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# Understanding expansion in calcium sulfoaluminate–belite cements

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ABSTRACT

Calcium sulfoaluminate–belite (CSAB) cements are promoted as sustainable alternatives to portland cement because of their lower energy and $CO_2$ emissions during production and comparable performance. However, the formation of ettringite, the main hydration product in CSAB cements, can be expansive, sometimes resulting in cracking. The factors controlling expansive behavior in CSAB cements have not been completely elucidated. In this study, three CSAB cements synthesized from reagent-grade chemicals with varied phase compositions were examined for dimensional stability in water and sulfate solutions. The interdependent effects of $C_4A_3\hat{S}$ (Ye'elimite) content, calcium sulfate content, water-to-cement ratio, and particle fineness on CSAB cement expansion were evaluated. The results show that the expansive behavior can be controlled by altering chemical and physical factors in CSAB clinker, cement, and paste.

## 1. Introduction

Calcium sulfoaluminate–belite (CSAB) cement is promoted as a sustainable alternative to portland cement (PC) because of lower energy used and $CO_2$ emitted during production. All 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 PC production [1]; the lower formation temperature also lowers the energy requirement and $CO_2$ emissions from fossil fuel burning. Further, due to high porosity, CSAB clinker is more friable than PC clinker, which reduces the energy needed for grinding [2]. CSAB cement principally utilizes $C_4A_3\hat{S}$[2] (Ye'elimite), instead of $C_3S$, as the primary early-age strength gaining phase and utilizes $C_2S$ to develop additional long-term strength. By using phases that are lower in CaO than $C_3S$, there is a reduction of $CO_2$ emissions during the calcination of limestone in cement kilns. To illustrate the wide variation in CaO content in cement phases, the CaO content by weight of several cement phases are listed: $C_3S$ 73.7%, $C_2S$ 65.1%, $C_3A$ 62.2%, $C_4AF$ 46.2%, $C_4A_3\hat{S}$ 36.7%. $C_4A_3\hat{S}$ has the lowest CaO content of any cement phase, making it an attractive option for developing a sustainable cement.

CSAB cements have exhibited rapid setting, high early-age strength, self stressing, and shrinkage compensating properties due to the fast reacting $C_4A_3\hat{S}$ and the expansive nature of ettringite [2]. In field practices, CSAB cements have been used mainly in pre-cast concrete applications and cold environments and have shown good dimensional stability, low permeability, low alkalinity, good durability, and comparable compressive strength to PC [3–6]. However, despite the increasing interests in CSAB cement, industrial scale production and usage are mostly limited to China [7].

Since ettringite formation in PC has been linked to expansion and degradation in several forms of sulfate attack including delayed ettringite formation and external sulfate attack [8,9], the dimensional stability and durability of CSAB cement, which relies on ettringite to provide early strength, needs to be extensively studied.

The hydration reactions of $C_4A_3\hat{S}$ and calcium sulfates ($C\hat{S}$ and $C\hat{S}H_2$) initiates rapidly and forms ettringite ($C_6A\hat{S}_3H_{32}$) and $AH_3$, which contribute to the early-age property development in CSAB cement. Eqs. (1)–(6) show some of the common hydration reactions in CSAB cements [10].

$$C\hat{S} + 2H \rightarrow C\hat{S}H_2 \tag{1}$$

$$C_4A_3\hat{S} + 2C\hat{S}H_2 + 34H \rightarrow C_6A\hat{S}_3H_{32} + 2AH_3 \tag{2}$$

$$C_4A_3\hat{S} + 8C\hat{S}H_2 + 6CH + 74H \rightarrow 3C_6A\hat{S}_3H_{32} \tag{3}$$

$$AH_3 + 3CH + 3C\hat{S}H_2 + 20H \rightarrow C_6A\hat{S}_3H_{32} \tag{4}$$

$$3C_4AF + 12C\hat{S}H_2 + 110H \rightarrow 4\,C_6(A,F)\hat{S}_3H_{32} + 2(A,F)H_3 \tag{5}$$

$$C_2S + 2H \rightarrow CH + C{-}S{-}H \tag{6}$$

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[2] Cement chemistry notation used ( $C = CaO$, $\hat{S} = SO_3$, $A = Al_2O_3$, $F = Fe_2O_3$, $S = SiO_2$, & $H = H_2O$ ).

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The formation of ettringite from the hydration reactions of $C_4A_3\hat{S}$ with calcium sulfates can be expansive [10]. It has been suggested that if most of the ettringite forms before hardening, then non-expansive and rapid hardening CSAB cement can be achieved, but significant ettringite formation after hardening can cause expansion and cracking [11]. Specific factors that have been shown to affect expansion in CSAB cements have been identified as: $C_4A_3\hat{S}$ content, pore structure, water to cement ratio (w/c), sulfate content, free lime content, alkali hydroxide content, and particle fineness. These factors are discussed in more detail next.

The phase assemblage in CSAB clinker has been shown to affect expansion; specifically, higher amounts of $C_4A_3\hat{S}$ have been linked to higher expansions. Beretka et al. [12] showed that CSAB cements containing mainly $C_4A_3\hat{S}$, $C_5S_2\hat{S}$, and $C\hat{S}$ expanded and cracked with $C_4A_3\hat{S}$ contents higher than 50% using a w/c of 0.4. These results agree with those of Janotka et al. [13] who found that CSAB cement with a low $C_4A_3\hat{S}$ content (20.2% $C_4A_3\hat{S}$, 50.3% $C_2S$, 9.7% $C\hat{S}$, and 19.5% $C_4AF$) and a w/c of 0.5 had limited expansion (0.25%), although it expanded more than PC mortar (−0.10%).

The effect of $C_4A_3\hat{S}$ content on expansion is mainly dependent on the amount of ettringite that formed after cement hardened according to Eq. (2), but the cement pore structure at the time of ettringite formation also plays an important role [11,14]. The cement pore structure affects the mobility of ions and the amount of space for reaction products to form. It has been suggested that the formation of ettringite confined to the vicinity of aluminum-bearing grains results in large expansions [14]. Therefore, ettringite formation in pastes with denser pore structures could cause more expansion. Bernardo et al. [15] showed that CSAB cement that contained a relatively high amount of $C_4A_3\hat{S}$ (53.0% $C_4A_3\hat{S}$, 13.2% $C_2S$, 18.6% $C\hat{S}$, and 10.3% $C_{12}A_7$) using a w/c of 0.5 hardened rapidly due to the fast formation of ettringite. The initial hydration products quickly reduced the internal pore space. After 6 h of hydration, the smaller pores (~25 nm) dominated over the capillary pores (~200 nm) and the system developed a bimodal pore structure, which generally correlates to a disconnected pore structure and a denser microstructure. Portland cement, on the other hand, showed a unimodal or continuous pore structure at early ages, which generally correlates to a more porous microstructure. Portland cement only developed a bimodal pore structure after 7 days of hydration, demonstrating the disconnected nature of the pore system as the larger pore volume decreased. These results suggest that the high $C_4A_3\hat{S}$ cement examined by Bernardo et al. [15] should be expansive. While Bernardo et al. [15] did not measure expansion on their specimens, the high $C_4A_3\hat{S}$ cements tested by Beretka et al. [12] earlier would presumably have a similarly dense microstructure and these did expand. On the other side of the spectrum, Janotka et al. [13] found that their low $C_4A_3\hat{S}$ content CSAB cement (20.2% $C_4A_3\hat{S}$, 50.3% $C_2S$, 9.7% $C\hat{S}$, and 19.5% $C_4AF$) with a w/c of 0.5 had higher porosity and coarser pore structure than PC mortar at 90 days of hydration and both were non-expansive, as discussed earlier.

The w/c affects the amount of space (porosity) available for hydration product formation and the amount of water available to hydrate the cement phases, both of which can alter expansion in CSAB cements. At lower w/c, cement develops a denser pore structure, which affects the mobility of ions and the amount of space for reaction products to form that could lead to expansive behavior in CSAB cements, as discussed in the previous paragraph. Furthermore, at lower w/c, high $C_4A_3\hat{S}$-bearing CSAB cements can undergo self-desiccation because the formation of ettringite requires large amounts of water according to Eq. (2) [2]. Therefore, more cement particles remain unhydrated, even at later ages. Having large amounts of unhydrated cement after setting can lead to expansion if the cement is later exposed to external water from the environment, since unhydrated phases can react to form secondary ettringite. Beretka et al. [12] tested a range of w/c with CSAB cements that mainly contained $C_4A_3\hat{S}$, $C_5S_2\hat{S}$, and $C\hat{S}$. It was observed that when using a w/c of 0.4, the CSAB cements with $C_4A_3\hat{S}$ content higher than 50% expanded and cracked after curing in 100% relative humidity (RH). At w/c of 0.4, the initial water content was not enough for the large amount of $C_4A_3\hat{S}$ to completely react according to Eq. (2). Therefore, the secondary ettringite formed from the unhydrated $C_4A_3\hat{S}$ and $C\hat{S}$ during curing after the paste hardened combined with the denser pore structure from the low w/c and high $C_4A_3\hat{S}$ content (more ettringite formation) resulted in the expansion and cracking at later ages. However, when using higher w/c of 0.65–0.7, the high $C_4A_3\hat{S}$ cements remained dimensionally stable during curing in 100% relative humidity because water in the system was sufficient for $C_4A_3\hat{S}$ to fully react at early ages and the microstructure is more porous. It should be noted that secondary ettringite formation and associated expansion depends on the curing environment [16]. When curing at low humidity, ettringite formation stops after a few days of hydration due to the loss of free water in the system.

Dimensional stability of commercial CSAB cement has been shown to be dependent on the amount of $C\hat{S}H_2$ available in the system, with higher $C\hat{S}H_2$ contents linked to higher expansions [2,17]. Yanmou et al. [17] experienced ~0.15% and ~0.70% expansion with 15% and 35% $C\hat{S}H_2$, respectively, with a CSAB clinker that contained 58.4% $C_4A_3\hat{S}$ and 11.6% $C_2S$. Glasser and Zhang [2] showed that a different commercial CSAB cement (unreported phase assemblage) shrunk slightly at 18% $C\hat{S}H_2$ addition, showed zero dimensional change at 22–24% $C\hat{S}H_2$ addition, and became expansive at 24–25% of $C\hat{S}H_2$ addition.

Type K cements [18] which are designed to be expansive contain CSAB cement as an additive to PC. The degree of expansion in Type K cement has been linked to free lime content. While investigating Type K cements, Kurdowski and Thiel [19] found that a cement containing 3.9% free lime produced much greater expansion than a low free lime cement (0.8%). When the two pastes were examined in a scanning electron microscope (SEM) at 1 and 7 days of hydration, the free lime accelerated the formation of ettringite but did not appear to affect the size of the ettringite crystals. In contrast, Mehta [20] found that the hydration of $C_4A_3\hat{S}$ in the presence of $C\hat{S}H_2$ and free lime resulted in ettringite crystals that were significantly smaller than ettringite crystals formed from the hydration of $C_4A_3\hat{S}$ in the presence of $C\hat{S}H_2$ only, suggesting a faster ettringite crystal formation rate when free lime is available. The presence of free lime may make the reaction pathway in Eq. (3) more favorable than the reaction pathway of Eq. (2); consequently, each unit of $C_4A_3\hat{S}$ would produce 3 units of ettringite instead of 1. The larger amount of ettringite produced per unit of $C_4A_3\hat{S}$ in Eq. 3 would result in a larger potential for expansion.

Alkali hydroxides have been shown to increase the dissolution rate of the aluminate phases in PC [21], and Min and Mingshu [14] found that alkali hydroxides increased the expansion in a sulfoaluminate cement, presumably through increasing the dissolution rate of $C_4A_3\hat{S}$ and formation of ettringite.

Cement particles can remain unhydrated through means other than self-desiccation. If the CSAB cement contains high quantities of coarser particles, then those larger particles will be slow to hydrate [22]. In Type K cements, the particle size of the $C_4A_3\hat{S}$-bearing cement has been shown to affect the amount and timing of the expansion [23]. When finer ground expansive Type K clinker was added to PC, the $C_4A_3\hat{S}$ particles reacted faster with calcium sulfates to form ettringite and the cement paste expanded at a high early rate for only a few days. However, when coarser ground expansive Type K clinker was used, the $C_4A_3\hat{S}$ particles reacted slower with calcium sulfates to form ettringite and the cement paste expanded at a slower rate for a longer period of time, which led to abnormal behavior. The delayed expansion and strength drop in coarser blends could be attributed to the formation of ettringite crystals on larger grains of $C_4A_3\hat{S}$ after the C–S–H matrix had formed, which caused localized mechanical failures in the matrix.

**Table 1**
CSAB cement clinker phase composition and gypsum replacement requirement.

| Clinker | $C_4A_3\hat{S}$ | $C_4AF$ | $C\hat{S}$ | $C_2S$ | Gypsum required (stoichiometric) | Gypsum required (experimental) |
|---|---|---|---|---|---|---|
| HS | 65.3% | 3.2% | 8.9% | 22.4% | 23.2% | 25% |
| MS | 42.0% | 6.1% | 6.8% | 44.9% | 19.2% | 15% |
| LS | 15.4% | 7.2% | 6.6% | 70.8% | 9.5% | 8% |

While previous research has identified variables that contribute to CSAB cement expansion, each study attributed expansion of the system to individual factors. Oftentimes identifying the cause of expansion was not the goal of the research; consequently, factors affecting expansion were not controlled in these studies. Also, many published studies do not give the phase composition of the CSAB cements tested. This study attempts to elucidate the interdependency of $C_4A_3\hat{S}$ content, particle fineness, w/c, and calcium sulfate content and show how CSAB cement expansion can be controlled by altering chemical and physical factors in CSAB clinker, cement, and pastes. The results should provide insights for future usage of CSAB cements as potential direct alternatives to PC in specialty applications.

## 2. Materials and methods

### 2.1. CSAB cements

Three different CSAB cements were synthesized from reagent grade chemicals with varying phase assemblages in order to test the effects of phase assemblage on expansion. The synthesis of the clinkers was described by Chen and Juenger [24] in detail. These contained high (HS), medium (MS), and low (LS) amounts of the sulfoaluminate phase (Table 1). The compositions in Table 1 were determined by Rietveld quantitative X-ray diffraction analysis of the clinkers. The particle size distributions of the synthesized clinkers were determined through laser diffraction (Fritsch Analysette 22) and are shown in Fig. 1. The particle size distribution (PSD) of a commercially-produced PC (TXI Hunter Type I/II portland cement) is shown for context. The amounts of gypsum replacement required stoichiometrically to the clinkers to form ettringite from $C_4A_3\hat{S}$ and $C_4AF$ (assuming completion of the reactions) and the amounts required according to experimental calorimetry testing [24] are given in Table 1.

### 2.2. Dimensional stability and sulfate resistance

Dimensional stability and sulfate resistance of the synthesized CSAB cements were tested by adapting a test method for concrete sulfate resistance [25]. The small molds were selected to minimize the cement used in testing; the molds are made of polytetrafluoroethylene (PTFE) and produce small prisms (40 × 10 × 10 mm). Cement paste was hand-mixed with a stainless steel spatula for 3 min to homogeneity in a 250 ml glass beaker, cast in the PTFE molds, cured at 23 °C and 100% relative humidity, and demolded after 1 day. For dimensional stability tests, the bars were transferred and cured in ultra-pure water from 1 to 4 days at room temperature (23 °C). 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 (18 MΩ) at room temperature (23 °C) for 6 days after demolding and then transferred to a 5% $Na_2SO_4$ solution at room temperature (23 °C) for 84 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, three small bars were measured from each batch of paste and the expansion was averaged. The measurements' errors were within 10% standard deviation.

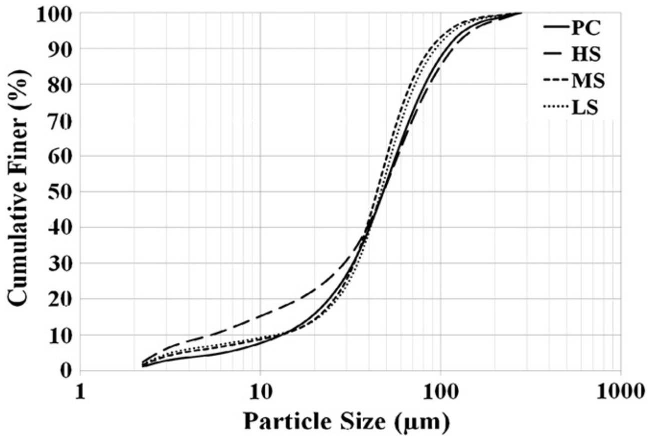

**Fig. 1.** Particle size distributions for a commercial PC and the CSAB cement clinkers.

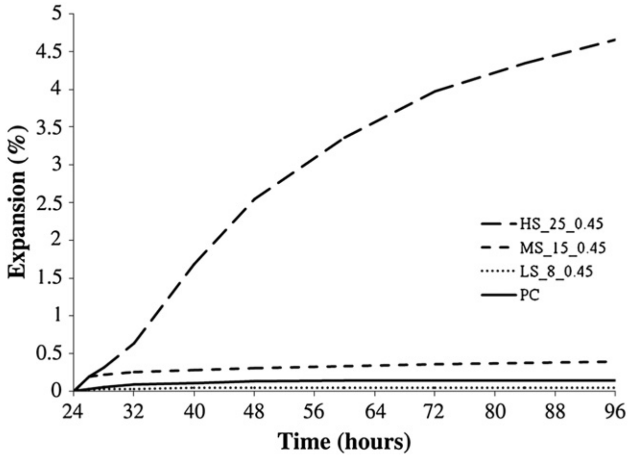

**Fig. 2.** Dimensional stability of a commercial PC and CSAB cements with experimentally-determined gypsum contents using w/c of 0.45 cured in ultra-pure water after demolding at 1 day.

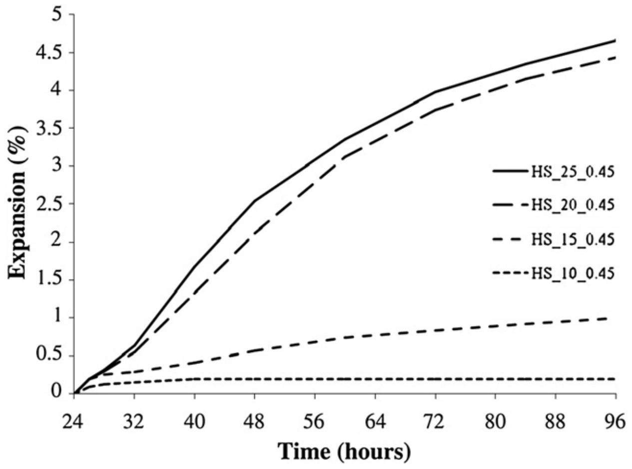

**Fig. 3.** Dimensional stability of the HS CSAB cement pastes with different amounts of gypsum using w/c of 0.45 cured in ultra-pure water after demolding at 1 day.

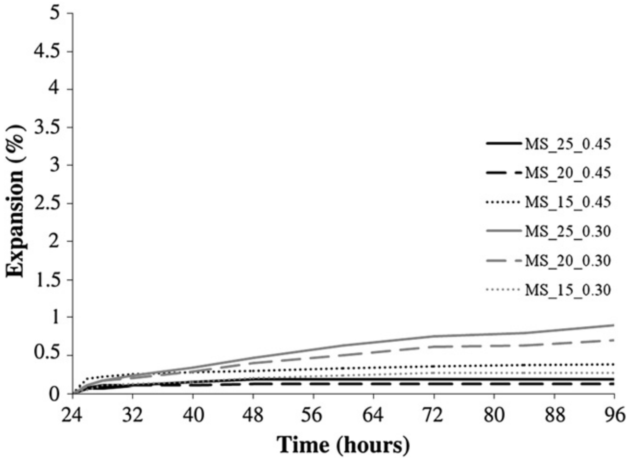

**Fig. 4.** Dimensional stability of MS CSAB cement pastes with different amounts of gypsum and w/c cured in ultra-pure water after demolding at 1 day.

### 2.3. X-ray diffraction

X-ray diffraction (XRD) (Siemens D500 Powder Diffractometer; Cu $K_{\alpha 1}$, $\lambda = 1.5046$ Å) was used to determine phase compositions for the hydrated CSAB cements at 3 h and 1, 3, 7, 28, and 90 days. Pastes were cast in 25 ml polyethylene cups using 5 g of cement and a w/c of 0.45, demolded at 1 day, and stored in ultra-pure water at room temperature (23 °C) until testing. Hydration was stopped by soaking in an excess of ethanol for 24 h followed by drying in a vacuum dessicator. The diffractometer was operated under 40 keV and 30 mA, the step size used was 0.02°/6 s, and the scan range used was 5°–70° 2θ. 20% rutile ($TiO_2$) was ground into the hydrated 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 and pastes was obtained using the Hanawalt manual and the Jade program (MDI) [26]. Quantitative information was determined using Rietveld analysis (with an accuracy of about 1%) by fitting the lattice parameters of the phases present in the synthetic clinkers to their XRD patterns [27,28]. To avoid interactions with the sample holder, the 2θ range of the XRD patterns that was quantitatively analyzed was restricted to 15°–70° 2θ. TOPAS-Academic software (Bruker AXS) was used for the analysis.

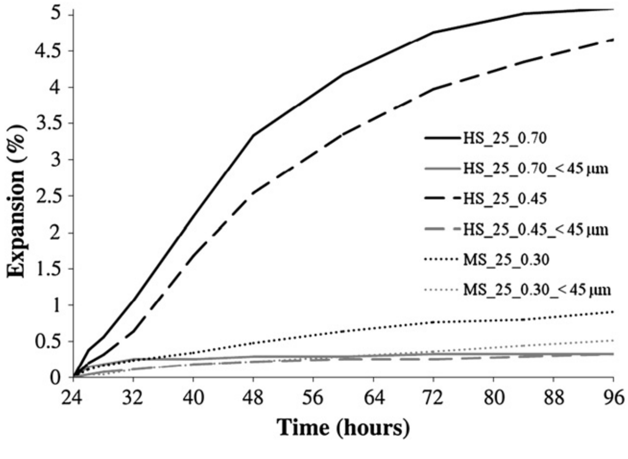

**Fig. 5.** Dimensional stability for the HS and MS CSAB cement pastes with differing PSDs and w/c cured in ultra-pure water after demolding at 1 day.

### 2.4. Scanning electron microscopy

Scanning electron microscopy (SEM, JEOL JSM-5610) was used to study phase distribution of the hydrated synthesized CSAB cements. Pastes were prepared as for XRD. Samples were prepared for SEM by placing the paste sample (about 5 mm thick) at the bottom of a cylindrical mold (30 mm diameter). Optical-grade epoxy (EPO-TEK 353ND) was then slowly poured in the cylindrical mold to cover the paste. The samples were then placed under vacuum to draw the remaining air out of the samples and were brought back to atmospheric pressure to allow epoxy to fill in the voids of the paste. The samples were 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 [29].

## 3. Results and discussion

### 3.1. Dimensional stability

Dimensional stability in water results for PC and the CSAB cements with their experimentally-determined gypsum contents according to calorimetry testing and w/c of 0.45 are shown in Fig. 2. The specimens are labeled by the cement (PC, HS, MS, or LS), the gypsum content (percent replacement by mass), and w/c. For example, HS_25_0.45 would indicate the high sulfoaluminate clinker with 25% gypsum, w/c of 0.45, and the PSD shown in Fig. 1. If the PSD was altered from that given in Fig. 1, then an additional label would indicate the modification.

The HS CSAB cement expanded about 5% after demolding and curing in ultra-pure water for 3 days. Slight cracking was observed after curing in ultra-pure water for 2 days. On the other hand, the MS and LS CSAB cements that contained lower $C_4A_3\hat{S}$ contents showed limited expansion, comparable to the commercially-produced PC (TXI Hunter Type I/II portland cement). From these data alone it appears that the $C_4A_3\hat{S}$ content is directly correlated with expansion, but there are other differences between the cements that could account for expansion, such as the amount of gypsum blended with the clinker to make the cement.

In order to understand the effects of gypsum levels on dimensional stability, the HS CSAB cement clinker was tested with 10%, 15%, 20%, and 25% gypsum replacement. Expansion for the HS CSAB cement clinker increased with increasing amount of gypsum (Fig. 3). HS CSAB pastes with 20% and 25% gypsum replacement to the clinker resulted in similarly high expansions, and both cracked slightly after demolding and curing in ultra-pure water for 2 days. The similar expansion amounts for the specimens with 20% and 25% gypsum may be because both gypsum levels are close to the stoichiometric requirement of 23.2%. It is not expected that all stoichiometric gypsum be consumed immediately since larger particles hydrate slower, so not all of the $C_4A_3\hat{S}$ and $C_4AF$ grains are immediately accessible to reaction. It can be considered that both the sample with 20% gypsum and the sample with 25% gypsum have more than enough gypsum for the early-age reactions. It can be inferred from Fig. 3, therefore, that samples with enough gypsum to accommodate early reactions expand and those with low amounts of gypsum do not. However, given that effects of gypsum on expansion are confounded with a high $C_4A_3\hat{S}$ content, another expansion-causing factor, it was necessary to examine the role of gypsum on expansion in a cement with a lower $C_4A_3\hat{S}$ content to separate the two factors.

To determine the effects of gypsum content on expansion in CSAB cement with less $C_4A_3\hat{S}$ than the HS cement, the gypsum amount was increased from the experimentally determined 15% in MS cement pastes to 20% and 25%; the stoichiometric gypsum amount was calculated to be 19.2%. Contrary to the results with the HS pastes, the MS pastes with gypsum contents at or above the stoichiometric amount did not expand significantly at a w/c of 0.45 (Fig. 4).

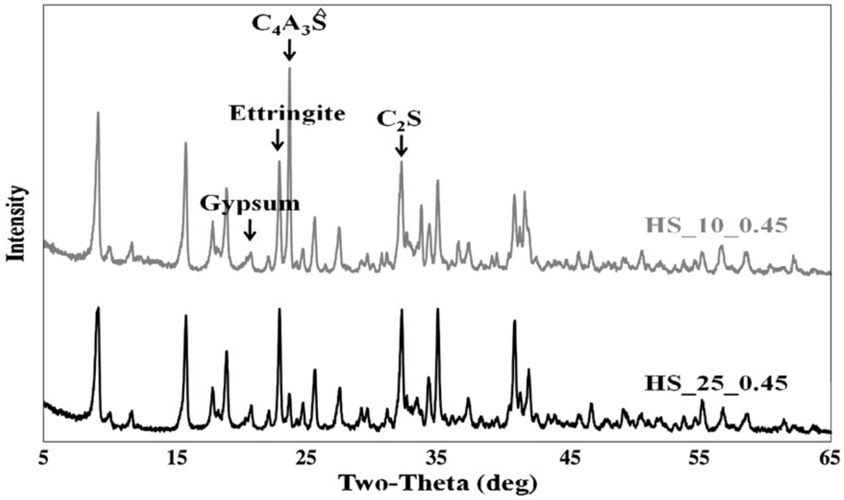

**Fig. 6.** X-ray diffraction patterns for the HS CSAB cement clinker with 10% and 25% gypsum using w/c of 0.45 after 7 days curing in water.

Therefore, high gypsum content alone does not cause expansion; it must be accompanied by other factors that cause expansion such as high $C_4A_3\hat{S}$ content.

In the literature it has been reported that low w/c mixtures experienced higher expansion due to a denser pore structure, which affects the mobility of ions and the amount of space for reaction products to form, and self-desiccation, which limits the early reaction of $C_4A_3\hat{S}$ [12]. It has also been observed that when cement paste with low w/c was later given access to externally-supplied water, expansive ettringite formed in an already hardened dense matrix, causing expansion [2]. This concept was tested with the MS CSAB clinker, as shown in Fig. 4. When the w/c was lowered to 0.30, it was observed that the expansion increased as the gypsum content increased. It should be noted that these expansions (~1%) were not nearly as severe as in the high-gypsum HS cement pastes (~5%) and no cracking was observed perhaps due to the lower $C_4A_3\hat{S}$ content, which correlates to a lower amount of ettringite formation and a more porous microstructure. However, these data confirm the concept that limiting water can result in expansion due to both a denser pore structure and self-desiccation.

**Table 2**
Phase compositions for the hydrated CSAB cements (w/c = 0.45) with experimentally-determined gypsum contents.

| Sample | Phase composition (wt.%) | | | | | |
|---|---|---|---|---|---|---|
| | $C_2S$ | $C_4A_3\hat{S}$ | $C_4AF$ | Gypsum | Ettringite | Amorphous |
| HS_3h | 10.5 | 16.0 | 1.1 | 43.4 | 19.1 | 7.4 |
| HS_1D | 12.0 | 14.6 | 1.0 | 33.2 | 26.8 | 11.0 |
| HS_3D | 12.0 | 8.2 | 0.9 | 15.0 | 40.5 | 22.3 |
| HS_7D | 10.6 | 3.9 | 0.8 | 9.8 | 49.7 | 24.1 |
| HS_28D | 9.1 | 2.6 | 0.5 | 4.5 | 51.7 | 30.8 |
| HS_90D | 8.2 | 2.0 | 0.7 | 1.9 | 60.4 | 24.0 |
| MS_3h | 25.7 | 15.0 | 2.9 | 12.8 | 20.6 | 20.5 |
| MS_1D | 24.6 | 10.1 | 2.9 | 6.3 | 24.5 | 29.3 |
| MS_3D | 24.5 | 4.8 | 3.0 | 2.7 | 34.6 | 29.2 |
| MS_7D | 25.2 | 3.1 | 2.6 | 1.9 | 38.5 | 27.6 |
| MS_28D | 23.3 | 3.5 | 2.3 | 2.3 | 40.0 | 27.3 |
| MS_90D | 20.7 | 3.9 | 2.6 | 2.1 | 40.9 | 26.8 |
| LS_3h | 55.4 | 10.5 | 3.8 | 8.2 | 12.7 | 6.3 |
| LS_1D | 55.3 | 4.9 | 4.2 | 3.0 | 17.6 | 12.1 |
| LS_3D | 55.8 | 1.8 | 4.0 | 1.9 | 21.1 | 13.6 |
| LS_7D | 53.5 | 1.8 | 4.0 | 1.3 | 23.8 | 14.6 |
| LS_28D | 52.5 | 1.9 | 4.1 | 1.4 | 24.5 | 15.0 |
| LS_90D | 47.6 | 1.2 | 4.4 | 0.8 | 31.4 | 14.1 |

To see if the HS pastes shown in Fig. 2 expanded due to inadequate access to water, rather than due to high $C_4A_3\hat{S}$ or gypsum, HS pastes with higher w/c of 0.70 were tested (Fig. 5). No corresponding decrease in expansion was observed, implying that the expansions exhibited by HS pastes were not due to limited pore space and water, but instead were caused by high $C_4A_3\hat{S}$ and gypsum and coarse $C_4A_3\hat{S}$ particles (discussed next).

Similar to the idea that restricting early water access allows for later ettringite formation once water is available, the early access to the other critical reactants, $C_4A_3\hat{S}$ and $C_4AF$, can be restricted if particle size is too large. Large particles dissolve and react more slowly and leave large reserves of unreacted material that can form ettringite and cause localized mechanical failures in the matrix at later ages [14]. Furthermore, Cohen and Richards [23] showed that expansion depends on the amount of expansive product formed in a unit volume where coarser particles resulted in larger localized expansion, leading to deleterious behavior. Fig. 1 suggests that the HS clinker had 55% of the particles larger than 45 μm. To determine the effect of particle size on expansion, the HS and MS clinkers were ground to pass a #325 (45 μm) sieve. The cases of worst expansion were chosen from the previously discussed tests in order to try to reduce expansion by reducing particle size; HS_25_0.45, HS_25_0.70, and MS_25_0.30 paste bars were made utilizing the finer PSD. Fig. 5 shows that expansion in the HS_25_0.45 and HS_25_0.70 systems were dramatically reduced from about 5% to about 0.4% after 3 days in water, and expansion for the MS_25_0.3 system was reduced to from 0.9% to 0.5% after 3 days in water. None of the specimens with particles smaller than 45 μm showed signs of cracking. It is clear that reducing particle size could eliminate expansion and associated cracking, even in cases with restricted water (MS_25_0.30) or high amounts of solid reactants (HS_25).

### *3.2. Hydration product development*

The results of dimensional stability testing suggest that limiting access to reactants at early times (water and $C_4A_3\hat{S}/C_4AF$) through a low w/c or large particles increases expansion. High amounts of $C_4A_3\hat{S}$ and gypsum exacerbate expansion, but moderate expansion can occur even in systems with relatively modest amounts of $C_4A_3\hat{S}$ and gypsum if the w/c is low. In order to confirm that the timing of ettringite growth is responsible for expansion, pastes were followed with XRD to quantify ettringite contents.

Two cement paste samples were prepared from the HS CSAB cement clinker with 10% and 25% gypsum replacement. Both samples were demolded at 1 day of hydration and cured in ultra-pure water

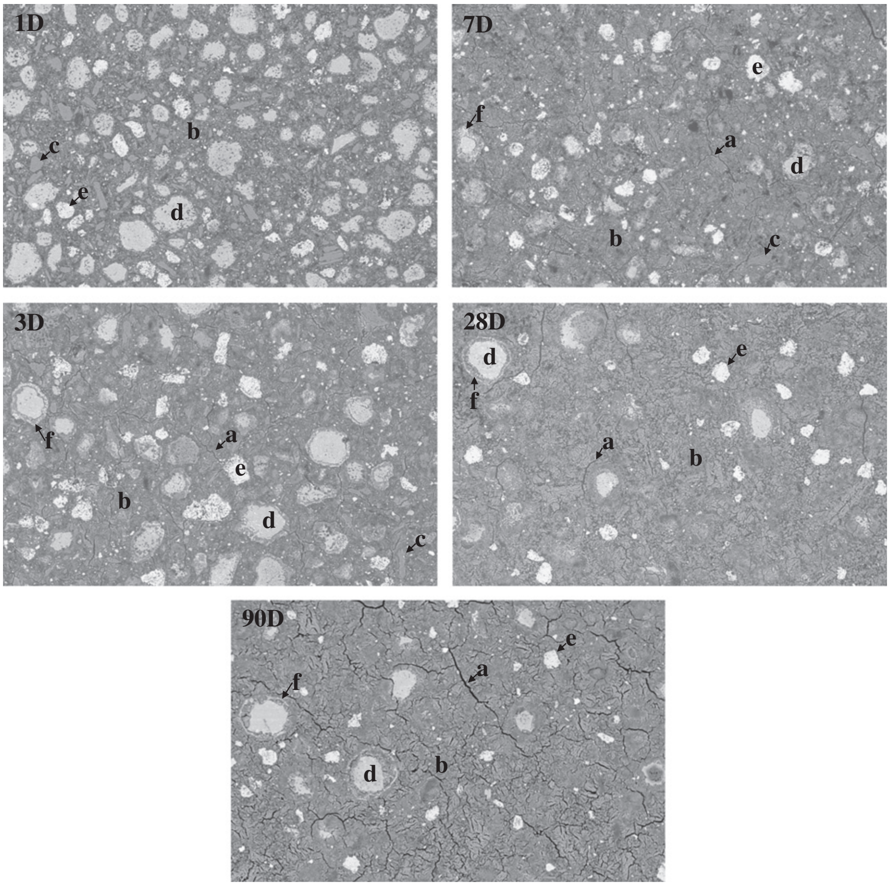

**Fig. 7.** Backscattered electron images for the hydrated HS CSAB cement from reagent-grade chemicals [a (black): pores and cracks, b (dark gray background): ettringite and amorphous content, c (dark gray particles): gypsum, d (gray): $C_4A_3\hat{S}$, e (light gray): $C_2S$, and f: reaction rims; field width: 1250 μm].

from 1–7 days at room temperature; at this point the specimen with 25% gypsum had expanded significantly and cracked and the one with 10% gypsum had not. X-ray diffraction patterns (Fig. 6) for the two cement paste samples indicate that gypsum had mostly reacted in both cement samples, and less ettringite formed and more $C_4A_3\hat{S}$ remained unhydrated in the HS clinker with 10% gypsum replacement. Therefore, this result suggests that gypsum was a limiting reagent in the system with 10% gypsum, not allowing enough ettringite to form to cause expansion [30]. However, it should be noted, even though adding less gypsum can improve dimensional stability, it might adversely affect property development in CSAB cements as more $C_4A_3\hat{S}$ remained unhydrated.

To establish if ettringite formation after setting was causing the expansion, the CSAB cements with their calorimetry-determined gypsum contents and w/c of 0.45 (expansions shown in Fig. 2) were cured in water and studied over 90 days with XRD utilizing Rietveld analysis. The measurements taken at 3 h represent the system at approximately the time of setting. Quantitative XRD results (Table 2) show that in the HS sample ettringite increased from 19.1% of the dried paste at 3 h to 40.5% of the dried paste after 3 days of hydration, in the MS dried pastes ettringite increased in this 3-day period from 20.6% to 34.6%, and in the LS dried pastes from 12.7% to 21.1%. Given the large differences in expansion in HS compared to MS, it was expected that ettringite growth rates would be very different. The data in Table 2 suggest slightly different ettringite growth in HS and MS dried pastes during the expansion testing period. Also surprisingly, ettringite content increased significantly in the LS samples between 3 h and 3 days, without any accompanying expansion. The 3 day to 90 day data meet expectations; however, the HS specimen forms more ettringite over time due to the slow diffusion-limited hydration of the $C_4A_3\hat{S}$ phase, present in higher quantities in this cement.

### 3.3. Microstructure

Ettringite increased from 20.6% to 40.9% and 12.7% to 31.4% in the MS_15_0.45 and LS_8_0.45 pastes between 3 h and 90 days, respectively, yet no corresponding large expansion occurred. If ettringite forms without accompanying expansion, then this means that the ettringite has room to grow without exerting pressure on a rigid matrix. Therefore, it was hypothesized that the MS_15_0.45 and LS_8_0.45 pastes had open porosity that the ettringite could grow in, whereas the HS_25_0.45 paste did not. An SEM investigation of the three CSAB pastes with their experimentally-determined optimum gypsum contents and w/c of 0.45 (expansions shown in Fig. 2) was performed to determine if differences in the microstructure of the pastes could help explain the differences in expansion.

Backscattered electron images allowed the examination of phase distribution and porosity in the hydrated CSAB cements with their calorimetry-determined gypsum contents and w/c of 0.45 (expansions shown in Fig. 2). The samples were cured in water and studied over 90 days, see Figs. 7–9. The black areas represent pores and cracks (formed by expansion and/or vacuum drying during sample preparation). The dark gray background represents ettringite and the amorphous phases (mainly $AH_3$), the dark gray particles represent unhydrated gypsum, the gray particles represent unhydrated $C_4A_3\hat{S}$, and the light gray particles represent unhydrated $C_2S$. For the hydrated HS CSAB cement with high $C_4A_3\hat{S}$:$C_2S$ ratio (Fig. 7), substantial amounts of $C_4A_3\hat{S}$ and gypsum remained unhydrated at 1 day of hydration. From 1–

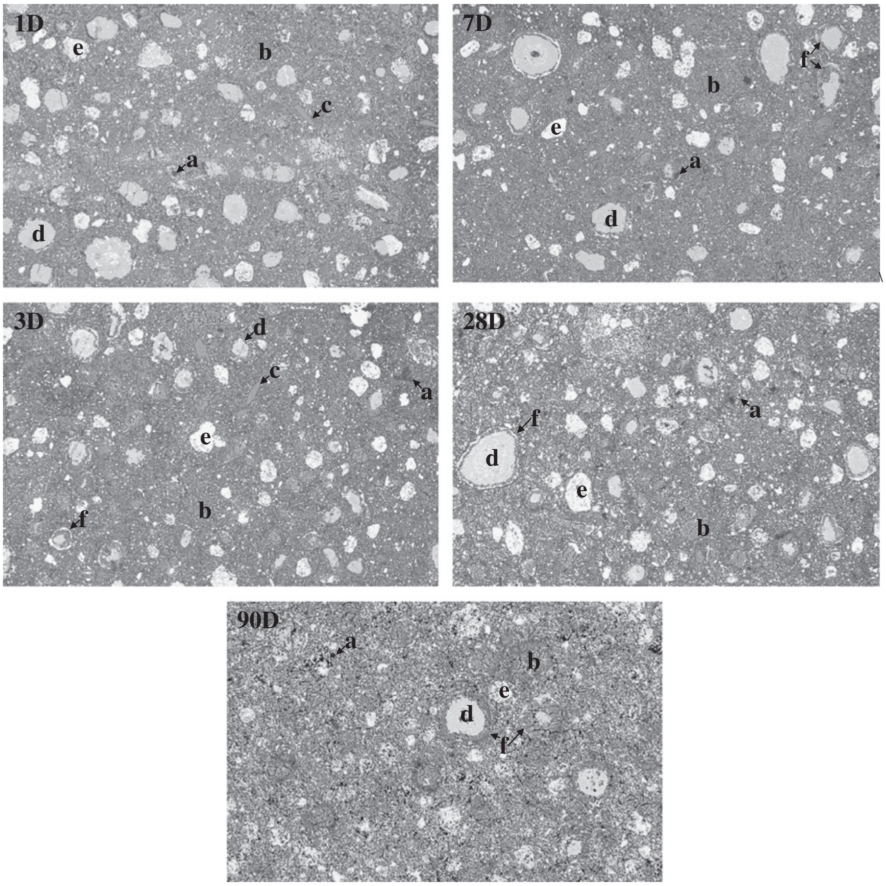

**Fig. 8.** Backscattered electron images for the hydrated MS CSAB cement from reagent-grade chemicals [a (black): pores and cracks, b (dark gray background): ettringite and amorphous content, c (dark gray particles): gypsum, d (gray): $C_4A_3\hat{S}$, e (light gray): $C_2S$, and f: reaction rims; field width: 1250 μm].

28 days of hydration, the amounts of $C_4A_3\hat{S}$ and gypsum decreased significantly, consistent with XRD results in Table 2. At 28 days of hydration, all the gypsum seemed to have reacted and only a few large $C_4A_3\hat{S}$ particles can be observed. Large $C_4A_3\hat{S}$ particles seemed to preferentially remain unhydrated. Moreover, rings were observed around the large unhydrated $C_4A_3\hat{S}$ particles starting at 3 days of hydration. Energy dispersive spectroscopy analysis showed that the rings had similar composition to the unhydrated $C_4A_3\hat{S}$ particles, perhaps indicating that the hydration of large $C_4A_3\hat{S}$ particles initiated from the outer layer but slowed down and became diffusion-controlled after the paste developed a dense microstructure. The dense microstructure confining the large $C_4A_3\hat{S}$ grains may explain why raising the w/c in the HS_25 system did not reduce the expansion. The reaction products formed during later ages could be confined to the vicinity of the large $C_4A_3\hat{S}$ grains, creating localized sites of expansion.

For the hydrated MS and LS CSAB cements with lower $C_4A_3\hat{S}$–$C_2S$ ratios (Figs. 8, 9) at 1 day of hydration, substantial amounts of $C_4A_3\hat{S}$ and $C_2S$ remained unhydrated; however, most of the gypsum seemed to have reacted and only a few gypsum particles can be observed. This is consistent with the hypotheses presented earlier that early gypsum depletion in these systems limited expansion. From 1–7 days of hydration, the amount of $C_4A_3\hat{S}$ decreased significantly and only a few large $C_4A_3\hat{S}$ particles can be observed at 7 days of hydration. Again, large $C_4A_3\hat{S}$ particles seemed to preferentially remain unhydrated. From 1–90 days of hydration, $C_2S$ particles seemed to be reacting and breaking down. However, significant amounts of $C_2S$ remained unhydrated at 90 days of hydration.

The microstructure of the hydrated MS CSAB cement appears to contain more porosity than the HS CSAB cement as evidenced by the fine black speckles in the images which represent the pores filled by epoxy. The additional porosity in the MS cement paste helps explain why MS_15_0.45 paste expands less than the HS_25_0.45 paste. The reaction products are able to form in the open pores instead of being confined near the $C_4A_3\hat{S}$ grains. With higher porosity, it is easier for the ions to migrate away from the dissolution sites, react in open space, and not cause expansion. By lowering the MS CSAB cement's w/c from 0.45 to 0.3, the amount of space available for products to form (porosity) reduces and the water available to hydrate the CSAB cement decreases. In combination with an excess of gypsum, this causes the CSAB cement's expansion potential to increase (Fig. 4).

The microstructure of the hydrated LS CSAB cement seemed to be even more porous due to its low $C_4A_3\hat{S}$ content (Fig. 9). Quantitative X-ray diffraction results (Table 2) show that 31.4% ettringite formed in the LS CSAB cement at 90 days of hydration compared to 60.4% and 40.9% ettringite formed in the HS and MS CSAB cements, respectively. Given the large differences in porosity between the MS and LS CSAB cements, it was expected that the amount of ettringite (40.9% and 31.4%, respectively) formed would be very different. However, if taking into account the amorphous content formed at 90 days of hydration, 14.1% amorphous content formed in the LS CSAB cement while 24.0% and 26.8% amorphous content formed in the HS and MS CSAB cements, respectively. The HS and MS CSAB cements showed almost twice as much amorphous content formation compared to the LS CSAB cement at 90 days of hydration; the hydration of CSAB cement to form amorphous hydration products reduces the porosity. Since $C_2S$ remained mostly unhydrated even at later ages (Table 2), the amorphous content should mainly be $AH_3$ according Eq. (2). The

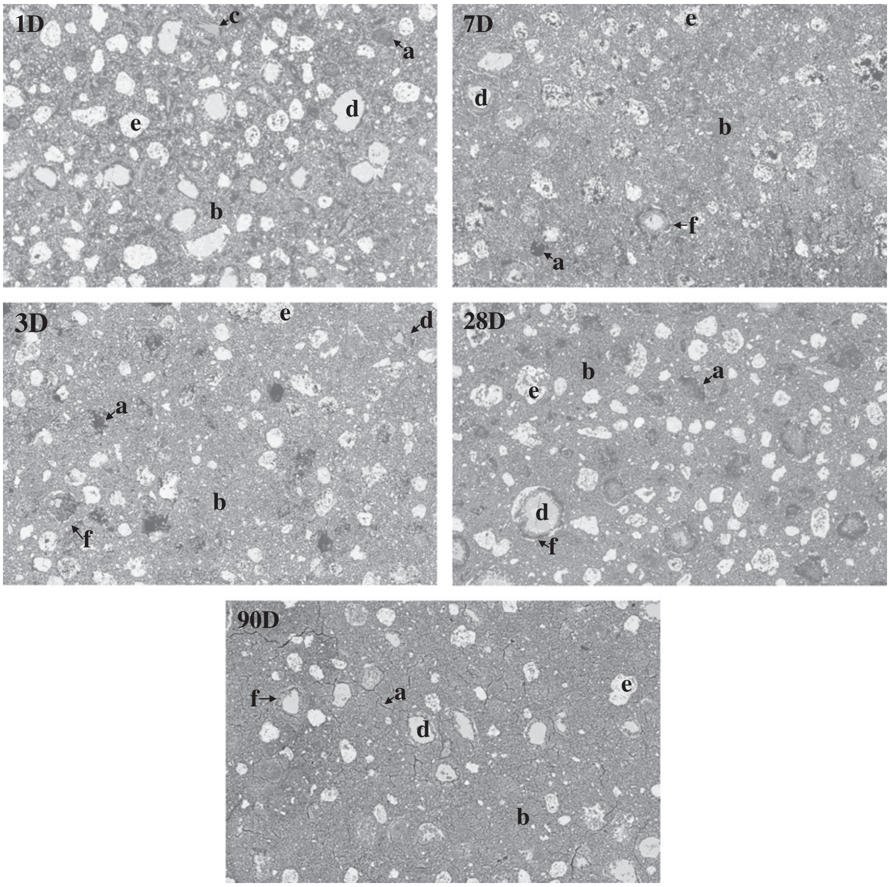

**Fig. 9.** Backscattered electron images for the hydrated LS CSAB cement from reagent-grade chemicals [a (black): pores and cracks, b (dark gray background): ettringite and amorphous content, c (dark gray particles): gypsum, d (gray): $C_4A_3\hat{S}$, e (light gray): $C_2S$, and f: reaction rim; field width: 1250 μm].

low amount of total hydration products forming in the LS CSAB cement ensured ample porosity for ettringite to form and not cause expansion.

The total amount of hydration products forming affects porosity and might be another factor for expansion. Quantitative X-ray diffraction results (Table 2) show that in the HS CSAB cement, ettringite increased from 19.1% to 40.5% and the amorphous content (mainly $AH_3$) increased from 7.4% to 22.3% while in the MS CSAB cement ettringite increased from 20.6% to 34.6% and the amorphous content increased from 20.5% and 29.2% between 3 hrs and 3 days of hydration. In contrast to the minor differences in ettringite growth during the expansion testing period, the large differences in amorphous content (mainly $AH_3$) formation might also be a significant factor for the differences in expansion shown in Fig. 2 between the HS_25_0.45 and MS_15_0.45 pastes.

### 3.4. Sulfate resistance

Expansion results in a 5% $Na_2SO_4$ solution for the HS CSAB pastes are presented in Fig. 10. Expansion increased with increasing gypsum

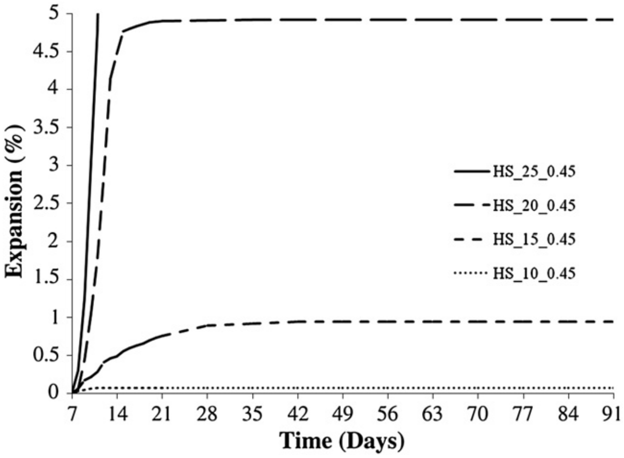

**Fig. 10.** Sulfate resistance for the HS CSAB cement with different amounts of gypsum using w/c of 0.45 stored in 5% $Na_2SO_4$ solution after 7 days of hydration.

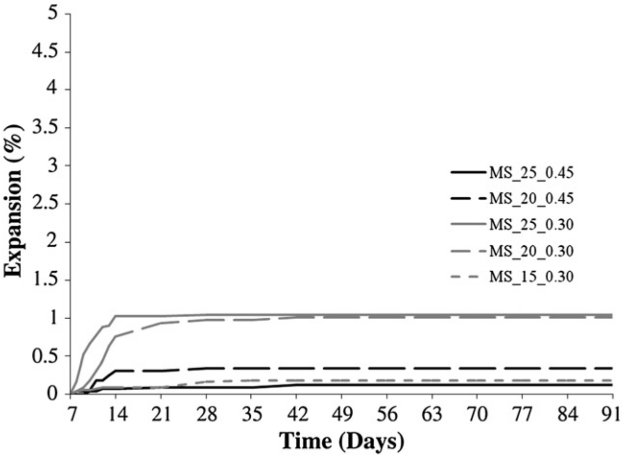

**Fig. 11.** Sulfate resistance for the MS CSAB cement with different amounts of gypsum using w/c of 0.45 and 0.3 stored in 5% $Na_2SO_4$ solution after 7 days of hydration.

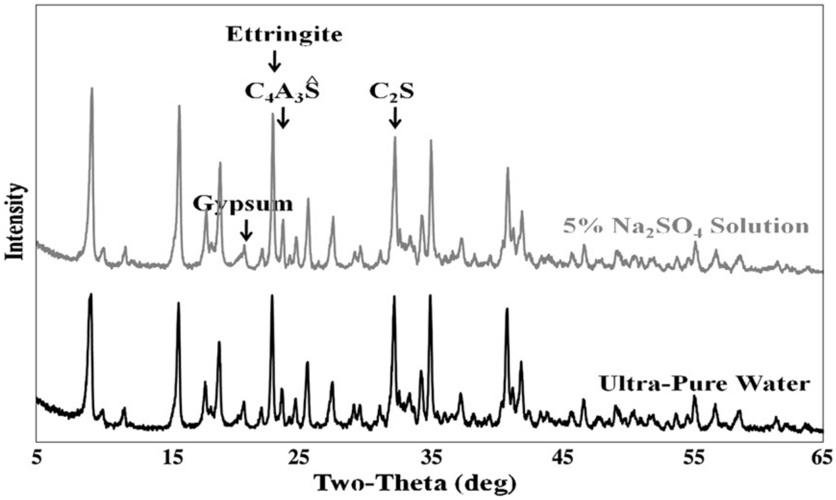

**Fig. 12.** X-ray diffraction patterns for the HS CSAB cement with 25% gypsum using w/c of 0.45 stored in ultra-pure water and 5% $Na_2SO_4$ solution for 3 days after 7 days of hydration.

content. This is the same trend as the dimensional stability tests (expansion before sulfate resistance testing shown in Fig. 3). Fig. 6 demonstrates that more $C_4A_3\hat{S}$ reacted with increasing gypsum, as evidenced by the smaller $C_4A_3\hat{S}$ peak. Therefore, it is likely that curing the pastes in 5% $Na_2SO_4$ would provide additional sulfate ions and cause the $C_4A_3\hat{S}$ to hydrate more rapidly to form ettringite and amorphous phases (mainly $AH_3$) and cause a more rapid expansion. However, similar to the dimensional stability results, gypsum seemed to be a limiting reagent for $C_4A_3\hat{S}$ hydration and subsequent ettringite and amorphous phases (mainly $AH_3$) formation, perhaps due to the availability of Ca ions, which explains the decrease in expansion with decreasing gypsum content [30].

To determine the behavior of a CSAB cement with less $C_4A_3\hat{S}$ in an aggressive sulfate environment, MS CSAB pastes were tested in 5% $Na_2SO_4$ solution (Fig. 11; expansion before sulfate resistance testing shown in Fig. 4). Again the MS pastes that showed the most expansion in the dimensional stability tests showed the most expansion in the sulfate tests. The MS CSAB pastes needed a low w/c and an excess of gypsum to show significant expansion in 5% $Na_2SO_4$ solution.

In order to better understand the differences in hydration between pastes stored in water and 5% $Na_2SO_4$ solution, two cement paste samples were prepared from the HS CSAB cement with 25% gypsum. Both samples were demolded at 1 day of hydration and cured in ultra-pure water from 1–7 days at room temperature. One sample was continually stored in ultra-pure water from 7–10 days while the other was stored in 5% $Na_2SO_4$ solution. X-ray diffraction patterns for the two cement paste samples (Fig. 12) show that more ettringite formed in the paste sample stored in 5% $Na_2SO_4$ solution than in the paste sample stored in ultra-pure water. It is interesting to note that about the same amount of $C_4A_3\hat{S}$ remained unreacted in both paste samples, indicating that the sulfate ions perhaps did not accelerate $C_4A_3\hat{S}$ reaction but facilitate ettringite precipitation, causing a more rapid expansion.

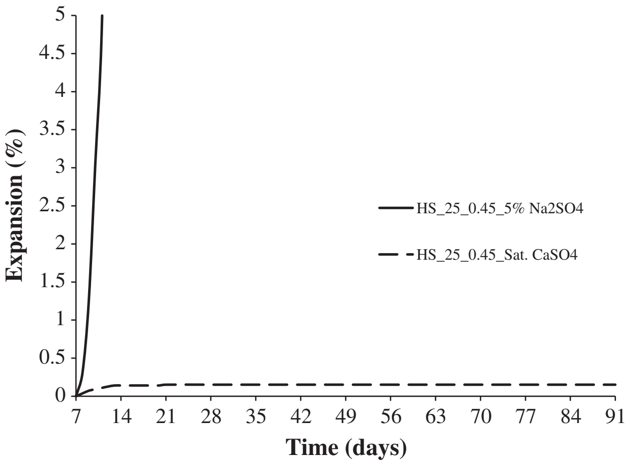

**Fig. 13.** Sulfate resistance for the HS CSAB cement with 25% gypsum blended using w/c of 0.45 stored in 5% $Na_2SO_4$ solution and saturated $CaSO_4$ solution after 7 days of hydration.

Finally, the effects of type of sulfate solution on sulfate resistance for the HS CSAB cement with 25% gypsum were studied by comparing immersion in a 5% $Na_2SO_4$ solution to a saturated $CaSO_4$ solution. Fig. 13 shows that the HS CSAB cement with 25% gypsum had nearly no expansion after curing and storing in saturated $CaSO_4$ solution (even though it had expanded about 5% and slightly cracked during curing in ultra-pure water; expansion before sulfate resistance testing shown in Fig. 3). The difference in expansion between sodium sulfate and calcium sulfate solutions might be due to the different concentrations of the sulfate solutions. The solubility of $CaSO_4$ in water is much lower than that of $Na_2SO_4$.

## 4. Conclusions

Three CSAB cements synthesized from reagent grade materials with different phase assemblages were examined for dimensional stability in water and sulfate solutions. The reactions were tracked using X-ray diffraction, and the microstructure development was observed utilizing a SEM. Hydration product development showed that $C_4A_3\hat{S}$ and gypsum reacted quickly and contributed to the formation of ettringite and amorphous phases (mainly $AH_3$). Most of the $C_4A_3\hat{S}$ and gypsum reacted by 7 days of hydration. However, $C_2S$ remained mostly unhydrated at 90 days of hydration in all the CSAB cements.

The dimensional stability tests and companion XRD and SEM studies showed that expansion in CSAB cement increases with:

1) Increasing $C_4A_3\hat{S}$ content. As the $C_4A_3\hat{S}$ content increases, the amounts of ettringite and amorphous phases (mainly $AH_3$) that can be formed increase. The large store of "potential" ettringite and amorphous phases (mainly $AH_3$) that can be formed increases the sensitivity of the cement to other factors that cause expansion.
2) Decreasing w/c. As the w/c decreases, there is less space for the formation of hydration products, including ettringite and amorphous phases (mainly $AH_3$). The expansive pressure from ettringite and amorphous phases (mainly $AH_3$) growth increases

when space is restricted. Also, since there is less water available for hydration reactions, fewer hydration products can form prior to self-desiccation, which could lead to expansion later when external water is supplied.

3) Increasing gypsum content. Increasing the amount of gypsum provides the calcium and sulfate ions necessary for the formation of ettringite and amorphous phases (mainly $AH_3$), increasing the amounts that can be formed and the risk for expansion.
4) Increasing PSD. Coarser cement grains result in the production of reaction rims around the hydrating $C_4A_3\hat{S}$ particles, confining the formation of ettringite and amorphous phases (mainly $AH_3$) to around the surface of the hydrating grains, resulting in localized expansion. Furthermore, since large grains hydrate slowly they can cause expansion for a longer period of time.
5) Increasing sulfate content in the curing environment. As more sulfate ions are available in the curing water, ettringite could form more rapidly and the potential for expansion increases.

From the dimensional stability results presented in the study, the $C_4A_3\hat{S}$ content had the most significant effect on CSAB cements expansive behavior. However, expansion could be mitigated even in high $C_4A_3\hat{S}$ content CSAB cements when appropriate measures were taken simultaneously. For example, providing enough water for the hydration reactions provided more pore space for hydration products to form and prevented self-desiccation, adding less gypsum reduced the formation of ettringite and amorphous phases (mainly $AH_3$), eliminating exposure to high sulfate environments prevented free sulfate ions from entering the system that could accelerate the formation of ettringite, and finally the most effective approach, reducing the PSD of the cements prevented localized expansion around coarser $C_4A_3\hat{S}$ particles. However, it should be noted that increasing the w/c and reducing the gypsum content might adversely affect other property development in CSAB cements as the higher w/c results in a more porous microstructure and the lower gypsum content prevents $C_4A_3\hat{S}$ from reacting.

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