lower than the temperature used in portland cement clinker manufacturing—reducing CO_2 emissions by about 30%.

Concrete products comprising CO_2-cured cement are manufactured using the same basic mixing and forming processes as those comprising portland cement. However, while mixing water is used, CO_2-cured cement is not a hydraulic cement because setting and hardening develop from reactions between the calcium silicates in the cement and CO_2 that's supplied during the mixing of the concrete. These reactions form calcite ($CaCO_3$) and silica (SiO_2), respectively, allowing concrete products to sequester up to 300 kg of CO_2 per tonne (600 lb of CO_2 per ton) of CO_2-cured cement. The reduced emissions during manufacturing of the cement and the sequestration of CO_2 during curing of the concrete reduces the carbon footprint of CO_2-cured cement by up to 70% relative to portland cement.[16]

Relevant Testing Standards

Relevant standards for testing ACMs are listed in Table 1. Currently, the standards are focused on hydraulic cements.

Gaps to Close for Industry Acceptance

Contracting procedures involve multiple stakeholders who all must agree to move forward on a project. This can be difficult when new products, regulations, or specifications are introduced. Broader familiarity with ACMs, particularly among contractors, will help alleviate some of this difficulty. Prescriptive codes and regulations can also restrict the widespread deployment of ACM concrete technology. Some items that need to be updated and improved are:

- Many building and transportation structure codes restrict supplemental cementitious materials (SCMs) constituents to a maximum of 25% for members that will be exposed to deicing chemicals. This limit is based on the results of aggressive lab tests that do not necessarily match field conditions and performance. Use of a realistic performance specification can help overcome this obstacle;
- Many guide specifications do not include ACMs. The industry must work to broaden the material lists in specification templates;
- Many architects and project engineers are not aware of the benefits of using ACMs. An education and promotion program is needed;
- Many packagers and producers may be unwilling to allocate resources to production of ACM concretes and products. Studies and white papers that show the economical and performance benefits of ACM concrete production can help overcome this obstacle; and
- Additional standards may be required for acceptance of nonhydraulic binders.

Table 1:
Relevant standards for alternative cements

Standard	Geo-polymers	Activated glassy cements	Hydraulic fly ash cements	Activated slag cements	Calcium aluminate cements	Calcium sulfoaluminate cements	Magnesia cements	CO_2-cured cements
ASTM C1157/C1157M	Possibly meets	N/A	Meets	Meets	Meets	Meets	No	N/A
ASTM C1600/C1600M	No	No	Meets	No	Meets	Meets	No	N/A
ACI 318-14	Possibly meets	N/A	Meets	Meets	Question-able	Meets	No	N/A

If sustainability is defined as service life (in years) per unit of nonrenewable resources used, ACMs are among the alternatives with the highest sustainability. The carbon footprint of ACMs is much lower, while the anticipated service life for ACM concrete is the same as or greater than that for concretes produced comprising generic cement. ACMs can therefore be expected to see increasing use.

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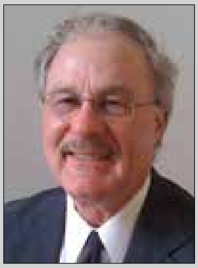
Note: Additional information on the ASTM standards discussed in this article can be found at **www.astm.org**.

Selected for reader interest by the editors.



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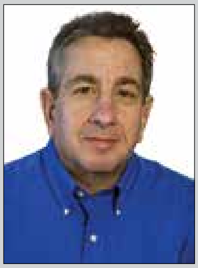

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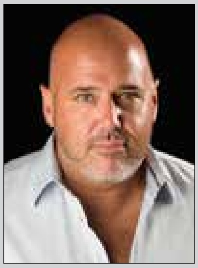

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