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Report on Alternative Cements

Reported by ACI Innovation Task Group 10



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Report on Alternative Cements

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This report addresses available and emerging alternative cements with the intent to facilitate the adoption of these new materials. Given the initiatives to address the sustainability of construction, owners, architects, and engineers are actively seeking alternatives to portland cement for concrete. An alternative cement is intended to be a replacement for portland cement in some applications. In some cases, alternative cements can also be used in combination with portland or blended hydraulic cements. In addition to a reduced environmental impact associated with their production and use, alternative cements offer improved performance over portland cement in some applications. Various alternative cement technologies are discussed, including their physical and compositional characteristics, methods of production, fresh and hardened properties, and example applications. Additionally, the applicability of existing tests methods for specifying alternative cements is discussed and new testing needs are identified.

Keywords: alkali-activated; alternative cementitious materials; alternative cements; calcium aluminate cement; calcium sulfoaluminate cement; carbonated calcium silicate cement; geopolymers; magnesium oxychloride cement; magnesium phosphate cement; supersulfated cement.

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CHAPTER 1—INTRODUCTION AND SCOPE

1.1—Introduction

This report provides a summary of alternative cement technologies currently available or emerging for construction use. This report also identifies the need for development of test methods to facilitate the use of alternative cements with the same level of reliability expected from portland cement. The goal of this document is to introduce the concrete construction community to alternative cements and increase their knowledge base, experience, and confidence in their

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use. Because of the long history of using portland cement as the exclusive or primary cement for concrete construction, concrete specifications and design codes have an inherent assumption, or in some cases a requirement, that portland cement is the primary cementitious binder material to be used. Supplementary cementitious materials are commonly used but very rarely as a complete replacement for portland cement. Because alternative cements are developing and their commercialization is increasing, it is important that engineers, architects, contractors, and owners become familiar with alternative cement properties and applications, and be knowledgeable of how to test these materials.

1.2—Scope

This report addresses available and emerging alternative cements, with the intent of introducing these materials and facilitating the development of test methods to address their safe and reliable use. The discussion herein includes material properties, production methods, and testing methodologies. References made to portland cement and portland cement production are for comparison purposes only. An in-depth discussion of portland cement is not within the scope of this report.

1.3—History

In its simplest conception, concrete consists of aggregates bonded together using a cohesive binder, or cement. More than 2000 years ago, concrete was produced with noteworthy cement technologies such as those used by the Romans in construction of the Pantheon and Colosseum (Kosmatka and Wilson 2011). These ancient concrete mixtures relied on lime or various natural cements and pozzolans for the cohesive binder. Since its introduction in 1824, portland cement has universally become the most common cement for concrete given its relatively low cost, uniformity, availability, and ease of use.

Portland-cement concrete (PCC) is the most widely used manmade material and is unrivaled for its versatility and durability. Because of these general characteristics, PCC is an indispensable ingredient of modern civilization, used in the construction of civil engineering and architectural structures, including roads, bridges, public water and sanitary systems, and buildings.

Like many manufacturing processes, portland cement production is not without detriment to the environment with respect to the energy-intensive nature of its production and the inherent release of greenhouse gas (GHG) emissions. Production of portland cement begins with a mixture of raw materials that includes limestone, which is primarily calcium carbonate (CaCO_3) and shale. These materials are heated in a rotary kiln to temperatures of approximately 2460 to 2640°F (1350 to 1450°C) to produce clinker. The conversion of calcium carbonate to calcium oxide by heating is called calcining. In this process, carbon dioxide (CO_2) and other GHG emissions are created. The primary source of CO_2 is the conversion of CaCO_3 to CaO . Additional CO_2 is released through burning fossil fuels to heat the kiln. The negative results of this process are a high energy demand due to the

temperatures needed for producing portland-cement clinker and the identified GHG emissions. Although portland cement is a minor ingredient in PCC, it is the principal source of embodied energy and GHG emissions for the material. There are numerous papers and references discussing the environmental footprint of portland cement with a brief list referenced here (Hanle et al. 2009; Kosmatka and Wilson 2011; NRMCA 2012; EPA 2012). With respect to both embodied energy and GHG emissions, the state of the art for portland cement production is approaching the point where only minimal additional reductions can be expected using existing production technologies.

Given recent initiatives to address the sustainability of everything we do as a society, owners, architects, and engineers are actively seeking alternatives to portland cement to meet the demand for concrete. It is unlikely that portland cement will be completely replaced as the primary cement for producing concrete, but there are applications in which available alternative cements can be used. Adoption of alternative cements can result in numerous environmental advantages, including the beneficial and effective incorporation of recycled and residual materials, and reductions in the embodied energy and GHG emissions associated with PCC.

In addition to environmental advantages, alternative cement concrete can perform better in specific applications when compared to PCC. Examples of performance improvements include faster setting times, increased wear resistance, and improved chemical or fire resistance.

CHAPTER 2—DEFINITIONS

ACI provides a comprehensive list of definitions in “ACI Concrete Terminology.” Definitions provided herein complement that source.

alkali activation—the process of using an alkali-based solution to cause the dissolution of an aluminosilicate precursor and to initiate the chemical reactions leading to the formation of reaction products.

alkali activator—an alkali-based solution that causes alkali activation, such as sodium hydroxide and sodium silicate solutions.

alternative cement—an inorganic cement that can be used as a complete replacement for portland or blended hydraulic cements, and that is not covered by applicable specifications for portland or blended hydraulic cements.

Note: An alternative cement or alternative cement blend could provide better performance than that of portland or blended hydraulic cement in some applications. An alternative cement, however, might not perform adequately as a replacement for portland or blended hydraulic cement in every application. In some cases, alternative cements can also be used in combination with portland or blended hydraulic cements.

ambient-cured—curing without the addition of heat above that available from room or the external environment.

calcined alternative cement—an alternative cement produced by calcining a raw material only, without further pyroprocessing, to produce additional mineral phases within the material.

clinkered alternative cement—an alternative cement produced using technologies similar to portland cement production, with process changes that preclude production of portland cement but positively affect the environmental impact of production.

functional addition—a substance other than water that is added to, or combined with, a material that is not hydraulic and causes a cementitious reaction to occur or accelerate.

geopolymer—an alternative cement produced from alumino-silicate precursors that form nonhydrated cementitious reaction products by alkali activation.

geopolymerization—a spontaneous reaction that results in the bonding of smaller inorganic polymers to form larger ones.

heat-cured—curing with the addition of heat above that available from room or external environment.

non-clinkered alternative cement—an alternative cement produced using precursors that require no pyroprocessing and set after addition of an activating solution to cause reactions that are not hydration or acid-base.

precursor—a solid raw material reacted with a functional addition to form an alternative cement

CHAPTER 3—BACKGROUND

3.1—Performance measures for alternative cements

To serve as an alternative to portland cement, a binder technology needs to offer demonstrable improvements in one or more areas, including environmental impact, life-cycle cost (LCC), and performance. The cost of an alternative cement needs to be competitive when compared to portland cement, but most importantly, an alternative cement will be expected to meet all specified functional performance requirements. Each of these factors will be briefly discussed.

3.1.1 Environmental impact—With respect to environmental impact such as greenhouse gas (GHG) emissions and embodied energy, alternative cement concrete typically compares favorably to PCC. The manufacture of portland cement accounts for approximately 70 percent of the total embodied energy and 88 percent of the CO₂ emissions for a 3000 psi (20 MPa) PCC mixture (Nisbet et al. 2002). By using alternative production techniques or precursor materials, alternative cement concretes can be produced with a reduced environmental impact.

There are numerous aspects to assessing environmental impact and in-depth analysis is beyond the expertise of most people in the construction industry. To summarize the environmental impacts of any product, the construction industry has responded to the need-to-know by issuing an environmental product declaration (EPD) for each product, which summarizes the various impacts associated with that product. An EPD is developed within the framework of a product category rule (PCR); as alternative cements enter the market, PCRs and the associated EPDs are developed, allowing comparisons between the various cementitious systems.

3.1.1.1 Life-cycle cost—Increasingly, construction alternatives are being considered in terms of their LCC, in addition to or in place of the initial cost. LCC considers the total cost of ownership of an asset from cradle-to-grave, or when recycling and reuse is possible, cradle-to-cradle. Typical life-cycle aspects considered when determining the LCC include planning, design, construction and acquisition, operations and user costs, maintenance, renewal and rehabilitation, depreciation and cost of finance, and replacement or disposal costs. Note that not all costs factored into an LCC are direct monetary costs. An example for concrete is that a portion of the materials LCC will be attributed to the environmental impact of producing the cement used. In an economic environment where carbon credits/taxes exist, this environmental impact can be assigned a monetary cost as well. In the absence of a tax or credit, converting these life-cycle aspects to monetary cost is more problematic.

The choice of binder system for a concrete will impact the LCC in various ways. As stated previously, if the material is produced with a smaller environmental footprint when compared to another material, nonmonetary environmental impact costs will be reduced. How the material performs in service could impact operation and maintenance costs. Characteristics of the material may also impact the renewal, rehabilitation, replacement, and disposal costs. As an industry, there is considerable experience with PCC and, therefore, the individual factors that contribute to LCC are more easily estimated. This is not the case for some alternative cements due to a more inexperienced industry. The LCC of a construction material is inextricably linked to its durability.

3.1.1.2 Initial cost—To be competitive with PCC, an alternative cement concrete does not necessarily need to have the same initial cost. In the past, an equal initial cost, or lower cost, would clearly be a necessary starting point, as initial cost was the only consideration. However, with LCC increasingly being used as a decision tool in selecting materials for construction, other factors are now considered. When comparing initial costs for a project, it is important to ensure the comparisons are made on an intellectually honest basis. One cannot compare the materials cost for an alternative cement concrete to the cost of PCC if either option cannot fulfill the requirements of the project.

When considering the initial cost, it is necessary to consider the in-place cost, including labor, equipment, curing methods, and construction time because performance improvements of the binder system may allow for savings in other areas of construction and ultimately reduce the total project cost. Construction contractors are constantly seeking ways to lower their total cost or improve their profitability and ability to compete; alternative cements provide a new opportunity to achieve lower project costs when all factors are considered. As one example, when rebuilding the Santa Monica Freeway after the 1994 Northridge earthquake, the contractor received a \$14.5 million bonus for early completion and one factor leading to the early completion was the use of an alternative cement for portions of the construction (Mitchell et al. 1995; Philips 2005).

3.1.1.3 Functional performance—Although modern construction practices demand more environmentally-friendly materials, and, to a degree, a smaller environmental footprint can offset a higher monetary cost, functional performance will always be the key measure. If a material cannot meet project requirements, the material should not be used in construction. Many performance benefits result from the use of alternative cements in concrete, including faster set times, rapid strength gain, low permeability, heat resistance, and others. However, as alternative cements seek to replace PCC in more conventional applications, unique qualities are less important and specifiers seek similar performance when alternative cement concrete is compared to PCC. This is mainly due to the empirical nature of the concrete design and construction environment.

Demonstrated performance, both in the laboratory and in practice, is required to ensure that life-safety considerations and performance are met when using alternative cement concrete in place of PCC. Providing this information to specifiers has been a challenge for alternative cement producers largely due to the lack of a clear testing protocol or, in some cases, the lack of applicable tests. Without needed information, it is difficult to provide a demonstrated example, or even an accurate prediction, of a design life for structures using new types of concrete. As mentioned previously, the LCC of a construction material is inextricably linked to its durability. Therefore, developing data on long-term durability is a necessary step to increasing use of alternative cements.

Another aspect of functional performance is constructability. To achieve the desired hardened properties, the concrete requires proper placement and curing in the field. This aspect alone may limit the application of some alternative cements, while for others it can be an advantage. Constructability also depends on the availability of knowledgeable professionals to place, troubleshoot, or adjust mixture designs to achieve the desired performance. This means it will be necessary to have a workforce that is trained to proportion, test, mix, place, and cure these new materials.

3.2—Summary

Concrete produced using alternative cements offers numerous advantages and opportunities, which will be discussed in subsequent chapters of this report. Along with the advantages, however, is a discussion of the challenges to be resolved before alternative cements can be more commonly used in everyday construction. One challenge is the industry's desire to compare these new materials to PCC using the same metrics and methods that have historically been used, which may not be appropriate.

The general criteria of initial cost and the material's functional performance in the existing design environment are key factors but are not the only considerations. The desire for a more sustainable construction industry requires consideration of LCCs that, in turn, allows the environmental advantages of alternative cement production to be considered.

Table 4.1a—Classification of commercially available and emerging alternative cement technologies

Clinkered alternative cements	Calcium aluminate Reactive belite Calcium sulfoaluminate Carbonated calcium silicate
Calcined alternative cements	Magnesium oxychloride Magnesium phosphate Magnesium ammonium phosphate Magnesium potassium phosphate
Non-clinkered alternative cements	Alkali-activated Fly ash Slag Recycled glass Supersulfated cement

CHAPTER 4—ALTERNATIVE CEMENT TECHNOLOGIES

4.1—Introduction

The purpose of this chapter is to introduce and discuss the properties of the various alternative cement technologies. The technologies discussed are grouped based on similar production factors. The categories used are defined in **Chapter 2** and include clinkered alternative cements, calcined alternative cements, and non-clinkered alternative cements. This chapter addresses alternative cements that are commercially available as well as those that are still in development. A summary of the state of the knowledge with respect to all these materials is presented. A list of the alternative cements is provided in Table 4.1a. Each subsection starts with a summary of the technology, which may suffice for understanding the advantages and disadvantages of each technology and how their properties compare to portland cement. Following the summary is a more in-depth synopsis of the pertinent literature regarding fresh and hardened properties of mixtures made using these technologies. Table 4.1b provides a comparison of technologies, summarizing key properties and applications for implementing alternative cement technology.

4.2—Clinkered alternative cements

Clinkered alternative cements are materials that represent an incremental change in binder technology when compared to portland cement. However, as is discussed in this report, the resulting materials have chemical and physical properties that are notably different than portland cement because they offer different performance attributes and, in some cases, require varying approaches to implementation. One example is different curing regimes. Therefore, despite their similarities to portland cement, these materials that do not meet current standards for portland or blended cement are considered alternative cements.

4.2.1 Calcium aluminate cement

4.2.1.1 Technology—Calcium aluminate cements (CACs) differ significantly from portland cement in composition because of the raw materials and, to some extent, manufacturing processes. Calcium aluminate cements are hydraulic

Table 4.1b—Comparison of commercially available alternative cement technologies

	CAC	CSA	MOC	MPC	AAFA	AAS	SSC
Hydraulic	Yes	Yes	No	No	No	No	No
Main hydration or reaction products	Calcium aluminate hydrates C_3AH_6 and AH_3	Ettringite, C-S-H, CH	Hydro-magnesite	Insoluble ammonium and phosphate phases	Variable, C-A-S-H, N-A-S-H	Variable, C-A-S-H	Ettringite, C-S-H
Set time relative to PC	Rapid	Rapid and expansive	Same or longer	Rapid	Rapid	Same or faster	Same or faster
Strength	High-early, late strength comparable to portland	High-early, slower rate of late strength gain compared to portland	High-early, late strength comparable to portland	Low-early, moderate late strength compared to portland	High-early, late strength comparable to portland	Low-early, late strength comparable to portland	Low-early, late strength comparable to portland
Key durability attributes	Good sulfate, ASR resistance	Good sulfate resistance	Good fire, abrasion, ASR resistance	Good sulfate, ASR performance	Good sulfate, acid, ASR, resistance	Good sulfate, corrosion, acid, ASR, resistance	Good sulfate resistance
	Abrasion resistant	Carbonation rates high	Good FT resistance	Good fire resistance	Good fire resistance	Good fire resistance	
Concerns	Conversion reactions increase porosity and reduce strength over time	Carbonation affecting corrosion resistance	Loses strength when exposed to water at early ages	Significant heat evolution	Performance varies with fly ash source	Performance varies with slag source	Limited field experience
	Significant heat evolution	Possible thaumasite formation	Significant heat evolution				
Applications	Refractory concrete, sulfate and acid resistance	Structural, precast cold-weather	Patching, wallboard	Fireproof coatings, patching	Same as PC	Same as PC	Same as PC

Note: Abbreviations used—PC: portland cement; C-S-H: calcium silicate hydrate, C-A-S-H: calcium aluminate silicate hydrate; N-A-S-H: sodium aluminate silicate hydrate; CH: calcium hydroxide; ASR: alkali-silica reactivity; FT: freezing-and-thawing.

cements; when CAC is placed in contact with water, hydration reactions occur and calcium aluminate (CA), also known as monocalcium aluminate, quickly dissolves, followed by a rapid precipitation of hydration products. This fast reaction leads to a significant temperature rise, even in relatively small volumes of cement (Scrivener 2003; Scrivener and Capmas 2003). Compared to portland cement, CACs have a lower CO₂ footprint (Juenger et al. 2011; Henry-Lanier et al. 2014). A thorough review of calcium aluminate cements is found in several sources (Scrivener 2003; Scrivener and Capmas 2003; Juenger et al. 2011).

In formulations where CAC comprises 100 percent of the binding material, conversion of the initially formed metastable hydrates to stable hydrates can result in a partial reduction of compressive strength. This reduction in strength from an apparent maximum strength to a lower strength is called conversion. From the 1930s to the 1970s, the improper use of CAC resulted in several failures attributed to this effect. This effect led to reduced use of CAC in the structural concrete applications. Later investigations found this misuse was primarily due to a lack of education about the conversion process (Concrete Society 1997; Scrivener and Capmas 2003). In the early 2000s, given known performance properties of CAC, a renewed interest in CACs for use in rapid repair emerged (Gosselin and Scrivener 2008;

Ideker 2008; Gosselin 2009; Gosselin et al. 2010; Juenger et al. 2011; Ideker et al. 2013). Calcium aluminate cements are well known for their rapid strength gain, especially at low temperatures, and their resistance to aggressive chemicals.

Calcium aluminate cement is now commonly used as a rapid repair material, as well as in refractory applications, typically as 100 percent CAC mixtures, and in ternary blends of CAC, portland cement, and gypsum. When using gypsum, the ternary blends are typically formulated with unique properties such as rapid set, early strength, expansion, or corrosion resistance. Use in refractories and formulated products, which is its main use, has seen steady growth since the 1950s.

4.2.1.2 Fresh properties—Curing at a constant temperature of 100°F (38°C), immediately after casting, leads to accelerated formation of the stable hydrates; a converted strength is typically realized within 5 to 7 days (EN 14647:2005). Figure 4.2.1.2 provides a schematic of the curing and strength development process. After conversion occurs and a minimum strength is reached, the water released by conversion continues to react with unhydrated cement, resulting in continued long-term strength gain (Fryda et al. 2001; Scrivener and Capmas 2003).

Assessing conversion is done through performance testing and can be evaluated using several accelerated laboratory

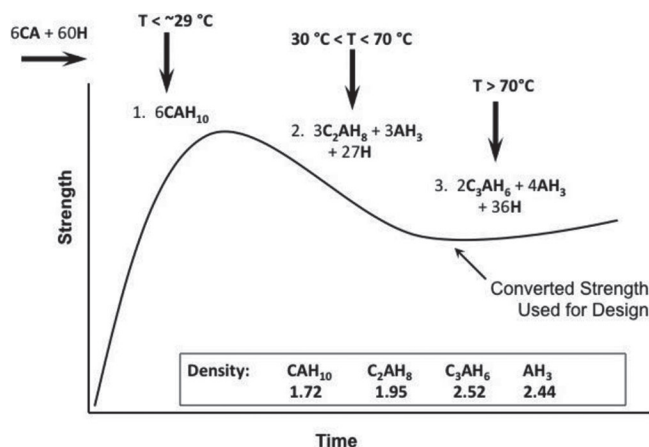


Fig. 4.2.1.2—Schematic of CAC conversion and strength reduction. Density shown in units of g/cm^3 (Juenger et al. 2011). (Note: $1 \text{ g/cm}^3 = 62.4 \text{ lb/ft}^3$; $^{\circ}\text{F} = (9/5)^{\circ}\text{C} + 32$.)

test methods. Three accelerated conversion test methods are given herein. These three methods rely on casting concrete cylinders, subjecting the cylinders to an increased temperature, and monitoring their strength over a specified period to determine the converted strength.

Method 1: Direct immersion of freshly cast cylinders in plastic molds at 100°F (38°C), demolding at 24 hours, and continued immersion at 100°F (38°C) until the converted strength is reached (EN 14647:2005).

Method 2: Standard curing of cast cylinders in plastic molds in a 73°F (23°C) ambient environment for 24 hours, then direct immersion in a 122°F (50°C) water bath until the converted strength is reached (Fryda et al. 2008).

Method 3: Direct placement of cast cylinders in plastic molds in a semi-adiabatic, highly insulated curing box immediately after casting for 24 hours, followed by standard 73°F (23°C) curing thereafter (Fryda et al. 2001; Texas Department of Transportation 2010).

It is important to account for the loss of strength due to conversion through proper mixture proportioning, design, and performance testing. The water-cementitious materials ratio (w/cm) is recommended to not exceed 0.40 and the minimum CAC content is recommended to be 400 kg/m^3 (674 lb/yd^3) (Hanson Cement 2009).

4.2.1.3 Hardened properties—Calcium aluminate cements were originally developed to resist sulfate attack. Calcium aluminate cement concrete has also performed well with respect to other forms of attack. For example, CACs are abrasion-resistant and are often combined with synthetic aggregate made from CAC to produce a highly resistant material for use in dam spillways or industrial floor slabs (Scrivener and Capmas 2003). Alkali-silica reaction (ASR) is thought to be unlikely when using calcium aluminate cements (Kurtis and Monteiro 1999). This is because the hydration products are different from those of calcium silicate cements. Specifically, because there is no calcium hydroxide formed, the pH of the pore solution is lower (~ 11.5 to 12.5) and, therefore, CAC by itself does not promote dissolution of silica (SiO_2) in reactive aggregates. However, blends of

CAC and portland cement may still induce ASR (Kurtis and Monteiro 1999).

Recent work by Yi and Thomas (2014) showed that unconverted CAC concrete exposed to artificial seawater had significantly enhanced chloride ion resistance as compared to PCC. However, they also showed that in converted CAC, the depth of penetration of chloride may be higher than in unconverted specimens (Yi and Thomas 2014). A possible reason for the observed durability of CAC concretes could be the formation of a dense, low-porosity outer layer that limits or greatly reduces the ingress of aggressive agents.

Information in the literature for CACs and corrosion is limited. Unpublished work indicates the rate of chloride ingress into a new, rapidly converted CAC concrete without the outer layer was rapid. Other work has shown that in unconverted CAC concrete, the electrical resistivity exceeded that of PCC by more than an order of magnitude (Juenger et al. 2011).

4.2.2 Reactive belite cement

4.2.2.1 Technology—Traditional portland cement clinker contains four principal mineral phases known as alite, belite, aluminate, and ferrite, with alite being the most abundant phase. The chemical nomenclature and relative abundance of these phases in concrete are summarized in Table 4.2.2.1.

Alite reacts rapidly with water, relative to the other clinker phases, and is responsible for most of the early strength development in portland cement. While belite is less reactive at early ages, it does contribute appreciably to strength at later ages. A reactive belite cement (RBC) has a significantly lower alite content, giving it a relatively higher belite content (Chatterjee 1996). Production of RBC allows for a lower kiln temperature, less limestone, and lower CO_2 and NO_x emissions (Chatterjee 1996). To achieve usable early strengths, belite is chemically modified or mineralized to improve its reactivity. Because the process of modification is complicated, the use of RBC alone has not grown. Calcium sulfoaluminate cements, however, which are a modified form of RBC, have been used in numerous applications (Burris et al. 2015). Calcium sulfoaluminate cements will be addressed further in a later section.

4.2.2.2 Fresh properties—The hydration of RBC produces the same hydration products formed in hydrated portland cement, but with lower heat evolution and smaller quantities of calcium hydroxide (CH) formation. The hydration of RBC is expected to be somewhat slower than observed in portland cement, which may result in a lower early heat of hydration and slightly longer setting time as compared to portland cement. The setting time, however, is typically acceptable for use in the construction industry for some applications. Additionally, hydrated RBC shows no change in volume after 28 days of hardening (Popescu et al. 2003).

4.2.2.3 Hardened properties—The compressive strength of hardened RBC is lower than a comparable portland cement at early ages. Reactive belite cement mortars have been shown to have higher strength gains beyond 28 days as compared to portland cement. The measured porosity after 5 years of hydration is relatively lower in RBC (Chatterjee 1996). Physical and mechanical tests performed on

Table 4.2.2.1—Chemical nomenclature and relative abundance of the principal phases in portland cement clinker (Taylor 1997)

Common name	Chemical name	Chemical formula	Cement chemist notation*	Relative abundance, %
Alite	Tricalcium silicate	Ca_3SiO_5	C_3S	50 to 70
Belite	Dicalcium silicate	Ca_2SiO_4	C_2S	15 to 30
Aluminate	Tricalcium aluminate	$\text{Ca}_3\text{Al}_2\text{O}_6$	C_3A	5 to 10
Ferrite	Tetracalcium aluminoferrite	$\text{Ca}_2\text{AlFeO}_5$	C_4AF	5 to 15

*Abbreviations are C: CaO ; A: Al_2O_3 ; S: SiO_2 ; F: Fe_2O_3 ; $\bar{\text{S}}$: SO_3 .

cement mortars of sodium fluoride (NaF) mineralized belite clinker have shown the heat of hydration and compressive strength to evolve quickly to reach 28-day values like those of alite clinker (Kacimi et al. 2009).

Given that RBC produces relatively higher amounts of C-S-H and lower CH contents, with denser, less permeable microstructures, the resulting concrete durability is expected to be good. The range of strengths of concrete made from RBC, and long-term durability data, have yet to be presented in the literature.

4.2.3 Calcium sulfoaluminate cement

4.2.3.1 Technology—As stated in 4.2.2.3, early compressive strengths of pastes, mortars, and concretes containing RBC are generally low. Early strength, however, can be increased using several techniques. One practical technique is the addition of a reactive component such as calcium sulfoaluminate ($\text{C}_4\text{A}_3\bar{\text{S}}$) in some cases together with calcium sulfate (CS), tetracalcium aluminoferrite (C_4AF), or some combination of the ingredients (Quillin 2001). This combination yields a belite-sulfoaluminate cement, commonly referred to as calcium sulfoaluminate cement (CSA) or calcium sulfoaluminate belite cement (CSAB). This cement is gaining attention from the cement and concrete industries as a lower-energy, lower- CO_2 alternative to portland cement. Calcium sulfoaluminate cement contains as a primary phase ye'elimite, or $\text{Ca}_4\text{Al}_6\text{SO}_{16}$ or $\text{C}_4\text{A}_3\bar{\text{S}}$ in cement chemist notation, also known as Klein's Compound, which was used by Alexander Klein in the 1960s as an expansive additive to portland cement (Klein 1966).

4.2.3.2 Fresh properties—Because ettringite ($\text{C}_6\text{A}\bar{\text{S}}_3\text{H}_{32}$) is the primary reaction product of ye'elimite, gypsum, and water, CSAs can exhibit rapid setting and early strength gains, as well as expansion (Uchikawa 1994). In practice, these properties can be controlled by manipulating cement composition, and through the addition of chemical retarders.

Gypsum content in cement is shown to be an important factor in phase evolution. Early strength development for CSA cement concrete is faster than observed in PCC, but strength gain at later ages, for example 28 days, is slower. Early strength development for CSA cements, however, is slower than found in CACs. Mechanical properties and dimensional stability for CSA cements are like that achieved by portland cement (Mehta 1980; Juenger and Chen 2011).

4.2.3.3 Hardened properties—Concrete made using CSA cement shows excellent sulfate resistance (Quillin 2001). However, under natural and accelerated conditions, carbonation rates for CSA concrete are high when compared with

PCC made using a similar mixture design (Quillin 2001). Therefore, corrosion of reinforcement may be an issue for concrete made using CSA cements. The rate of carbonation and diffusion coefficients can be lowered with the use of appropriate water-reducing admixtures. Although the mechanical properties and durability of CSA concrete are reported to rival portland cement (Quillin 2001), field experience is needed to fully vet the long-term material performance.

Calcium sulfoaluminate (CSA) cements are used for some structural applications, but are especially well suited for precast and cold-weather applications, which take advantage of the rapid strength gain of these materials (Su et al. 1997).

4.2.4 Carbonated calcium silicate cement

4.2.4.1 Technology—Carbonated calcium silicate cement (CCSC) is a nonhydraulic cement. As the name implies, the solidification process used involves carbonation of the cement. Water is used as the medium for the process but is not incorporated into the final hardened cement paste, as is the case with portland cement hydration.

Carbonated calcium silicate clinker is produced using the same raw materials and rotary kilns used for portland cement clinker production. The raw meal for CCSC production requires 50 percent less limestone as compared to producing portland cement. The resulting clinker is primarily composed of calcium silicate phases, such as wollastonite and rankinite. The carbon footprint of CCSC clinker is lower than PC clinker due to decreased calcination-related CO_2 from limestone, and less fuel-related CO_2 . Carbonated calcium silicate cement is an emerging technology, not yet fully commercialized.

4.2.4.2 Fresh properties—Carbonated calcium silicate cement is as much an alternative concrete technology as it is an alternative cement. Placement requires curing in a CO_2 -rich environment and, therefore, special equipment is required. Unlike the hydration reactions in portland cement, the carbonation reactions in CCSC occur relatively rapidly. Full curing of CCSC-based concrete is limited only by the ability of the gaseous CO_2 to diffuse throughout the material. Thin concrete products, such as roof tiles that are 10 mm (0.4 in.) thick, can be cured in less than 10 hours. Larger concrete parts, such as railroad ties, require a longer curing time, up to 24 hours.

The carbonation reactions CCSC undergoes during formation are exothermic. The heat generated during the reactions is dissipated through the evaporation of water. Kinetics of the curing process are controlled by counter diffusion of CO_2

and H₂O molecules in and out of the concrete. The finishing window for CCSC concrete is typically longer than PCC.

4.2.4.3 Hardened properties—Research performed to date on concrete prepared with CCSC reports hardened properties comparable to PCC. The Young's modulus and coefficient of thermal expansion (CTE) are similar to PCC, facilitating compatibility when used together (Jain et al. 2015). For CCSC-based concrete, compressive strengths of approximately 10,000 psi (70 MPa) and flexural strengths of approximately 1100 psi (8 MPa) have been reported (Jain et al. 2015). Testing performed to date also indicates that CCSC concrete has good freezing-and-thawing resistance (Farnam et al. 2016; Villani et al. 2015).

4.3—Calcined alternative cements

Calcined alternative cements are a combination of calcined magnesite and a crosslinking agent that, when combined, react to form a solidified binder matrix. While water is a product of the reaction, formation of the hardened matrix is the result of acid/base reactions in an aqueous environment.

The calcining temperature of the magnesite determines the reactivity of the magnesia (magnesium oxide [MgO]). Calcination at high temperatures, such as 2732 to 3632°F (1500 to 2000°C), produces nonreactive dead-burned magnesia. At lower calcining temperatures of 1832 to 2732°F (1000 to 1500°C), hard-burned magnesia is produced, which has a relatively low reactivity. Lower calcining temperatures of 1292 to 1832°F (700 to 1000°C) will produce light-burned magnesia—a significantly more reactive form sometimes referred to as caustic magnesia (Shand 2006). The magnesia reactivity used is dependent on the type of cement being produced, the desired plastic and hardened properties, and the nature and amount of fillers/aggregate that will be added to the binder (Matkovic et al. 1977).

4.3.1 Magnesium oxychloride cement

4.3.1.1 Technology—The first type of magnesia cement was developed by Stanislas Sorel in 1867 (Sorel 1867) and is now referred to as Sorel, magnesite, or magnesium oxychloride cement (MOC) (Phair 2006; Válek et al. 2012). MOC is formed by reaction of magnesium oxide with magnesium chloride in the presence of water. A common formulation is to use 1.2 parts magnesium oxide to 1 part of magnesium chloride hexahydrate, to 0.6 parts of water, by mass. The main bonding phase found in hardened MOC pastes is magnesium hydroxide.

4.3.1.2 Fresh properties—Magnesium oxychloride cement, during initial curing, is not stable in prolonged contact with water. Leaching of magnesium chloride can result, with reversal of the reaction and loss of strength (Lu et al. 1994). Atmospheric carbon dioxide (CO₂) has been reported to react with magnesium oxychloride to form a surface layer that slows the leaching process. Hydromagnesite (4MgO·3CO₂·4H₂O) forms, which is insoluble and enables the cement to maintain structural integrity (Cole and Demediuk 1955). These late carbonation reactions contribute to the claim that MOC has a low carbon footprint.

A variety of additives have been developed that will significantly slow down or block water penetration during

early ages, or expedite formation of hydromagnesite. Materials evaluated included phosphates (Deng 2003), fly ash and silica fume (Li and Yu 2010), and alkali metal fatty acids such as magnesium stearate, metal or alkali metal sulfates such as aluminum sulfate, or magnesium sulfate. Water resistance is further enhanced by either precarbonating the mixing water or the liquid magnesium chloride phase of the cements, or by adding a carbonate into the cement powder (Rademan et al. 2013).

Neat MOC paste is generally very fluid and, as such, is not suitable for casting. The addition of fillers/aggregates and other components provides the ability to control viscosity and workability. In general, the rheology of MOC can be controlled by selection of raw materials, and the molar ratio and concentration of the magnesium chloride solution. Admixtures are not necessary for the formulation of workable mixtures, and not all concrete admixtures are effective in MOC, but some admixtures are used. Because fresh MOC tends to be thixotropic, high-range water reducers used in PCC are generally applicable depending on the flowability requirements. Another material that improves flowability is magnesium lignosulfonate, although polyacrylates and carboxy-modified cellulose also yield good results (Zhou and Li 2012).

Because the initial stage of the reaction requires MgO dissolution, fresh mixtures start out looking dry. Mixing for a few minutes increases the fluidity, so once the two components are combined, they should be stirred for several minutes before application.

The set time for neat MOC paste can vary from a few hours to 48 hours (Yadav et al. 2013). Curing is affected by temperature, air flow, and humidity conditions. While heating can increase the rate of hardening, overheating the concrete may lead to cracking of the material (Yadav et al. 2012). No additional curing is necessary after set.

As an acid/base reaction, neat MOC paste develops a significant heat of hydration. Therefore, mixtures can develop significant temperatures. For example, 140 to 176°F (60 to 80°C) and temperatures above 212°F (100°C) have been reported (Newman et al. 1952). Precautions are required when handling neat paste to avoid thermal damage of substrates and forms, and to avoid personal injury. Temperature evolution is significantly decreased when fillers/aggregates are added to the paste, resulting in mixtures that are safe to handle and place. Also, the evolved heat dissipates quickly due to high thermal conductivity of the material.

Application method, material thickness, and nature of the substrate determine the applicability of specific MOC mixtures. Certain fillers/aggregates, such as magnesite or dolomite, can be used in quantities up to 50 to 60 percent without significant loss in compressive strength, whereas others will result in lower strength development. Reduced heat evolution from filler addition could result in a decreased degree of reaction and a reduced strength (Yadav et al. 2013).

4.3.1.3 Hardened properties—Concrete mixtures prepared with MOC can have high compressive strength—for example, 8000 to 10,000 psi (55 to 70 MPa) within 48 hours. The compressive strength is achieved early