J Mater Sci (2011) 46:2568–2577
DOI 10.1007/s10853-010-5109-9

Synthesis and hydration of calcium sulfoaluminate-belite cements with varied phase compositions

Irvin A. Chen · Maria C. G. Juenger

Received: 19 June 2010 / Accepted: 23 November 2010

Abstract The production of portland cement is energy intensive and contributes significantly to greenhouse gas emissions. One method of reducing the environmental impact of concrete production is the use of an alternative binder, such as calcium sulfoaluminate-belite (CSAB) cement. The relatively low lime requirement of CSAB cement compared to portland cement reduces energy consumption and carbon dioxide emissions from cement production. Moreover, CSAB cement can be produced at temperatures approximately 200 °C lower than portland cement, further reducing energy and carbon dioxide. Major drawbacks to the implementation of CSAB cements are the lack of standard phase composition and published data on composition-processing-performance relationships. In this study, three CSAB cement clinkers with different phase compositions were synthesized from reagent-grade chemicals. The synthetic clinkers were analyzed for phase composition using X-ray diffraction and phase distribution using scanning electron microscopy. The synthetic clinkers were then tested for hydration rate using isothermal conduction calorimetry to investigate the effects of phase composition and gypsum addition on early-age hydration behavior. A proportioning method for predicting phase composition was refined and an equation for calculating the minimum gypsum content for CSAB cement clinker was developed.

I. A. Chen (✉)
Calera Corporation, 14600 Winchester Blvd, Los Gatos,
CA 95032, USA
e-mail: ichen@calera.com

M. C. G. Juenger
Department of Civil, Architectural, and Environmental
Engineering, University of Texas at Austin,
1 University Station C1748, Austin, TX 78712, USA

Introduction

Portland cement concrete, the most widely used manufactured material in the world, is made primarily from water, mineral aggregates, and portland cement. Portland cement clinker is produced by high temperature firing of mineral deposits such as limestone and clay; the clinker is then ground with gypsum to make cement. Global production of portland cement is estimated at about 2.8×10^9 tonnes per year [1]. The production of portland cement is energy intensive, accounting for 2% of primary energy consumption and 5% of industrial energy consumption globally [2]. Moreover, portland cement manufacturing contributes significantly to greenhouse gases and accounts for 5% of the global CO_2 emissions resulting from human activity. About half of this CO_2 comes from the use of fossil fuels to heat the kilns, and the other half is produced through the calcination of limestone. One method of reducing the environmental impact of cement manufacturing is the use and adoption of an alternative, environmentally friendly binder, calcium sulfoaluminate-belite (CSAB) cement.

CSAB generally refers to cements that have the same basic components of $C_4A_3\bar{S}$[1] (calcium sulfoaluminate), C_2S (belite), and calcium sulfates, but the minor phases and the amounts of the phases present vary significantly [3–5]. CSAB cement can be produced by combing limestone, clay, bauxite, and gypsum to provide the necessary CaO, SiO_2, Al_2O_3, and SO_3 required for phase formation, respectively. Calcium sulfates can either be formed as anhydrite ($C\bar{S}$) in the clinker, be interground as gypsum ($C\bar{S}H_2$) after clinkering, or some combination of the two

---

[1] In cement chemistry notation, oxides are abbreviated by the first capital letter: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, H = H_2O, and $\bar{S}$ = SO_3.

[6]. The hydration reaction of $C_4A_3\bar{S}$ with calcium sulfates ($C\bar{S}$ and $C\bar{S}H_2$) initiates rapidly and forms ettringite ($C_6A\bar{S}_3H_{32}$) and AH_3, which contribute to the early-age property development in CSAB cement, as shown in Eqs. 1 and 2 [7]:

$$C\bar{S} + 2H \rightarrow C\bar{S}H_2 \quad (1)$$

$$C_4A_3\bar{S} + 2C\bar{S}H_2 + 34H \rightarrow C_6A\bar{S}_3H_{32} + 2AH_3 \quad (2)$$

The relatively slow hydration reaction of C_2S forms calcium silicate hydrate (C–S–H), as shown in Eq. 3 [8], which contributes to the long-term property development in CSAB cement:

$$C_2S + 2H \rightarrow CH + C{-}S{-}H \quad (3)$$

Calcium silicate hydrate is usually referred to as C–S–H because it does not have a fixed stoichiometry; the C/S ratio is generally between 1.5 and 2, with a highly variable amount of associated water.

Due to the different phase assemblage compared to portland cement, CSAB cement requires less lime for its formation. The relatively low lime requirement for CSAB cement production reduces energy consumption and CO_2 emissions from the calcination of limestone ($CaCO_3 \rightarrow CaO + CO_2$, $\Delta H = 178$ kJ/mol). Furthermore, all of the phases in CSAB cement can form and are stable at a temperature of approximately 1,250 °C, which is about 200 °C lower than the temperature used for portland cement production. The lower formation temperature further lowers the energy requirement and CO_2 emissions from cement manufacturing, and the resulting clinker is more friable (due to high porosity), which reduces the energy needed for grinding.

Previous research has shown successful production of CSAB cement from natural materials and waste materials [9–11], and these cements have been produced commercially in China for over 30 years. However, there are still many unanswered questions about this system. The effects of raw material composition and temperature on phase formation in clinkers are not well defined in the published literature, which limits our ability to predict phase composition in the final cement. The hydration chemistry is not nearly as well explored as that of portland cement, which hinders our ability to understand property development. This study aimed to address these questions.

In this study, three CSAB cement clinkers with different phase compositions were synthesized from reagent-grade chemicals to tightly control compositional variables. A phase assemblage of $C_4A_3\bar{S}{-}C_2S{-}C_4AF{-}C\bar{S}$ was used. C_4AF was included because most natural and waste materials suitable for cement manufacturing contain some amount of iron. Materials were proportioned using an adaptation of the Bogue method [12, 13] that is used to proportion portland cement clinker. The range of phase compositions was chosen because it allows full evaluation of the inter-relationship between phase composition and early-age hydration of the CSAB cement system. The synthetic CSAB cement clinkers were ground and tested for particle fineness by Blaine fineness [14]. The synthetic clinkers were analyzed for phase composition using X-ray diffraction and phase distribution using scanning electron microscopy. Different amounts of gypsum were added to the synthetic CSAB cement clinkers to control their hydration reactions. Hydration rates were tested with isothermal conduction calorimetry to investigate the effects of gypsum addition and phase composition on early-age hydration behavior.

Experimental

Materials proportioning

The reagent-grade chemicals used to synthesize CSAB cement clinkers were calcium oxide (96% + CaO; Arcos), silica gel (100% SiO_2; Fisher), aluminum oxide (100% Al_2O_3; Fisher), ferric oxide (100% Fe_2O_3; Fisher), and calcium sulfate dihydrate (99% $CaSO_4{\cdot}2H_2O$; Arcos). Materials were proportioned by adapting the Bogue method for CSAB cement clinker. The Bogue method is a technique used in the cement industry to estimate phase composition in portland cement clinker from the raw materials oxide composition using knowledge of phase equilibria and by solving linear equations [12, 13]. It was adapted for CSAB cement by assuming a phase assemblage of $C_2S{-}C_4A_3\bar{S}{-}C_4AF{-}C\bar{S}{-}C$, as shown in Eqs. 4–8. This phase assemblage was determined from review of the literature and preliminary testing [3–5].

$$\%C_4AF = 3.043(\%Fe_2O_3) \quad (4)$$

$$\%C_4A_3\bar{S} = 1.995(\%Al_2O_3) - 1.273(\%Fe_2O_3) \quad (5)$$

$$\%C_2S = 2.867(\%SiO_2) \quad (6)$$

$$\begin{aligned}\%C\bar{S} = {} & 1.700(\%SO_3) - 0.445(\%Al_2O_3) \\ & + 0.284(\%Fe_2O_3) \quad (7)\end{aligned}$$

$$\begin{aligned}\%C = {} & 1.000(\%CaO) - 1.867(\%SiO_2) \\ & - 1.054(\%Fe_2O_3) - 0.550(\%Al_2O_3) \\ & - 0.700(\%SO_3) \quad (8)\end{aligned}$$

Three target CSAB cement clinkers with different proportions of C_2S and $C_4A_3\bar{S}$ were synthesized (Table 1); HS designates a clinker with a high $C_4A_3\bar{S}$ content, MS has a medium amount of $C_4A_3\bar{S}$, and LS has low $C_4A_3\bar{S}$. These three phase compositions were chosen from preliminary testing of seven phase compositions. This range of phase compositions allows evaluation of the

Table 1 Phase compositions of the CSAB cement clinkers synthesized from reagent-grade chemicals (Calc.: target phases calculated from the Bogue equations; Actual: actual phases determined using Rietveld analysis); minimum gypsum contents of CSAB cements (Calc.: calculated using empirical model, Actual: measured using isothermal calorimetry); and measured Blaine fineness values of CSAB clinkers

Phase	Phase composition (weight %)					
	HS		MS		LS	
	Calc.	Actual	Calc.	Actual	Calc.	Actual
C_2S	20	22	40	45	60	71
$C_4A_3\bar{S}$	60	65	40	42	20	15
C_4AF	10	3	10	6	10	7
$C\bar{S}$	10	9	10	7	10	7
C	0	<1	0	<1	0	0
$C\bar{S}H_2$	23	25	19	15	10	8
Blaine (m^2/kg)	–	325	–	323	–	322

inter-relationship between phase composition and early-age hydration behavior of the CSAB cement system. The target C_4AF content was controlled at 10% for the CSAB cement clinkers because most natural and waste materials suitable for cement manufacturing contain some amount of iron. However, it is unusual to have suitable high iron-containing natural and waste materials to produce high C_4AF cement. The target $C\bar{S}$ content was controlled at 10% because it strongly affects hydration behavior; instead, the minimum gypsum ($C\bar{S}H_2$) content was evaluated and added to the synthetic clinkers during grinding [7].

Synthesis

The laboratory synthesis processes mimicked the processes that take place in industrial manufacturing, only on a much smaller scale. The proportioned raw ingredients were dispersed in ultra-pure water (1:2 volume ratio) and mixed using a rotary jar mill (U.S. Stoneware) for 8 h at 120 rpm in an HDPE bottle using 5–15 mm sphere high-purity ZrO_2 (Y_2O_3 stabilized) grinding media [15]. The suspension was poured in a steel pan and dried in a 105 °C oven for 72 h. The resulting product was hand-crushed into fine powder form using a mortar and pestle. The raw ingredients were then placed in alumina crucibles and fired in an electric muffle furnace (Sentrotech). Two cycles of firing were performed, with a 5 °C/min heating rate and a 2 °C/min cooling rate. In the first cycle, the raw ingredients were fired at 850 °C for 4 h to dehydrate and calcine the raw ingredients. Intermediate grinding by hand was performed between cycles to homogenize the raw ingredients. In the second cycle, covers were applied to the alumina crucibles to prevent sulfur emissions and the raw ingredients were fired at 1,250 °C for 12 h. The firing time in the furnace was much longer than the firing time in a rotary kiln used in industrial manufacturing because the raw ingredients remained stationary inside the crucibles during the laboratory firing process, which prevented materials from reacting as efficiently with each other. Finally, the resulting clinker was ground into fine powder form using a micro mill grinder (Scienceware/Bel-Art).

Analysis

Thermogravimetric analysis

Thermogravimetric analysis (Netzsch STA 409 PC Luxx) was used to follow the mass loss occurring with temperature for the raw ingredients of the CSAB cement clinkers during the firing process [16]. The instrument was operated from 25 to 1,300 °C, which is comparable to the temperature range in the furnace during synthesis of the clinkers. A 10 °C/min heating rate was used for the testing. Nitrogen gas filled the sample chamber to prevent oxidation during testing.

Particle fineness

The ground synthetic clinkers were tested by an air-permeability test according to ASTM C 204 [14]; the resulting specific surface area value is referred to as Blaine fineness. The test measures the rate of air passing thorough pressed powder and is the most common technique used by cement manufacturers to measure cement fineness. The test was performed to assure uniform median particle fineness between the synthetic clinkers. The Blaine fineness results were then compared to a commercially produced Type I/II portland cement (TXI Hunter).

X-ray diffraction

X-ray diffraction (Siemens D500 Powder Diffractometer; Cu $K_{\alpha 1}$, $\lambda = 1.5046$ Å) was used to determine phase compositions for the CSAB cement clinkers. The instrument was operated under 40 keV and 30 mA, the step size used was 0.02°/6 s, and the scan range used was 10°–80° 2θ. Qualitative information for the phases present in the CSAB cement clinkers was obtained using the Hanawalt manual and the Jade program (MDI) [17]. Quantitative information was collected using Rietveld analysis (accuracy about 1%) by fitting the lattice parameters of the phases present in the synthetic clinkers to their X-ray diffraction patterns, which was performed with TOPAS-Academic software (Bruker AXS) [18–20].

Scanning electron microscopy

Scanning electron microscopy (JEOL JSM-5610 SEM) was used to study phase distribution in the CSAB cement clinkers. Test samples were prepared by mixing the ground synthetic clinkers with optical-grade epoxy and casting in cylindrical epoxy sample disks that had four holes drilled into the surface. Test samples were then cured in a 40 °C oven for 24 h, and the surface was polished and coated with silver before backscattered electron imaging and compositional examination by energy dispersive spectroscopy [21].

Isothermal conduction calorimetry

The heat produced by cementitious materials in exothermic hydration reactions is a good indication of their early-age hydration behavior [22]. The CSAB cement clinkers were made into cements by blending different amounts of gypsum (99% $CaSO_4 \cdot 2H_2O$; Arcos) to control the hydration reaction of $C_4A_3\bar{S}$. The resulting cements were tested for rate of heat evolution using isothermal conduction calorimetry (Thermometric TAM Air) to study early-age hydration behavior. Hydration was evaluated for 3 days at 23 °C using a water-to-cement ratio by mass of 0.45. The results were compared to a commercially produced Type I/II portland cement (TXI Hunter Cement) [23]. The minimum amount of gypsum needed to control hydration was determined for each of the clinkers. The clinkers with the experimentally determined minimum amount of gypsum were then tested for rate of heat evolution at 5 and 38 °C to study the temperature-dependency of CSAB cement hydration.

Results and discussion

Synthesis

Sulfur emissions

The mass loss occurring with temperature for the raw ingredients of the CSAB cement clinkers during the firing process, obtained through thermogravimetric analysis, is shown in Fig. 1. Thermogravimetric analysis showed weight loss at 450 and 750 °C indicating the dissociation of water from $Ca(OH)_2$ and the calcination of $CaCO_3$, respectively [16]. $Ca(OH)_2$ and $CaCO_3$ both formed from CaO contained in the raw ingredients during the mixing process. The raw ingredients for the CSAB cement clinkers with higher target C_2S contents contained more CaO and showed higher mass losses at 450 and 750 °C, indicating that more $Ca(OH)_2$ and $CaCO_3$ formed during the mixing process. Furthermore, thermogravimetric analysis showed that a substantial amount of sulfur contained in the raw ingredients was emitted at temperatures above 1,200 °C, which can affect phase formation in CSAB cement clinker and the ability to predict phase composition from the initial raw materials composition. The raw ingredients for the CSAB cement clinkers with higher target $C_4A_3\bar{S}$ contents contained more sulfate and showed higher mass losses at temperatures above 1,200 °C. Therefore, during clinkering in the laboratory furnace, the raw ingredients were fired in covered and sealed crucibles to minimize sulfur emissions during the firing process. It was observed that the synthetic clinkers fired in covered crucibles contained higher $C\bar{S}$ contents (7–9%) compared to the synthetic clinkers fired in opened crucibles (1–2%), indicating that the sealed crucible covers successfully eliminated sulfur emissions from the raw ingredients at high temperature.

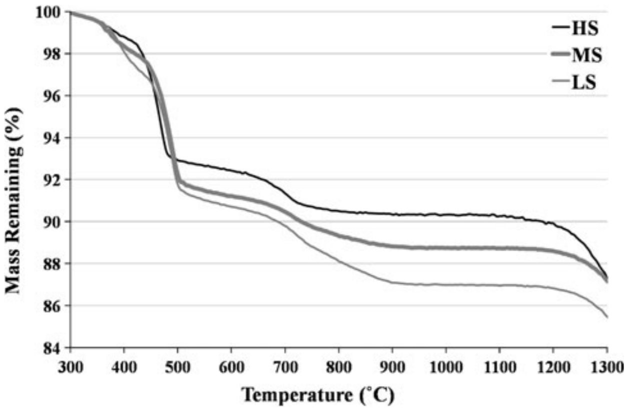

Fig. 1 Thermogravimetric analysis for the raw ingredients of the CSAB cement clinkers

Particle fineness

Measuring the particle fineness of the synthetic clinkers is critical because it strongly affects property development. The ground CSAB cement clinkers had uniform Blaine fineness after grinding with the micro mill grinder, as shown in Table 1. Therefore, differences in hydration rates due to particle fineness should be negligible. The Blaine specific surface areas for the synthetic clinkers were about 325 m^2/kg, which is higher than the minimum portland cement Blaine value (280 m^2/kg) specified in ASTM C 150 [23]. However, the synthetic clinkers had Blaine values about 20% lower than the commercial Type I/II portland cement used for comparison purposes in this study (403 m^2/kg).

Phase composition

A comparison of the measured X-ray diffraction patterns for the synthetic clinkers is shown in Fig. 2 and their

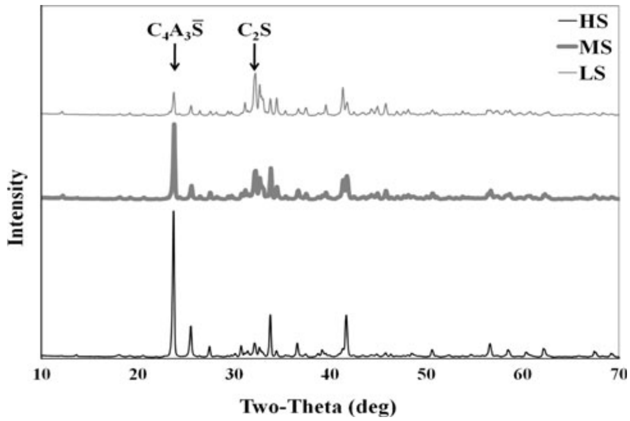

Fig. 2 X-ray diffraction patterns comparison for the CSAB cement clinkers

quantitative phase compositions determined through Rietveld analysis are shown in Table 1. The refined X-ray diffraction patterns calculated from the lattice parameters of the phases present in the synthetic clinkers agreed with the measured X-ray diffraction patterns very well, an indication of the reliability of the quantitative results. The phase analysis results show that the four major CSAB cement phases formed in every synthetic clinker. All of the synthetic clinkers had low free lime (C) contents (0–0.2%) indicating that the 1,250 °C firing temperature was sufficient for the raw ingredients to completely react in the furnace. Recently, Martín-Sedeño et al. [24] demonstrated that a firing temperature of 1,250 °C was sufficient for complete phase formation in an alumina-rich CSAB cement, but that the relative amount of $C_4A_3\bar{S}$ could be increased by using higher firing temperatures. They suggested that a firing temperature of 1,350 °C was more appropriate for clinkers without ferrite, such as theirs, but that iron-containing clinkers, such as the ones used in the present study, should be able to be synthesized at lower temperatures.

The phase compositions for the synthetic clinkers were reasonably close to their target phase compositions, indicating that the Bogue method refined for this research can effectively predict CSAB cement clinker phase composition from its raw materials oxide composition. The deviations from the target phase compositions were perhaps caused by the ability of phases to accommodate substitute ions [13]. The synthetic clinkers with higher $C_4A_3\bar{S}$ contents had lower C_4AF contents than predicted by the proposed Bogue-type equations (Eqs. 4–8). Strigac et al. [25] showed that $C_4A_3\bar{S}$ was able to accommodate up to 2 wt% Fe_2O_3 substitute ions, which could explain the low C_4AF content in high $C_4A_3\bar{S}$-containing synthetic clinker.

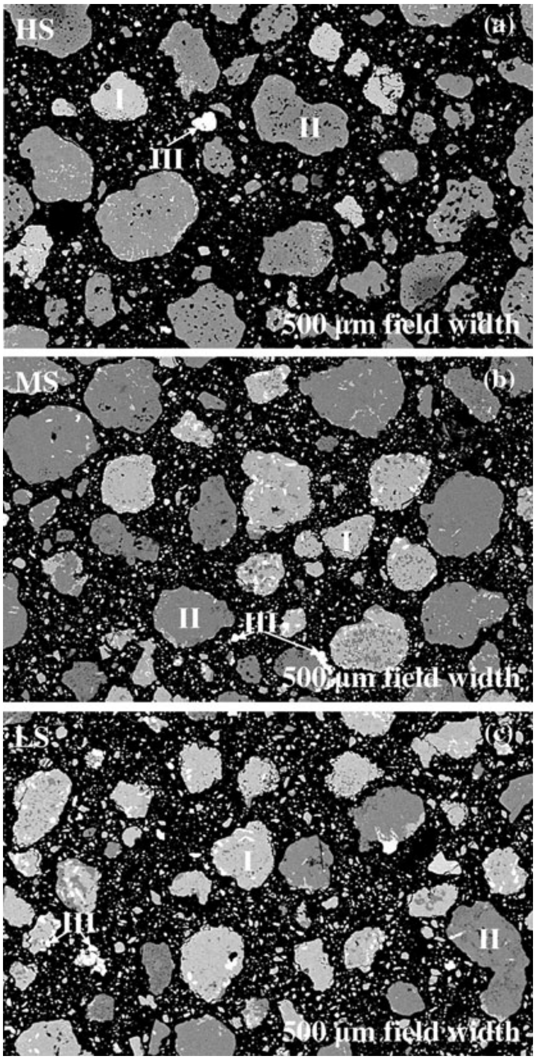

Fig. 3 Backscattered electron image for the CSAB cement clinkers [I (*light gray*): C_2S, II (*dark gray*): $C_4A_3\bar{S}$, and III (*white*): C_4AF], a. HS, b. MS, c. LS

Phase distribution

Backscattered electron images in Fig. 3 show particle size and phase distribution in the CSAB cement clinkers. The synthetic clinkers showed similar particle size distribution in the images, which confirms the Blaine fineness results (Table 1).

The lighter gray areas in the backscattered electron images represent C_2S while the darker gray areas represent $C_4A_3\bar{S}$. The synthetic clinkers that contained higher C_2S and lower $C_4A_3\bar{S}$ showed more light gray areas and less dark gray areas. The synthetic clinkers that contained higher $C_4A_3\bar{S}$ and lower C_2S showed more dark gray areas and less light gray areas, which agrees with the quantitative X-ray diffraction results (Table 1).

The small white areas that exist as separate particles and also inside the light gray (C_2S) and dark gray ($C_4A_3\bar{S}$) areas represent C_4AF (indicated in Fig. 4). The synthetic clinkers with higher $C_4A_3\bar{S}$ contents had fewer white areas (C_4AF), which agrees with X-ray diffraction results. Energy dispersive spectroscopy analysis on these samples showed that $C_4A_3\bar{S}$ was able to accommodate up to 1.5 wt% Fe_2O_3, which explains why high $C_4A_3\bar{S}$-containing synthetic clinkers contained less C_4AF.

It is clear in Fig. 4 that the clinker is highly porous, leading to lower energy needed for grinding. It is also interesting to note in Fig. 4 there are a variety of grain sizes of C_2S and $C_4A_3\bar{S}$. The presence of relatively large grains of each, on the order of 30–50 μm, is a result of slow cooling. However, many of the ground clinker particles contain several finely distributed phases, perhaps indicative of phases forming through solid-state reactions. The maximum synthesis temperature, 1,250 °C, was not high enough to melt aluminate and ferrite phases during the firing process and the reactions should mainly have been in the solid state. However, it was observed that the CSAB cement clinkers formed as very dense nodules, suggesting that some liquid phase was present during the firing process. The high sulfate content in the CSAB cement system could have acted as a mineralizer, thereby reducing the temperature required for liquid phase formation [13].

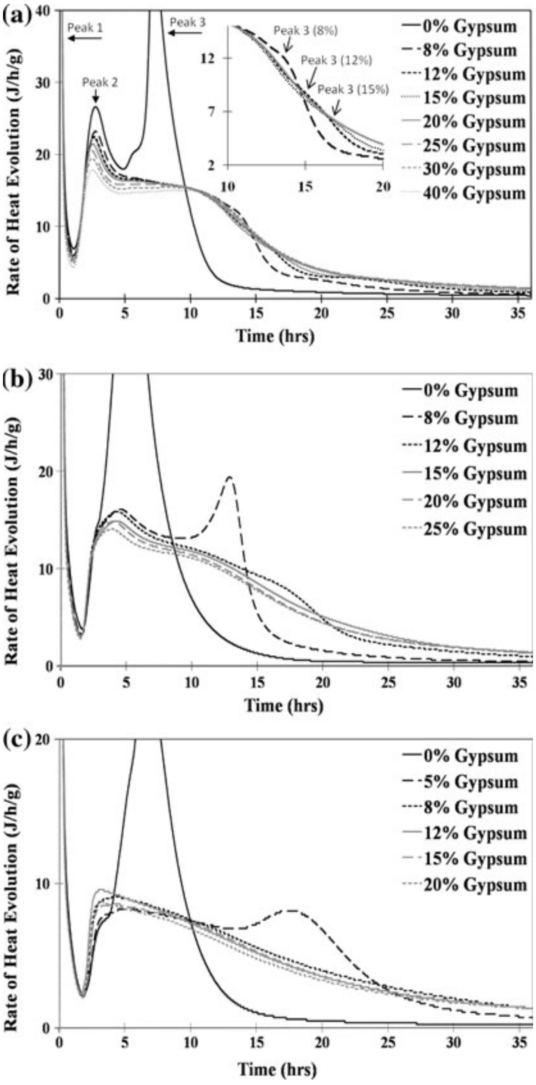

Fig. 4 Rate of heat evolution for the HS (**a**), MS (**b**), and LS (**c**) CSAB cement clinkers with different amounts of gypsum blended

Early-age hydration behavior

Minimum gypsum content

Because the effects of blended gypsum on CSAB cement early-age hydration behavior are not well known, different amounts of gypsum were blended with the synthetic clinkers. The resulting cements were tested for rate of heat evolution using isothermal conduction calorimetry to study the effects of gypsum on early-age hydration behavior and to determine the minimum gypsum content to control hydration. Rate of heat evolution results for the CSAB cement clinkers with different amounts of blended gypsum are shown in Fig. 4. The optimum gypsum content for portland cement was defined by Lerch [26] to be the minimum quantity of gypsum for which there are two ascending and descending cycles of heat release in the first 30 h, and these do not change shape appreciably with higher quantities of gypsum blended. Furthermore, portland cement containing its optimum gypsum content demonstrated the best performance. A similar approach was taken for the CSAB cements in this study; the shape of the second heat evolution cycle no longer changes shape with gypsum addition higher than the experimentally determined minimum amount. For properly sulfated CSAB cement, this heat evolution cycle is from the hydration reaction of $C_4A_3\bar{S}$ with calcium sulfates to form ettringite ($C_6A\bar{S}_3H_{32}$) and AH_3. Calcium sulfates in these cements are a combination of anhydrite ($C\bar{S}$) formed in clinker and gypsum ($C\bar{S}H_2$) interground after clinkering. The hydration reaction of $C_4A_3\bar{S}$ with calcium sulfates initiates rapidly and dominates the early-age hydration behavior and property development of CSAB cement, as shown in Eq. 2 [7]. The hydration reaction of C_4AF contained in the synthetic clinkers with calcium sulfates also contributes to ettringite formation, as shown in Eq. 9 [27]:

$$3C_4AF + 12C\bar{S}H_2 + 106H \rightarrow 4C_6(A_{0.75}, F_{0.25})\bar{S}_3H_{31} + 2FH_3 \quad (9)$$

In portland cement, the second heat evolution cycle is caused by the rapid hydration of the tricalcium silicate phase [22] and the rapid dissolution of C_3A after the depletion of sulfates from solution [28]. With increasing amounts of gypsum blended, the peak due to sulfate depletion shifts to later times [28]. Correspondingly, in the CSAB cements, it is likely that the second peak in the HS clinker with 0% blended gypsum (Fig. 4a) is the reaction of $C_4A_3\bar{S}$ with the $C\bar{S}$ present in the clinker and the very tall third peak is due to rapid dissolution/reaction of $C_4A_3\bar{S}$ and C_4AF after the sulfates in solution have been depleted due to the initial reaction. With 8–20% blended gypsum, the third sulfate depletion peak is visible, but is much weaker (more like a hump; shown in the magnified plot insert in Fig. 4a) and shifts to later times with increasing amounts of added gypsum. With 25% and more gypsum blended to this clinker, sulfates are likely still present in solution during the time of testing, so this peak no longer changes shape. Similarly, in the MS clinker with no blended gypsum (Fig. 4b), due to a lower amount of anhydrite present in the clinker than in the HS clinker (Table 1), the sulfate depletion peak overlaps with the $C_4A_3\bar{S}$ and $C\bar{S}$ reaction peak, resulting in a single, very large peak. With 8 and 12% blended gypsum, the third sulfate depletion peak/hump is visible, and shifts to later times. With additional gypsum the shape of the second heat evolution cycle does not change. The same is true for the LS clinker, with overlapping reaction and sulfate depletion peaks at 0% blended gypsum (Fig. 4c); a third peak is clearly present at 5% blended gypsum, but not with greater amounts of gypsum blended.

It is known that in portland cement, if insufficient gypsum is blended, ettringite reacts with the alumina containing phases (C_3A and C_4AF) to form calcium monosulfoaluminate ($C_4A\bar{S}H_{12}$) [8]. Calcium monosulfoaluminate is subject to transform back to ettringite in the presence of environmental sulfate, causing cracking. However, calcium monosulfoaluminate was not detected using X-ray diffraction in any of the synthetic clinkers with low amounts of gypsum blended even at 28 days; the only reaction products measured are ettringite and an amorphous phase (AH_3). Therefore, none of the calorimetry peaks refer to the reaction of ettringite to form calcium monosulfoaluminate [29]. Furthermore, X-ray diffraction of these samples show that less ettringite formed and more $C_4A_3\bar{S}$ remained unhydrated in the clinkers with less gypsum blended. This phenomenon confirms to Wang et al.'s results [30], which showed that the hydration reaction of $C_4A_3\bar{S}$ reached a lower degree of hydration with lower amounts of gypsum blended. Peng et al. [31] also showed that the transformation from ettringite to calcium monosulfoaluminate in portland cement after sulfate depletion had to overcome an energy barrier, which depended on the diffusion capability of the alumina ions. The transformation mostly took place during early ages before the development of a rigid microstructure. CSAB cement generally develops a denser microstructure during early ages compared to portland cement as shown by Bernardo et al. [32]. Therefore, the alumina ions might have a harder time diffusing, which stabilizes the unhydrated $C_4A_3\bar{S}$ and ettringite instead of forming calcium monosulfoaluminate. It should be noted that blending less gypsum than the minimum amount might adversely affect mechanical property development in CSAB cement as more $C_4A_3\bar{S}$ remained unhydrated. Blending in more gypsum than the minimum amount needed to control hydration may adversely affect dimensional stability.

A shoulder during the second heat cycle appears in the HS and MS cements at the minimum gypsum content and higher, even though a clear third "peak" is not present. This could be due to the difference in reaction rates between the clinkers and anhydrite compared to gypsum [33], a difference in reaction time of C_4AF compared to $C_4A_3\bar{S}$, or different reaction rates of particles due to size or spatial distribution of phases within particles. More detailed investigation of phase formation during this period is necessary in order to understand the progress of the hydration reaction better and explain the shape of the heat evolution curve for CSAB cements with minimum gypsum contents.

Cumulative heat results over 72 h for the CSAB cement clinkers with different amounts of gypsum blended are shown in Fig. 5. With the minimum gypsum content, the synthetic CSAB cement clinkers showed the highest cumulative heat after 3 days, an indication of optimum reaction rate throughout this period.

The minimum gypsum contents determined through calorimetry for all of the synthetic clinkers are shown in Table 1. An equation for calculating the minimum gypsum content for CSAB cement clinker was developed for future reference based on the $C\bar{S}$ content of CSAB cement clinker and the hydration reactions of $C_4A_3\bar{S}$ and C_4AF with gypsum to form ettringite and AH_3 (Eqs. 2 and 9), as shown in Eq. 10:

$$\begin{aligned}&126.45 \times [0.4461(\%C_4A_3\bar{S}) + 1.1205(\%\ C_4AF)\\&\quad - 1.000(\%C\bar{S})] / \{100 + 1.2645 \times [0.4461(\%C_4A_3\bar{S})\\&\quad + 1.1205(\%\ C_4AF) - 1.000(\%C\bar{S})]\}\end{aligned} \tag{10}$$

The calculated minimum gypsum contents for the synthetic clinkers agreed with their measured minimum gypsum contents from the heat evolution rate results, as shown in Table 1.

Effects of phase composition

Rate of heat evolution and cumulative heat results for the synthesized CSAB cements containing their minimum

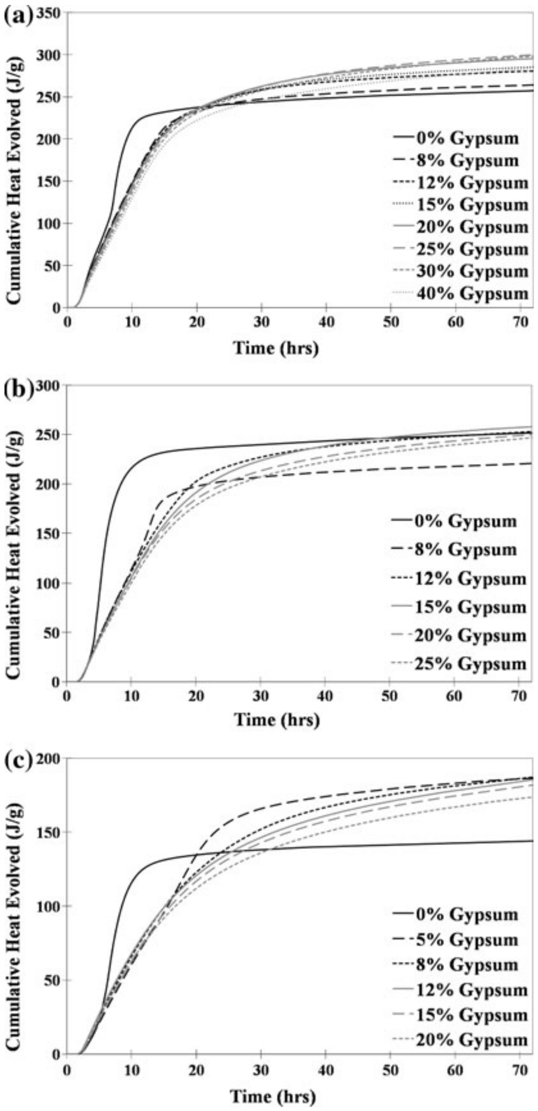

Fig. 5 Cumulative heat for the HS (**a**), MS (**b**), and LS (**c**) CSAB cement clinkers with different amounts of gypsum blended

gypsum contents and a commercial Type I/II portland cement are compared in Fig. 6. The results show that the synthesized cements with higher $C_4A_3\bar{S}$ contents had higher maximum rates of heat evolution and cumulative heats than the synthesized cements with lower $C_4A_3\bar{S}$ contents. In these cements, $C_4A_3\bar{S}$ reacts very rapidly to form ettringite and amorphous AH_3; a higher proportion of $C_4A_3\bar{S}$ results in a faster rate of reaction. The commercial Type I/II portland cement reacted slower and had a lower maximum rate of heat evolution than all of the CSAB cements. This difference can be attributed to the faster rate of reaction of $C_4A_3\bar{S}$ in CSAB cement compared to C_3S in portland cement. The cumulative heat for portland cement was initially lower than that of the synthesized cements, but it eventually caught up.

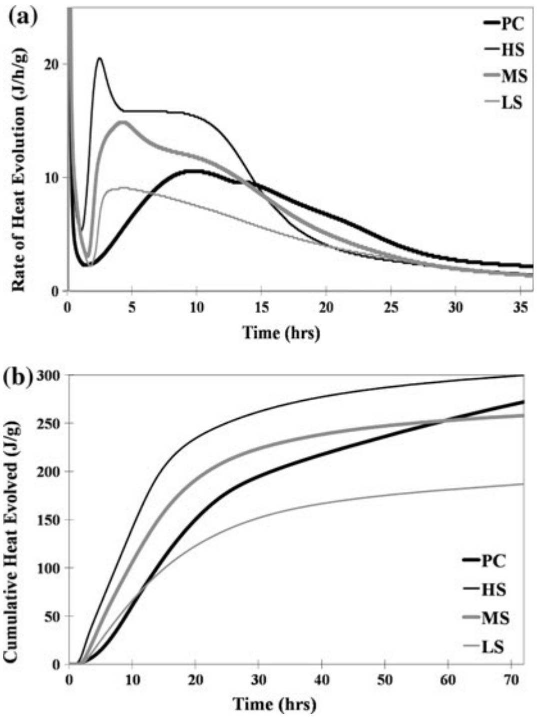

Fig. 6 Rate of heat evolution (**a**) and cumulative heat (**b**) for a commercial Type I/II portland cement (PC) and the CSAB cements (containing minimum gypsum content)

The rate of reaction in CSAB cements has an influence on fresh and hardened concrete properties. A very fast reaction, such as that exhibited by the HS cement, results in rapid setting and little available time for mixing and placing concrete. In these cases, a chemical retarder must be used to control the reaction and setting time when the cements are used in construction. On the other hand, faster reactions correlate with faster strength gains, which is often desirable.

Effects of temperature

Rate of heat evolution and cumulative heat results for the synthesized CSAB cements containing their minimum gypsum contents at 5, 23, and 38 °C are shown in Figs. 7 and 8. The results show that temperature had a dramatic effect on the rate of reaction. The time of commencement of acceleration, the slope of the acceleratory period, the maximum rate of heat evolution, and the width of the peak were all affected by a temperature from 23 to 38 °C. This indicates that the rate of reaction is quite sensitive to an increase in temperature, suggesting more rapid strength gain at higher temperatures, such as occurs with portland cement. At 5 °C, the reaction was extraordinarily slow, with the second heat evolution cycle only beginning after about 30 h. However, the reaction does appear to progress slowly, still producing heat after 72 h. Such a slow reaction

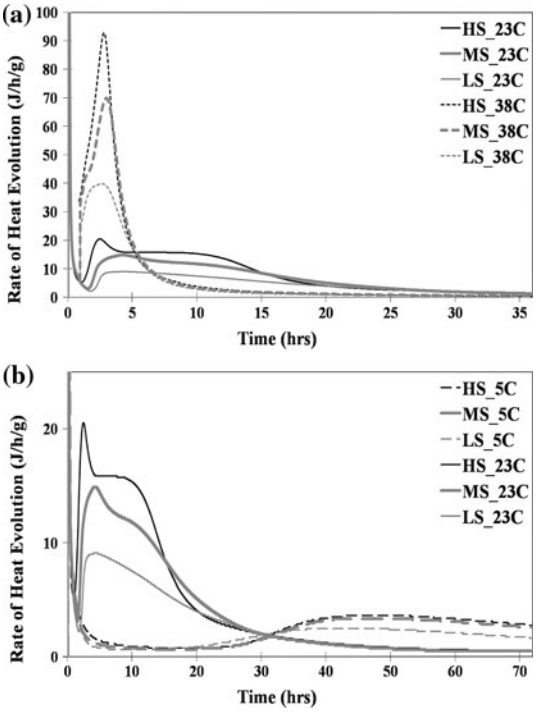

Fig. 7 Rate of heat evolution for the CSAB cements at 38 °C (**a**) and 5 °C (**b**) compared to 23 °C

is not useful for use in field concrete in the absence of chemical accelerators, as is also the case with portland cement.

Conclusions

Three CSAB cement clinkers with a range of target phase compositions were successfully synthesized from reagent-grade chemicals. A clinkering temperature of 1,250 °C was sufficient for complete reaction of the raw material and for the desired phase formation and spatial distribution. The ground CSAB cement clinkers had uniform particle fineness, comparable to commercial portland cement. The phase compositions for the CSAB cement clinkers were reasonably close to their target phase compositions, indicating that the Bogue method refined for this research can effectively predict CSAB cement clinker phase composition from its raw materials oxide composition. However, the synthetic clinkers with higher $C_4A_3\bar{S}$ contents had lower C_4AF contents than predicted by the proposed Bogue-type equations because $C_4A_3\bar{S}$ was able to accommodate up to 1.5 wt% Fe_2O_3, as shown by energy dispersive spectroscopy analysis. It was also observed that sulfur contained in the raw ingredients of CSAB clinker evaporates at temperatures above 1,200 °C. The loss of sulfur changes the final phase composition of the clinker. Therefore, special care should be taken during the firing process to minimize sulfur loss.

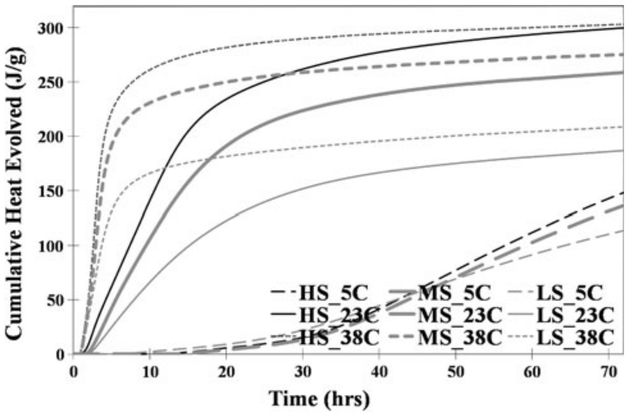

Fig. 8 Cumulative heat for the CSAB cements at 38 and 5 °C compared to 23 °C

Rate of heat evolution and cumulative heat results showed that the minimum gypsum contents for the CSAB cement clinkers synthesized from reagent-grade chemicals mainly depended on their $C_4A_3\bar{S}$ contents. Minimum gypsum content was defined as the lowest amount of gypsum for which the shape of the second heat evolution peak no longer changes with higher amounts of gypsum blended. Also, the CSAB cement clinkers show the highest cumulative heat with their minimum gypsum contents. An equation for calculating the minimum gypsum content for CSAB cement clinker was developed for future reference based on the $C\bar{S}$ content of CSAB cement clinker and the hydration reactions of $C_4A_3\bar{S}$ and C_4AF with gypsum to form ettringite and AH_3. The synthesized CSAB cements with higher $C_4A_3\bar{S}$ contents had higher maximum rates of heat evolution and cumulative heat than the CSAB cements with lower $C_4A_3\bar{S}$ contents. The hydration of CSAB cements at high temperatures (38 °C) was significantly faster, indicating poor field performance due to rapid setting in the absence of chemical retarders. The reactions at low temperatures (5 °C) were very slow, indicating poor performance in the field in the absence of chemical accelerators.

The results from this study represent a first approach at predicting phase formation in CSAB clinkers and examining the effects of phase composition and gypsum content on hydration rates. Reagent-grade chemicals were used to reduce the number of variables in the study. Since impurities affect phase formation and reaction behavior, it will be important to examine composition-property relationship in CSAB cements made from natural and waste raw materials to extrapolate these results to more realistic systems. It is also critical to comprehensively examine the effects of composition on hydration product development, strength development, volume stability, and long-term durability before these cements can successfully be utilized in the field.

Acknowledgements The authors express their thanks to the National Science Foundation (Grant No. CMMI 0448983) and Portland Cement Association (Project No. F08-07) for financial support and to Mr. Paul Stutzman from NIST for providing the phase lattice files used in Rietveld analysis.

References

1. US Geological Survey (2009) Mineral commodity summaries 2009
2. Hendricks CA, Worrell E, Price L, Martin N, Ozawa Meida L, de Jager D, Riemer P (1998) In: Proceedings of the 4th international conference on greenhouse gas control technologies, Interlaken, Austria
3. Mehta PK (1980) World Cem Technol 11:167
4. Sharp JH, Lawrence CD, Yang R (1999) Adv Cem Res 11:3
5. Majling J, Sahu S, Vlna M, Roy DM (1993) Cem Concr Res 23:1351
6. Glasser FP, Zhang L (2001) Cem Concr Res 31:1881
7. Kasselouri V, Tsakiridis P, Malami Ch, Georgali B, Alexandridou C (1995) Cem Concr Res 25:1726
8. Mindess S, Young JF, Darwin D (2003) Concrete, 2nd edn. Pearson Education Inc., Upper Saddle River, NJ
9. Roy DM, Silsbee MR, Xie Z (1999) In: Proceedings of the 1999 international ash utilization symposium, Center for Applied Energy Research, University of Kentucky, Lexington, KY
10. Beretka J, Santoro L, Sherman N, Valenti GL (1992) In: Proceedings of the 9th international congress on the chemistry of cement, New Delhi, India, 1992
11. Sahu S, Majling J (1994) Cem Concr Res 24:1065
12. Bogue RH (1929) Ind Eng Chem Res 1:192
13. Taylor HFW (1997) Cement chemistry, 2nd edn. Thomas Telford, London
14. ASTMC 204 (2007) Standard test methods for fineness of hydraulic cement by air-permeability apparatus. American Society of Testing and Materials, West Conshohocken, Pennsylvania
15. Richerson DW (1992) Modern ceramic engineering: properties, processing, and use in design, 2nd edn. Marcel Dekker Inc., New York
16. Ramachandran VS (1969) Applications of differential thermal analysis in cement chemistry. Chemical Publishing Company Inc., New York
17. JCPDS, International Centre for Diffraction Data (1989) Powder diffraction file search manual (Hanawalt method): inorganic
18. Young RA (1995) In: Young RA (ed) IUCr monographs of crystallography, vol 5. The Rietveld method. Oxford University Press, New York
19. Stutzman PE, Leigh S (2002) Phase composition analysis of the NIST reference clinkers by optical microscopy and X-ray powder diffraction. NIST Technical Note 1441, 44 pp
20. Whitfield PS, Mitchell LD (2003) J Mater Sci 38:4415. doi: 10.1023/A:1026363906432
21. Stutzman P (2004) Cem Concr Compos 26:957
22. Gartner EM, Young JF, Damidot DA, Jawed I (2002) In: Bensted J, Barnes P (eds) Structure and performance of cements. Spon Press, New York
23. ASTMC 150 (2005) Standard specification for portland cement. American Society of Testing and Materials, West Conshohocken, Pennsylvania
24. Martín-Sedeño MC, Cuberos AJM, De la Torre AG, Álvarez-Pinazo G, Ordónez LM, Gateshki M, Aranda MAG (2010) Cem Concr Res 40:359
25. Strigac J, Palou MT, Kristin J, Majling J (2000) Ceramics-Silikaty 44:26
26. Lerch CW (1947) The influence of gypsum on the hydration and properties of portland cement pastes. Proc Am Soc Test Mater 46:1252
27. Fukuhara M, Goto S, Asaga K, Daimon M, Kondo R (1981) Cem Concr Res 11:407
28. Minard H, Garrault S, Regnaud L, Nonat A (2007) Cem Concr Res 37:1418
29. Chen IA (2009) Synthesis of portland cement and calcium sulfoaluminate-belite cement for sustainable development and performance. PhD Dissertation, The University of Texas at Austin, Austin, TX
30. Wang Y, Su M, Yang R, Liu B (1992) In: Proceedings of the 9th international congress on the chemistry of cement, New Delhi, India
31. Peng J, Zhang J, Qu J (2006) J Wuhan Univ Technol (Mater Sci Edn) 21:158
32. Bernardo G, Telesca A, Valenti GL (2006) Cem Concr Res 36:1042
33. Sahu S, Havlica J, Tomková V, Majling J (1991) Thermochim Acta 175:45