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Incorporation of coal combustion residuals into calcium sulfoaluminate-belite cement clinkers

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ABSTRACT

In recent years, calcium sulfoaluminate-belite (CSAB) cement has been promoted as a sustainable alternative to Portland cement due to lower energy used and less CO_2 emitted during production, while providing comparable performance. However, a potential problem facing the widespread adoption and production of CSAB cement is the cost and availability of raw materials and it is therefore desirable to find alternative raw materials to keep costs competitive. In this study, two CSAB cement clinkers with a similar target phase composition were synthesized from combinations of natural and waste materials (coal combustion residuals). The two CSAB cement clinkers were compared against a CSAB clinker made from reagent-grade chemicals, enabling examination of the effects of impurities on performance. Cements made from the clinkers were examined for hydration rate, hydration product formation, dimensional stability, and compressive strength.

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1. Introduction

Calcium sulfoaluminate-belite (CSAB) cement generally refers to cements that have the same basic components of $C_4A_3\bar{S}$ (calcium sulfoaluminate)[1], C_2S (belite), and calcium sulfates, but the minor phases and the amounts of the phases present vary significantly depending on raw materials and applications [1–3]. CSAB cements can exhibit rapid setting, high early-age strength, self-stressing ability, and shrinkage-compensating properties, due to the fast reaction of $C_4A_3\bar{S}$ with calcium sulfates and water, and the expansive nature of the primary reaction product, ettringite ($C_6A\bar{S}_3H_{32}$). CSAB cements have been produced in China for over 40 years [4], with applications mainly in pre-cast concrete and cold environments. CSAB cement concrete has shown good dimensional stability, low permeability, low alkalinity, good durability, and comparable compressive strength to Portland cement concrete.

In the US and Europe, CSAB cement is being produced on a rather limited scale by a few companies, e.g. CTS Cement [5], Lafarge [6], and Buzzi Unicem [7]. While traditionally, CSAB cement was promoted as an expansive or rapid setting cement [5], in recent years, CSAB cement has been promoted as a sustainable alternative to Portland cement because of lower energy used and less CO_2 emitted during production [6]. Due to the different phase assemblage compared to Portland cement, CSAB cement requires less limestone for its formation [1]. The relatively low limestone 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 1250 °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 reduces CO_2 emissions from cement manufacturing, and the resulting clinker is more friable (due to a high porosity), which also reduces the energy needed for grinding [8].

CSAB cement can be produced by high temperature firing of minerals deposits such as limestone, clay, bauxite, and gypsum to provide the necessary CaO, SiO_2, Al_2O_3, and SO_3 required for phase formation, respectively. The hydration reaction of $C_4A_3\bar{S}$ with calcium sulfates 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) [9]:

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

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

Calcium sulfates can either be formed as anhydrite ($C\bar{S}$) in the clinker, be interground as gypsum ($C\bar{S}H_2$), hemihydrate ($C\bar{S}H_{0.5}$), and anhydrite ($C\bar{S}$) after clinkering, or some combination of the two [9]. On the other hand, the relatively slow hydration reaction of

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[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 $\bar{S} = SO_3$.

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C_2S forms calcium silicate hydrate (C–S–H) and calcium hydroxide, as shown in Eq. (3) [10], which contributes to long-term property development:

$$C_2S + (2 - x + y)H = C_xSH_y + (2 - x)CH \tag{3}$$

where x and y are not necessarily integers, $1.5 < x < 2$, and y is highly variable. C_xSH_y is typically abbreviated as C–S–H because of its variable stoichiometry.

A potential problem facing the widespread adoption and production of CSAB cement is the cost and availability of alumina bearing raw materials such as bauxite. Therefore, it is desirable to find alternative raw materials to keep costs competitive. If the raw materials are waste products of other industries, the environmental benefit of CSAB cement becomes even greater than simply a reduction in energy usage and CO_2 emissions, because the cement becomes a useful repository for waste materials that would otherwise enter landfills. Incorporating waste materials high in CaO rather than $CaCO_3$ further reduces energy consumption and CO_2 emissions, thereby further reducing the environmental impact. Furthermore, the high sulfate requirement for CSAB cement production allows sulfate-containing industrial byproducts to be used as raw materials for CSAB cement production [11]. Suitable waste materials for CSAB cement production include lime dust, fly ash, granulated blast furnace slag, fluidized bed ash, and flue gas desulfurization sludge for their high CaO, Al_2O_3, and SO_3 contents [12–16].

Previous research has shown successful production of CSAB cement from natural materials and waste materials [12–16]. However, the effects of impurities from natural and waste materials may significantly affect CSAB cement phase formation, hydration chemistry, and properties, and these effects have not been fully explored. Therefore, in this study, three CSAB cement clinkers with a similar target phase composition were synthesized from reagent-grade chemicals or combinations of natural (limestone and bauxite) and waste materials (coal combustion residuals: flue gas desulfurization sludge, fly ash, and fluidized bed ash). The CSAB cement clinker synthesized from reagent-grade chemicals served as a reference against which the clinkers made with natural and waste materials were compared. The final goals were to produce satisfactory CSAB cements with minimal natural and maximal waste material contents and to evaluate the effects of impurities from natural and waste materials used on phase formation, hydration chemistry, and properties.

2. Experimental

A phase assemblage of $C_4A_3\overline{S}$—C_2S—C_4AF—$C\overline{S}$ was chosen. C_4AF was included as a minor phase because most natural and waste materials suitable for cement manufacturing contain some amount of iron. A phase composition with equal (40%) C_2S and $C_4A_3\overline{S}$ contents (Table 1) was determined by Chen et al. [17,18] to have a good balance between CSAB cement property development and dimensional stability and was, therefore, chosen as the target phase composition for this study. The synthetic clinkers were ground into fine powder form and characterized. Different amounts of gypsum were added to the synthetic clinkers and the resulting cements were tested for heat evolution rate using isothermal conduction calorimetry to determine a minimum gypsum content based on early hydration behavior. The synthesized CSAB cements containing their minimum gypsum contents were monitored for hydration product development using X-ray diffraction. Finally, dimensional stability, sulfate resistance, and compressive strength development for the synthesized cements were studied. The results were compared to a commercial Type I/II Portland cement [19].

Table 1

Phase compositions (Calc.: target phases calculated from the adapted Bogue equations; Actual: actual phases determined using Rietveld analysis); gypsum ($C\overline{S}H_2$) contents expressed as the percent of cement replaced (Calc.: calculated using empirical equation, Actual: evaluated using isothermal calorimetry); and measured Blaine fineness values of the CSAB cement clinkers.

Phase	Phase composition (weight%)					
	MS		MC		MF	
	Calc.	Actual	Calc.	Actual	Calc.	Actual
C_2S	40	45	42	43	41	41
$C_4A_3\overline{S}$	40	42	40	44	39	42
C_4AF	10	6	8	8	7	8
$C\overline{S}$	10	7	4	2	7	4
C	0	<1	1	<1	2	<1
$C_5S_2\overline{S}$	N/A	0	N/A	1	N/A	3
MgO	N/A	0	N/A	2	N/A	2
$C\overline{S}H_2$	19	15	26	20	24	20
Blaine (m^2/kg)	–	323	–	324	–	312

2.1. Raw materials

The reagent-grade chemicals used for the synthesis of CSAB cement clinkers were calcium oxide (96% + CaO; Acros), 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% $CaSO_4{\cdot}2H_2O$; Acros). The natural and waste materials used to synthesize CSAB cement clinkers were limestone (Texas Lehigh Cement), bauxite (C–E Minerals), flue gas desulfurization sludge (Boral Material Technologies), Class C [20] fly ash (Headwaters/ISG), and fluidized bed ash (Tucson Electric Power); their oxide compositions from X-ray fluorescence analysis are shown in Table 2.

The reason for using flue gas desulfurization sludge, Class C fly ash, and fluidized bed ash was because of their high CaO, SO_3, and Al_2O_3 contents. The Class C fly ash and fluidized bed ash chosen had high CaO contents, rather than the $CaCO_3$ that is present in limestone, so replacement of limestone with ash could reduce CO_2 emissions from cement manufacturing. Moreover, Class C fly ash and fluidized bed ash are less used in concrete as supplementary cementitious materials than Class F fly ash. Furthermore, the fluidized bed ash has a high sulfate content, which could cause durability problems if used as a supplementary cementitious material in Portland cement concrete [21].

2.2. Materials proportioning

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 [22,23]. It was adapted for CSAB cement by assuming a phase assemblage of C_2S–$C_4A_3\overline{S}$–C_4AF–$C\overline{S}$–C, as shown in Eqs. (4)–(8). This phase assemblage was determined from review of the literature and preliminary testing [1–3].

$$\%C_4AF = 3.043(\%Fe_2O_3) \tag{4}$$

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

$$\%C_2S = 2.867(\%SiO_2) \tag{6}$$

$$\%C\overline{S} = 1.700(\%SO_3) - 0.445(\%Al_2O_3) + 0.284(\%Fe_2O_3) \tag{7}$$

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

Three CSAB cement clinkers were synthesized from reagent-grade chemicals or natural and waste materials for a similar target phase composition (Table 1). MS designates a clinker with equal

Table 2
Oxide compositions of the natural materials and industrial waste materials used for the MC and MF CSAB cement clinkers.

Oxide	Amount in sample (weight%)				
	Limestone	Bauxite	Flue gas desulfurization sludge	Class C fly ash	Fluidized bed ash
SiO_2	6.0	6.1	2.8	33.6	21.4
Al_2O_3	1.7	85.8	0.2	18.5	11.2
Fe_2O_3	0.6	2.2	0.2	6.6	3.5
CaO	49.0	0.5	37.9	27.1	37.8
MgO	0.9	0.2	0.2	6.1	3.7
Na_2O	0.1	0.1	0.1	1.9	2.0
K_2O	0.3	0.2	0	0.4	0.4
TiO_2	0	4.0	0	1.3	0.8
MnO_2	0	0	0	0	0
P_2O_5	0.1	0.3	0	1.2	0.9
SrO	0.1	0.1	0	0.5	0.2
BaO	0	0	0	0.7	0.4
SO_3	0.8	0	52.0	1.8	10.2
LOI*	40.4	0.5	6.6	0.3	7.5
Moisture	0.5	0.1	0.3	0.1	0.4

* LOI is mass lost on ignition to 750 °C.

amounts C_2S and $C_4A_3\overline{S}$ (40%) synthesized from reagent-grade chemicals. MC designates a clinker with the same C_2S and $C_4A_3\overline{S}$ contents synthesized from a high amount of Class C fly ash while MF designates a clinker with medium C_2S and $C_4A_3\overline{S}$ contents synthesized from a high amount of fluidized bed ash. The target C_4AF contents were controlled at about 10% for all of the synthetic clinkers because the natural and waste materials used for the synthesis of MC and MF CSAB cement clinkers contained some amount of iron. The target $C\overline{S}$ contents were kept low in all of the synthetic clinkers because it strongly affects hydration behavior [9]; instead, the minimum gypsum ($C\overline{S}H_2$) content was evaluated experimentally and blended with the clinkers before testing.

The proportions of raw ingredients for the MC and MF CSAB cement clinkers are shown in Table 3. The MC CSAB cement clinker was synthesized from limestone, bauxite, flue gas desulfurization sludge, and Class C fly ash while the MF CSAB cement clinker was synthesized from limestone, bauxite, flue gas desulfurization sludge, and fluidized bed ash. Waste materials composed 30% and 41% of the raw ingredients on a mass basis for the MC and MF CSAB cement clinkers, respectively.

2.3. 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 ratio) and mixed using a rotary jar mill (US 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 [24]. The solution was poured into 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 run, 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 1250°C for 12 h. The firing time in the furnace was much longer compared to the firing time in a rotary kiln used in industrial manufacturing because the raw ingredients remained stationary inside the crucibles during the firing process, which prevented materials from efficiently reacting with each other. Finally, the resulting clinker was ground into fine powder form using a micro mill grinder (Scienceware/Bel-Art).

Table 3
Proportion of raw ingredients for the MC and MF CSAB cement clinkers from natural and waste materials.

Raw materials	Proportion of materials (weight%)	
	MC	MF
Limestone	56	45
Bauxite	14	14
Flue gas desulfurization sludge	10	6
Class C fly ash	20	0
Fluidized bed ash	0	35

2.4. Analysis and testing

2.4.1. Particle fineness and size distribution

The ground synthetic clinkers were tested by an air-permeability test according to ASTM C 204 [25]; the resulting specific surface area value is referred to as Blaine fineness. A laser diffraction particle size distribution analyzer (Fritsch Analysette 22) was used to study the particle size distribution for the CSAB cement clinkers [26]. Both the Blaine fineness and the particle size distribution results were compared to a commercially-produced Type I/II Portland cement (TXI Hunter). Both tests were performed to assure uniform particle fineness and distribution between the synthetic clinkers.

2.4.2. X-ray diffraction

X-ray diffraction (Siemens D500 Powder Diffractometer; Cu $K_{\alpha1}$, $\lambda = 1.5046$ Å) was used to determine phase compositions for the CSAB cement clinkers and the hydrated synthesized CSAB cements at 3 h, 1, 3, 7, 28, and 90 days. For the hydrated synthesized cement samples, pastes were cast in 25 ml polyethylene cups using a water-to-cement ratio of 0.45 by mass, demolded at 1 day of hydration, and cured in ultra-pure water at room temperature until testing. Ultra-pure water was used to cure samples as it is difficult to control desiccation and carbonation, especially when curing small samples, even with humidity control. Furthermore, saturated lime solution, which is commonly used to cure Portland cement, can react with the AH_3 phase from CSAB cement hydration to form ettringite and was therefore considered not suitable for CSAB cement. Hydration was stopped by soaking the sample in ethanol followed by drying in a vacuum desiccator. The desiccator was attached to a 1/8 HP diaphragm vacuum pump with a max pressure of 0.41 MPa and a max vacuum of 648 mm-Hg to keep the relative humidity close to 0%. The X-ray diffraction 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 for the synthetic clinkers and 5–70° 2θ for the hydrated synthesized cements. 20% rutile (TiO_2) was ground into the hydrated synthesized cements to serve as an internal standard in order to quantify the amorphous content. Qualitative information for the phases present in the CSAB cement clinkers was obtained using the Hanawalt manual and the Jade program (MDI) [27]. Quantitative information was collected using Rietveld analysis (with an accuracy of about 3% for major phases and 1% for minor phases) by fitting the lattice parameters of the phases present in the synthetic clinkers to their X-ray diffraction patterns, which was performed with the TOPAS-Academic software (Bruker AXS) [28,29].

2.4.3. Scanning electron microscopy

Scanning electron microscopy (JEOL JSM-5610 SEM) was used to study phase distribution in the CSAB cement clinkers. Samples for the synthetic clinkers were prepared by mixing the ground synthetic clinkers with optical-grade epoxy (EPO-TEK 353ND) and casting in cylindrical epoxy sample disks. The 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 [30].

2.4.4. Isothermal conduction calorimetry

The heat produced by cementitious materials in exothermic hydration reactions is a good indication of their early-age hydration behavior [31]. The CSAB cement clinkers were made into cements by blending different amounts of gypsum (99% $CaSO_4 \cdot 2H_2O$; Acros) to control the hydration reaction of $C_4A_3\bar{S}$. The resulting cements were tested for heat evolution rate using isothermal conduction calorimetry (Thermometric TAM Air) to study the early-age hydration behavior. Hydration was evaluated for 3 days at 23°C using a water-to-cement ratio of 0.45. The results were compared to a commercially-produced Type I/II Portland cement (TXI Hunter). The minimum amount of gypsum (percentage of cement replacement) needed to control hydration was determined for each of the clinkers.

2.4.5. Dimensional stability and sulfate resistance

Dimensional stability and sulfate resistance of the synthesized CSAB cements were measured by adapting a test method for concrete sulfate resistance [32]. The small molds were selected to minimize the cement used in testing, as it is limited by the quantity that can be produced in the laboratory furnace. The molds are made of PTFE and produce small prisms (40 × 10 × 10 mm). Cement paste (water-to-cement ratio of 0.45) was hand-mixed to homogeneity in a 250 ml glass beaker, cast in the PTFE molds, cured at room temperature and 100% relative humidity, and demolded after 1 day. For dimensional stability tests, the bars were cured in ultra-pure water from 1 to 4 days at room temperature. Dimensional stability of the synthesized CSAB cements was tested by measuring length change of the prisms relative to an Invar bar of similar length using calipers accurate to ±0.01 mm. The initial length was taken to be that after demolding and prior to immersion in water.

To determine sulfate resistance, the paste bars were cured in ultra-pure water at room temperature for 6 days after demolding and then transferred to a 5% Na_2SO_4 solution at room temperature for 90 days. The initial length was taken to be that after water curing and before immersion in sulfate solution, thus at a paste age of 7 days. For both the dimensional stability and the sulfate resistance tests, six small bars were measured from each batch of paste and the expansion was averaged. The standard deviations of the measurement were within 10%. The results were compared to a commercially-produced Type I/II Portland cement (TXI Hunter).

2.4.6. Compressive strength development

Compressive strength development of the synthesized CSAB cements was tested with cubes (50 × 50 × 50 mm) of standard mortar (cement + sand + water; water-to-cement ratio of 0.45) according to ASTM C 109 [33]. The mortar cubes were demolded at 1 day and cured in ultra-pure water at room temperature. Ultra-pure water instead of saturated lime solution (specified by ASTM C 109) was used for curing the mortar cubes to prevent reactions between the AH_3 phase from CSAB cement hydration and $Ca(OH)_2$. Compressive strength was tested at 1, 3, 7, 28, and 90 days. Three mortar cubes were tested at each age for each sample type and the strengths were averaged. The standard deviations of the measurement were within 10%. The results were compared to a commercially-produced Type I/II Portland cement (TXI Hunter).

3. Results and discussion

3.1. Synthesis

3.1.1. Particle fineness and size distribution

Measuring the particle fineness and size distribution of the synthetic clinkers is critical because these factors strongly affect performance. The ground synthetic 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 [19]. However, the synthetic clinkers had Blaine values about 20% lower than the commercial Type I/II Portland cement (403 m^2/kg). Blaine fineness measures the rate of air passing through a pressed powder and its results could be affected by particle surface chemistry, morphology, and porosity, which could be different between CSAB cement and Portland cement, resulting in different measured Blaine values [34].

The particle size distributions obtained from laser light scattering for the synthetic clinkers were similar to that of the commercial Type I/II Portland cement; all had median particle sizes (d_{50}) of approximately 45 μm, as shown in Fig. 1. However, the MC and MF CSAB cement clinkers from natural and waste materials contained more fine particles (<20 μm) than the MS CSAB cement clinker from reagent-grade chemicals and the commercial Type I/II Portland cement.

3.1.2. Phase composition

A comparison of the measured X-ray diffraction patterns for the synthetic clinkers is shown in Fig. 2 and their quantitative phase compositions determined through Rietveld analysis are shown in Table 1. The phase analysis results show that the four targeted CSAB cement phases (C_2S, $C_4A_3\bar{S}$, C_4AF, and $C\bar{S}$) formed in all of the synthetic clinkers. The synthetic clinkers had low free lime (C) contents, indicating that the 1250C firing temperature was sufficient for CSAB cement clinker synthesis when using either reagent-grade chemicals or natural and waste materials as raw

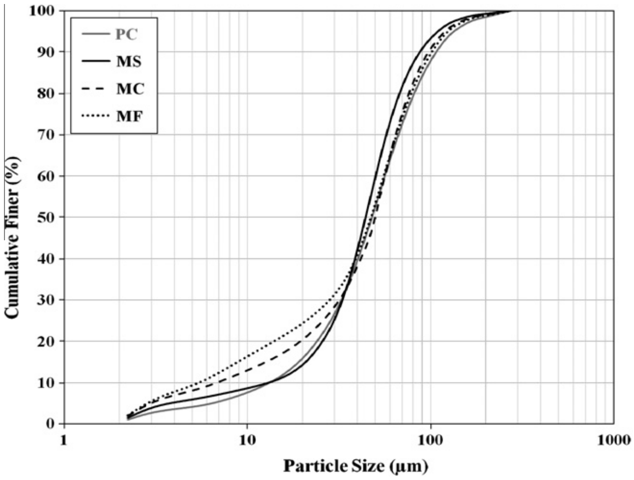

Fig. 1. Particle size distribution for a commercial Type I/II Portland cement (PC), MS CSAB cement clinker from reagent-grade chemicals, MC and MF CSAB cement clinkers from natural and waste materials.

materials. The phase compositions for the MS CSAB cement clinker from reagent-grade chemicals, and MC and MF CSAB cement clinkers from natural and waste materials were reasonably close to their target phase compositions, indicating that the adapted Bogue method can effectively predict CSAB cement clinker phase composition from its raw materials oxide composition when using either reagent-grade chemicals or natural and waste materials as raw materials. The slight deviations from the target phase compositions were perhaps caused by the ability of phases to accommodate substitute ions in forming solid solutions [23]. The impurities contained in the natural and waste materials slightly affected phase formation as $C_5S_2\overline{S}$ and periclase (MgO) formed in both the MC and MF CSAB cement clinkers. However, their contents were about 2% and should not significantly affect performance.

3.1.3. Phase distribution

Backscattered electron images clearly show phase and particle size distribution in the synthetic clinkers, as shown in Fig. 3. The lighter gray areas in the images represent C_2S while the darker gray areas represent $C_4A_3\overline{S}$. The small amount of white areas that formed individually and inside the light gray (C_2S) and dark gray ($C_4A_3\overline{S}$) areas represent C_4AF. The MS CSAB cement clinkers from reagent-grade chemicals, and the MC and MF CSAB cement clinkers from natural and waste materials contained similar amounts of light gray (C_2S) and dark gray ($C_4A_3\overline{S}$) areas, which agrees with the quantitative X-ray diffraction results (Table 1). Furthermore, the MC and MF CSAB cement clinkers contained more fine particles than the MS CSAB cement clinker, which conforms to the laser light scattering particle size distribution analysis results (Fig. 1) that show higher fine particle (<20 μm) contents in the MC and MF CSAB cement clinkers.

It is clear in Fig. 3 that the synthetic clinkers are highly porous, leading to lower energy needed for grinding than for Portland cement [8]. It is also interesting to note that in Fig. 3, many of the ground clinker particles contain several finely distributed phases, perhaps indicative of phases forming through solid-state reactions. The maximum synthesis temperature, 1250 °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 and ferrite contents in the CSAB cement system could have acted as mineralizers, thereby reducing the temperature required for liquid phase formation [23].

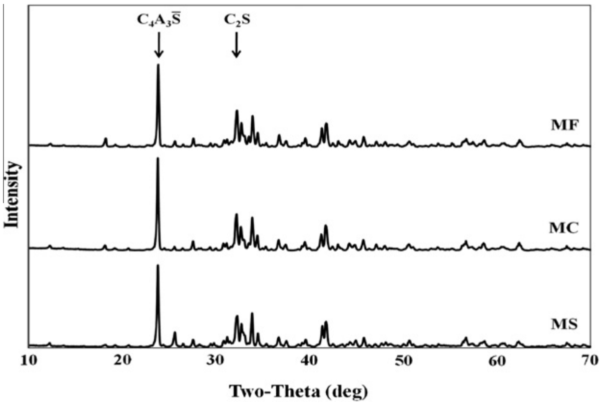

Fig. 2. X-ray diffraction pattern comparison for the MS CSAB cement clinker from reagent-grade chemicals and MC and MF CSAB cement clinkers from natural and waste materials.

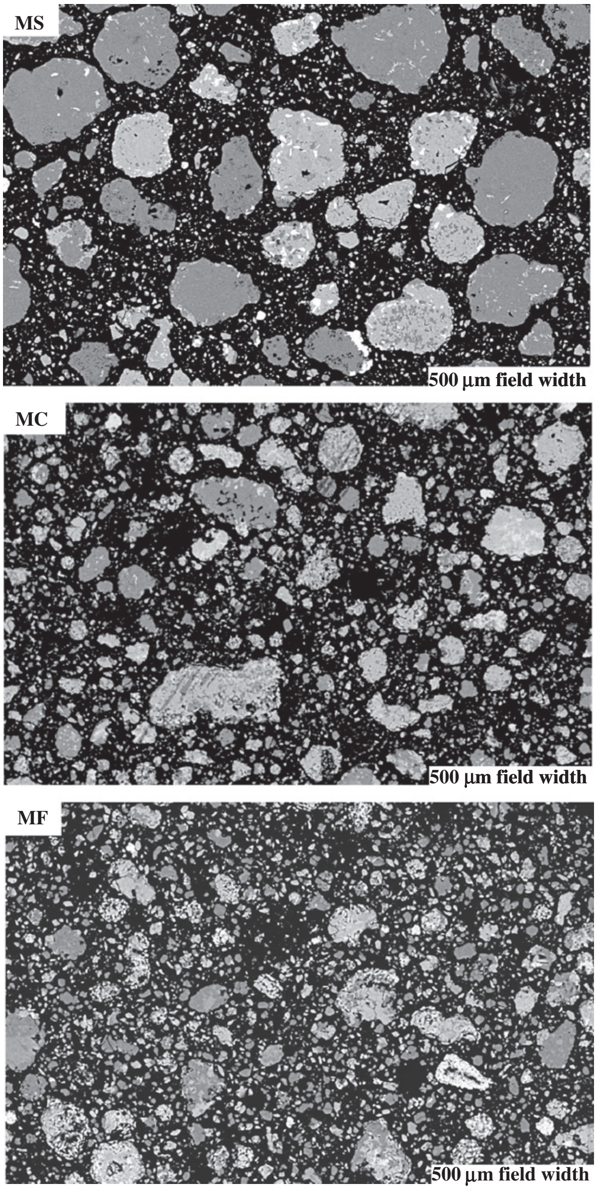

Fig. 3. Backscattered electron image for the MS CSAB cement clinker from reagent-grade chemicals, MC and MF CSAB cement clinkers from natural and waste materials (light gray: C_2S, dark gray: $C_4A_3\overline{S}$, and white: C_4AF).

3.2. Hydration behavior

3.2.1. Minimum gypsum content

To study the effects of blended gypsum on early-age hydration behavior and to determine the minimum gypsum content to control hydration, different amounts of gypsum were blended with the synthetic clinkers. The resulting cements were tested for rate of heat evolution using isothermal conduction calorimetry. Rate of heat evolution results for the synthetic clinkers with 0–25% blended gypsum (percentage of cement replacement) are shown in Fig. 4; note that the *x*-axis for MS shows the first 36 h of hydration while MC and MF show only the first 12 h. The minimum gypsum contents for the synthetic clinkers were determined using a method described by Chen and Juenger [18], where the shapes of cycles of heat release in the first 30 h do not change appreciably with higher quantities of gypsum blended than the experimentally determined minimum amount. For properly sulfated CSAB cements, the first heat released on contact with water is mainly from the dissolution of the cement phases, while the second heat evolution cycle is mainly from the hydration reactions of $C_4A_3\overline{S}$ and C_4AF with calcium sulfates to form ettringite $C_6A\overline{S}_3H_{32}$) and AH_3 according to Eqs. (1) and (2). Calcium sulfates in these cements are a combination of anhydrite ($C\overline{S}$) formed in the clinker and gypsum ($C\overline{S}H_2$) interground after clinkering. The reactions of $C_4A_3\overline{S}$ and C_4AF with calcium sulfates can either be concurrent, thus resulting in one cycle of heat release (or one cycle with two humps), or they can be separate, occurring as two distinct peaks. MS shows a single cycle with two humps for properly sulfated cement, MC shows a single peak (due to overlap of the hydration heat cycle with the initial heat dissolution cycle), and MF shows two distinct peaks (Fig. 4). For improperly sulfated cements, another heat release cycle occurs when gypsum is depleted [35]. This gypsum depletion peak is clearly apparent in MS, MF, and MC cements for 0–12% added gypsum. With the minimum gypsum content, the synthetic clinkers showed the highest cumulative heat after 3 days (data not shown), an indication of optimum reaction rate throughout this period.

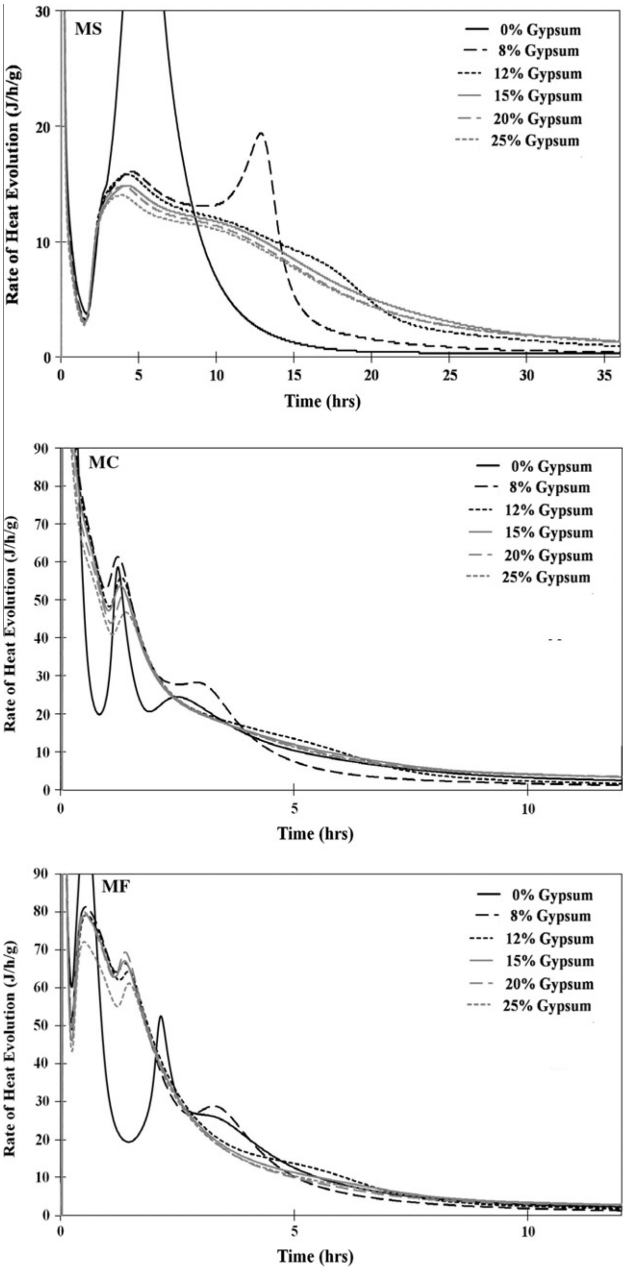

Fig. 4. Rate of heat evolution for the MS CSAB cement clinker from reagent-grade chemicals, MC and MF CSAB cement clinkers from natural and waste materials with different amounts of gypsum blended.

The minimum gypsum contents determined through calorimetry for all of the synthetic clinkers are shown in Table 1. The minimum gypsum contents for the MC and MF CSAB cement clinkers from natural and waste materials were determined to be 5% higher than the MS CSAB cement clinker from reagent-grade chemicals due to their lower $C\overline{S}$ contents (Table 1).

An alternative way of determining the minimum gypsum content for CSAB cement clinker is based on the $C\overline{S}$ content of CSAB cement clinker and the hydration reactions of $C_4A_3\overline{S}$ and C_4AF with gypsum to form ettringite and AH_3, as shown in Eq. (9):

$$\begin{aligned}&126.45\times[0.4461(\%C_4A_3\overline{S})+1.1205(\%C_4AF)\\&\quad-1.000(\%C\overline{S})]/\{100+1.2645\times[0.4461(\%C_4A_3\overline{S})\\&\quad+1.1205(\%C_4AF)-1.000(\%C\overline{S})]\}\end{aligned}\tag{9}$$

As shown in Table 1, determining the minimum amount of gypsum stoichiometrically through Eq. (9) overpredicts the minimum amount of gypsum compared to the experimental method, because it assumes that all phases will react to completion. It is interesting to note, however, that the over prediction is not severe, and Eq. (9) can be used effectively to predict the minimum gypsum content for CSAB cement clinker in order to minimize experimentation.

3.2.2. Early-age hydration behavior

Rate of heat evolution results for the MS CSAB cement from reagent-grade chemicals, and the MC and MF CSAB cements from natural and waste materials with their minimum gypsum contents added showed that the MC and MF CSAB cements reacted extremely quickly and had much higher maximum heat evolution rates than the MS CSAB cement even though they had similar clinker phase compositions, as shown in Fig. 5. However, cumulative heat results after three days for the MC, MF, and MS CSAB cements were similar, as shown in Fig. 6.

In order to understand the mechanism for the accelerating effect, the cements were examined for hydration product development. Interestingly, the MC and MF paste samples expanded, cracked, and completely crumbled after demolding and curing in ultra-pure water for 2 days (3 days of hydration), as shown in Fig. 7. Quantitative X-ray diffraction results for the hydrated MS, MC, and MF CSAB cements are shown in Table 4. At 3 h, the MC and MF CSAB cements contained only 3–4% unhydrated $C_4A_3\overline{S}$ and 9–10% unhydrated gypsum, while the MS CSAB cement contained 15% unhydrated $C_4A_3\overline{S}$ and 13% unhydrated gypsum. Accordingly, at 3 h of hydration, more ettringite and amorphous products formed in the MC and MF CSAB cements (24–26% of each) than in the MS CSAB cement (20% of each). Since C_2S is slow-reacting and remained mostly unhydrated at early ages (Table 4), the amorphous content should mainly contain AH_3 according to Eq. (2), and not C–S–H. The rapid initial hydration reaction of $C_4A_3\overline{S}$ and calcium sulfates to form ettringite and AH_3 in the hydrated MC and MF CSAB cements caused the paste samples to harden quickly. It was visually observed that the MC and MF CSAB cements hardened within 2 h after mixing while the MS CSAB cement was still soft 3 h after mixing. These results indicate that perhaps more ettringite and AH_3 formed in the MC and MF CSAB cements after the cement paste achieved set and resulted in the severe expansion and cracking in the paste samples [17].

The MS CSAB cement from reagent-grade chemicals, and the MC and MF CSAB cements from natural and waste materials had similar clinker phase compositions. The only differences are that the MC and MF CSAB cements synthesized from natural and waste

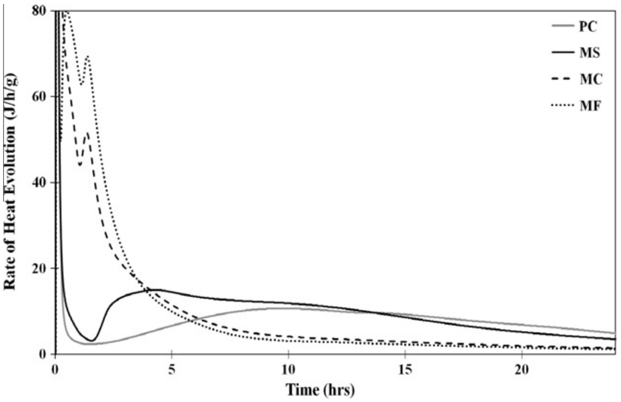

Fig. 5. Rate of heat evolution for a commercial Type I/II Portland cement (PC), MS CSAB cement from reagent-grade chemicals, MC and MF CSAB cements from natural and waste materials.

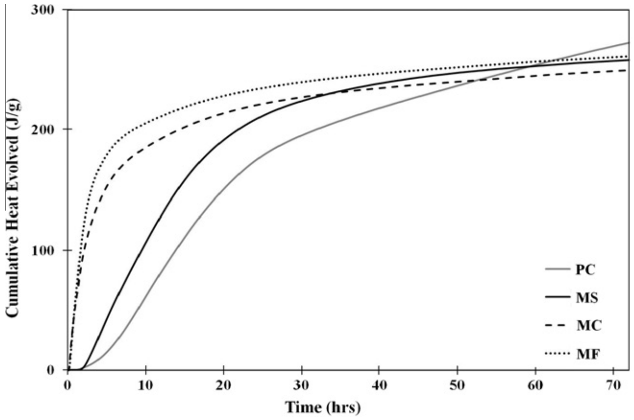

Fig. 6. Cumulative heat for a commercial Type I/II Portland cement (PC), MS CSAB cement from reagent-grade chemicals, MC and MF CSAB cements from natural and waste materials.

materials contained more fine particles (<20 μm; Fig. 1) and had higher impurity contents. The differences in fine particles are rather minor (<10%) and should not alone contribute to the significant differences observed in the hydration rate (Fig. 5) and hydration product development (Table 4) results. On the other hand, Table 2 shows that the Class C fly ash and fluidized bed ash used both had high alkali contents. Jawed and Skalny [36] showed that alkalis can increase the dissolution rate of the aluminate phases in Portland cement. Therefore, alkalis contained in the MC and MF CSAB cements (about 1%) might have accelerated the dissolution of $C_4A_3\overline{S}$ to form ettringite and AH_3 according to Eq. (2). To confirm this concept, 1% and 2% NaOH (by mass of cement) were added to the MS CSAB cement to evaluate the effect of alkalis. Rate of heat evolution results (Fig. 8) show that with 2% NaOH addition, the MS CSAB cement reacted much faster and had much higher maximum heat evolution rates, which were similar to those of the MC and MF CSAB cements. The results demonstrate, therefore, that alkalis can significantly accelerate hydration kinetics of the CSAB cement system.

To slow down the hydration reaction of $C_4A_3\overline{S}$ and calcium sulfates, 0.5–2% of citric acid, which is a common retarder used for both Portland cement and CSAB cement [37,38], was added to the MC and MF CSAB cements from natural and waste materials. Rate of heat evolution results for the MC and MF CSAB cements (Fig. 9) show that 1% citric acid addition (by weight of cement) was enough to effectively retard the hydration reactions in both the MC and MF CSAB cements to occur at about the same time as those of the MS CSAB cement; however, the maximum heat evolution rates were still much higher. Cumulative heat results (Fig. 10) show that the MC and MF CSAB cements had lower cumulative heat at 3 days with citric acid addition, which could affect CSAB cement performance.

3.2.3. Hydration product development

Quantitative X-ray diffraction results for the hydrated MS CSAB cement from reagent-grade chemicals and the hydrated MC and MF CSAB cements from natural and waste materials, with and without 1% citric acid addition, are shown in Tables 4 and 5, respectively. The results show that less $C_4A_3\overline{S}$ and gypsum reacted and less ettringite formed in the MC and MF CSAB cements at early ages (before 3 days) with 1% citric acid addition than without citric acid addition, as expected, since citric acid acts as a retarder (Fig. 9). However, $C_4A_3\overline{S}$ and gypsum in the MC and MF CSAB cements with 1% citric acid addition still reacted faster and more ettringite formed at early ages (before 3 days) than in the MS CSAB cement, which agrees with the calorimetry results in Fig. 9. Furthermore, more C_2S reacted at later ages (after 7 days) in the MC and MF CSAB cements with and without 1% citric acid addition than in the MS CSAB cement. The MS, MC, and MF CSAB cements had similar clinker phase compositions, the only difference being that the MC and MF CSAB cements synthesized from natural and waste materials had higher impurity contents, as shown in Table

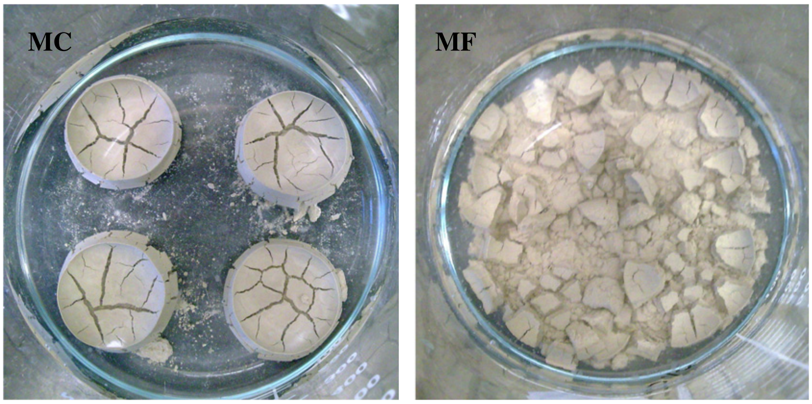

Fig. 7. Photographs of the MC and MF CSAB cements after 3 days of hydration, showing severe cracking due to expansion.

Table 4
Phase compositions for the hydrated MS CSAB cement from reagent-grade chemicals, MC and MF CSAB cements from natural and waste materials determined through Rietveld quantitative X-ray diffraction analysis.

Sample	Phase composition (weight%)									
	C_2S	$C_4A_3\bar{S}$	C_4AF	$C\bar{S}$	Periclase	$C_5S_2\bar{S}$	Gypsum	Ettringite	Amorphous	Calcite
MS 3 h	26	15	3	3	N/A	N/A	13	20	20	N/A
MS 1 day	25	10	3	2	N/A	N/A	6	25	29	N/A
MS 3 days	25	5	3	1	N/A	N/A	3	35	28	N/A
MS 7 days	25	3	3	1	N/A	N/A	2	39	27	N/A
MS 28 days	23	4	2	1	N/A	N/A	2	40	28	N/A
MS 90 days	21	4	3	1	N/A	N/A	2	41	26	2
MC 3 h	29	4	4	3	1	1	9	24	25	N/A
MC 1 day	29	3	5	2	1	1	7	31	21	N/A
MC 3 days	28	1	5	2	1	1	2	40	20	N/A
MC 7 days	28	2	5	1	1	1	1	45	16	N/A
MC 28 days	21	1	5	2	1	1	1	50	17	1
MC 90 days	13	1	4	1	0	1	1	48	29	2
MF 3 h	29	3	3	3	1	1	10	24	26	N/A
MF 1 day	30	2	4	3	1	1	7	30	22	N/A
MF 3 days	28	1	4	2	1	1	4	41	18	N/A
MF 7 days	28	1	4	2	1	1	2	44	17	N/A
MF 28 days	24	1	4	2	1	1	1	48	17	1
MF 90 days	14	1	4	1	1	1	1	46	29	2

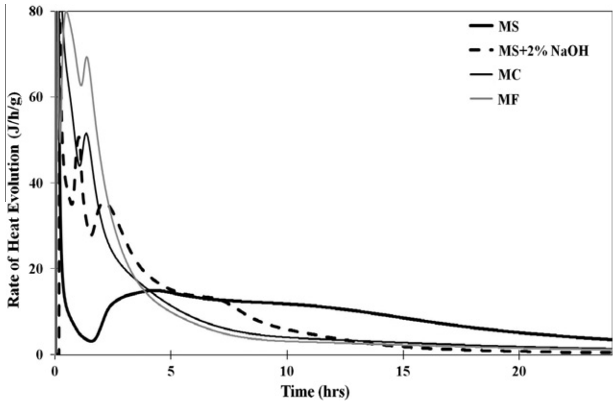

Fig. 8. Rate of heat evolution for the MS CSAB cement from reagent-grade chemicals with 2% NaOH addition, MC and MF CSAB cements from natural and waste materials.

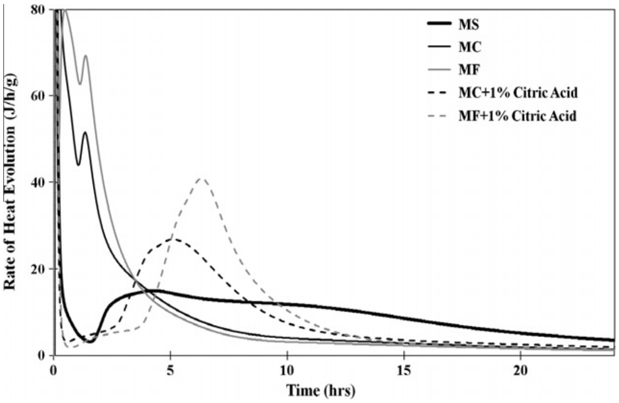

Fig. 9. Rate of heat evolution for the MS CSAB cement from reagent-grade chemicals, MC and MF CSAB cements from natural and waste materials with 1% citric acid (retarder) addition.

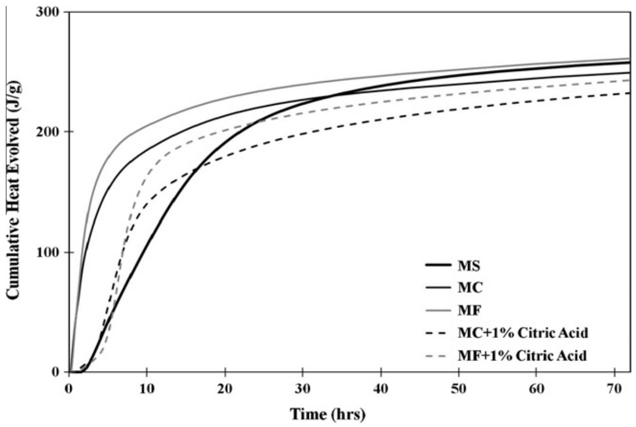

Fig. 10. Cumulative heat for the MS CSAB cement from reagent-grade chemicals, MC and MF CSAB cements from natural and waste materials with 1% citric acid (retarder) addition.

2. Gies and Knöfel [39] and Cuesta et al. [40] suggested that the incorporation of impurities such as alkalis, phosphorus, and boron in the C_2S lattice can increase its hydraulic reactivity by stabilizing the $\alpha'_H - C_2S$ modification, which is likely the reason for the increased reactivity of C_2S in MC and MF cements. It should be noted, though, that significant amounts of C_2S still remained unhydrated after 90 days of hydration in the MC and MF CSAB cements with and without 1% citric acid addition. It should also be noted that carbonation of the hydrated synthesized cements was observed as small amounts of calcite started to form in the MC and MF CSAB cements at 28 days of hydration with and without 1% citric acid addition and the MS CSAB cement at 90 days of hydration. The carbonation reaction occurred because of CO_2 diffusing through the curing water over time.

3.3. Dimensional stability and sulfate resistance

Dimensional stability results for the MS CSAB cement from reagent-grade chemicals, MC and MF CSAB cements from natural and waste materials with 1% citric acid addition (retarder), and a commercial Type I/II Portland cement are shown in Fig. 11. Even though the CSAB cements expanded more (~0.45%) than the Portland cement (~0.15%), the CSAB cements showed no signs of cracking, which should not seriously affect performance. Furthermore, the MC and MF CSAB cements showed comparable expansion to the MS CSAB cement (~0.45%), indicating that the severe expansion and cracking caused by the alkalis from the waste materials (Fig. 7) can be successfully reduced by slowing down the

Table 5
Phase compositions for the hydrated MS CSAB cement from reagent-grade chemicals, MC and MF CSAB cements from natural and waste materials with 1% citric acid (retarder) addition determined through Rietveld quantitative X-ray diffraction analysis.

Sample	Phase composition (weight%)									
	C_2S	$C_4A_3\overline{S}$	C_4AF	$C\overline{S}$	Periclase	$C_5S_2\overline{S}$	Gypsum	Ettringite	Amorphous	Calcite
MS 3 h	26	15	3	3	N/A	N/A	13	20	20	N/A
MS 1 day	25	10	3	2	N/A	N/A	6	25	29	N/A
MS 3 days	25	5	3	1	N/A	N/A	3	35	28	N/A
MS 7 days	25	3	3	1	N/A	N/A	2	39	27	N/A
MS 28 days	23	4	2	1	N/A	N/A	2	40	28	N/A
MS 90 days	21	4	3	1	N/A	N/A	2	41	26	2
MC 3 h	27	12	4	2	1	1	17	17	19	N/A
MC 1 day	27	5	4	1	1	1	10	25	26	N/A
MC 3 days	28	2	4	1	1	1	5	34	24	N/A
MC 7 days	27	1	4	1	1	1	3	38	24	N/A
MC 28 days	22	1	4	1	1	1	1	40	28	1
MC 90 days	18	1	4	1	1	1	2	42	28	2
MF 3 h	28	11	3	2	1	2	16	18	19	N/A
MF 1 day	27	4	3	2	1	2	9	27	25	N/A
MF 3 days	28	1	3	2	1	1	6	35	23	N/A
MF 7 days	27	1	3	1	1	1	4	40	22	N/A
MF 28 days	23	1	3	1	1	1	2	42	25	1
MF 90 days	18	1	3	1	1	1	2	43	27	3

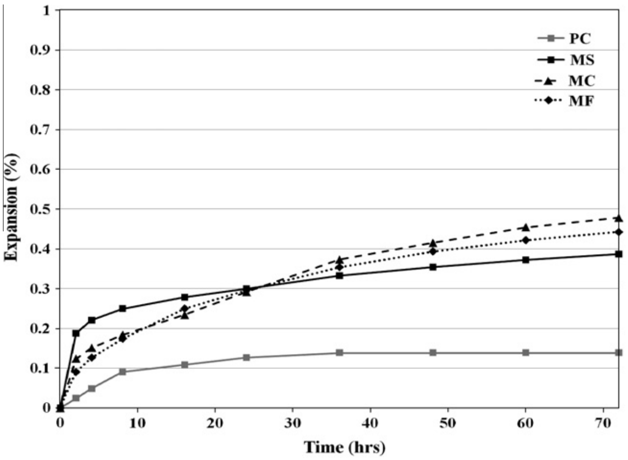

Fig. 11. Dimensional stability for a commercial Type I/II Portland cement (PC), MS CSAB cement from reagent-grade chemicals, and MC and MF CSAB cements from natural and waste materials with 1% citric acid (retarder) addition.

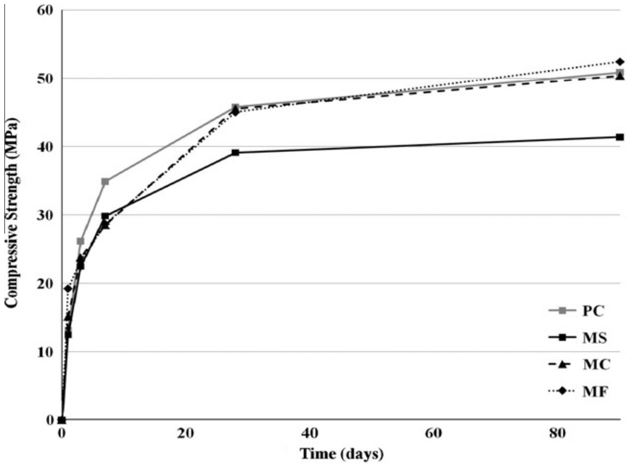

Fig. 12. Compressive strength development for a commercial Type I/II Portland cement (PC), MS CSAB cement from reagent-grade chemicals, and MC and MF CSAB cements from natural and waste materials with 1% citric acid (retarder) addition.

hydration rate with the addition of a retarder. On the other hand, sulfate resistance results for the MS CSAB cement from reagent-grade chemicals MC and MF CSAB cements from natural and waste materials with 1% citric acid addition (retarder), and a commercial Type I/II Portland cement all show nearly no expansion (<0.02% at 90 days).

3.4. Compressive strength development

Compressive strength results for the MS CSAB cement from reagent-grade chemicals, MC and MF CSAB cements from natural and waste materials with 1% citric acid (retarder) addition, and a commercial Type I/II Portland cement are shown in Fig. 12. The MC and MF CSAB cements developed compressive strength exceeding the MS CSAB cement even though they had similar phase compositions. This is because more C_2S reacted in the hydrated MC and MF CSAB cements at later ages and contributed to the long-term compressive strength development, as shown in the hydration product development results (Table 5). Furthermore, the MC and MF CSAB cements showed similar compressive strength development to the Portland cement. These results suggest that the MC and MF CSAB cements have the potential to replace Portland cement in concrete, without compromising dimensional stability, sulfate resistance, or compressive strength.

4. Conclusions

CSAB cement clinkers were successfully synthesized from reagent-grade chemicals, natural and waste materials. Waste materials composed 30% and 41% of the raw ingredients for the MC and MF CSAB cement clinkers from natural and waste materials, respectively. The phase compositions for the synthetic clinkers were reasonably close to their target phase compositions, indicating that an adapted Bogue method can effectively predict CSAB cement clinker phase composition from its raw materials oxide composition when using either reagent-grade chemicals, or natural and waste materials as raw materials. Impurities contained in the natural and waste materials slightly affected phase formation, as $C_5S_2\overline{S}$ and periclase (MgO) formed; however, their contents were about 2% and should not significantly affect performance. The MC and MF CSAB cements from natural and waste materials (with the experimentally-determined minimum gypsum contents added) reacted extremely quickly and had much higher maximum heat evolution rates than the MS CSAB cement from reagent-grade chemicals even though they had similar clinker phase compositions, which resulted in the severe expansion and cracking in the paste samples. The accelerating effect was caused by the alkali impurities from waste materials contained in the MC and MF CSAB cements. However, 1% citric acid was shown to be enough to effectively retard the hydration reactions. Hydration product development results from X-ray diffraction showed that C_2S reacted faster at later ages in the MC and MF CSAB cement from natural and waste materials with and without citric acid addition than in the MS CSAB cement from reagent-grade chemicals. The impurities incorporated in C_2S lattice likely increased its hydraulic reactivity. Dimensional stability and sulfate resistance results showed that the MC and MF CSAB cements with 1% citric acid addition had limited expansion, comparable to the MS CSAB cement and the commercial Type I/II Portland cement. Finally, compressive strength results showed that the MC and MF CSAB cements with 1% citric acid addition developed compressive strengths exceeding the MS CSAB cement and comparable to the Portland cement.

The CSAB cement clinkers from reagent-grade chemicals, natural and waste materials were successfully synthesized at a maximum temperature of 1250 °C, which is 200 °C lower than the maximum temperature used for Portland cement clinker synthesis. The lower synthesis temperature reduces energy consumption and CO_2 emissions from cement manufacturing. Moreover, raw ingredients for the MC and MF CSAB cement clinkers synthesized from natural and waste materials composed of 49.0% and 39.4% $CaCO_3$, which are much less compared to the raw ingredients for traditional Portland cement clinkers (70–80% $CaCO_3$). The low limestone requirement for CSAB cement production further reduces energy consumption and CO_2 emissions ($CaCO_3 \rightarrow CaO + CO_2$, $\Delta H = 178$ kJ/mol) from cement manufacturing. Finally, the reuse of high aluminum-containing waste materials such as Class C fly ash and fluidized bed ash reduces the use of expensive alumina bearing raw materials such as bauxite, thereby reducing cost and the environmental impact of cement manufacturing. However, special attention needs to be taken when using waste materials as raw materials for CSAB cement production, as the impurities contained in the waste materials could significantly affect CSAB cement formation, hydration chemistry and properties. For future research, a more comprehensive understanding on the effects of the different potential impurities will be beneficial for the large-scale implementation of CSAB cement production from waste materials.

Acknowledgements

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