



# Calcium sulfoaluminate (Ye'elimite) hydration in the presence of gypsum, calcite, and vaterite



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## ABSTRACT

Six calcium sulfoaluminate-based cementitious systems composed of calcium sulfoaluminate, calcite, vaterite, and gypsum were cured as pastes and mortars for 1, 7, 28 and 84 days. Pastes were analyzed with X-ray diffraction, thermogravimetric and differential thermal analyses. Mortars were tested for compressive strength, dimensional stability and setting time. Furthermore, pastes with a water/cementitious material mass ratio of 0.80 were tested for heat evolution during the first 48 h by means of isothermal conduction calorimetry.

It has been found that: (1) both calcite and vaterite reacted with monosulfoaluminate to give monocarboaluminate and ettringite, with vaterite being more reactive; (2) gypsum lowered the reactivity of both carbonates; (3) expansion was reduced by calcite and vaterite, irrespective of the presence of gypsum; and (4) both carbonates increased compressive strength in the absence of gypsum and decreased compressive strength less in the presence of gypsum, with vaterite's action more effective than that of calcite.

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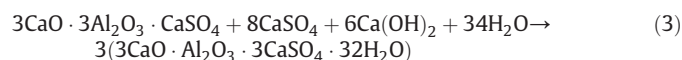
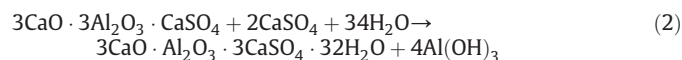
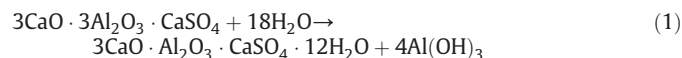
## 1. Introduction

Calcium sulfoaluminate (Ye'elimite) was first synthesized by Ragozina in 1957 [1], and its composition was first correctly identified as  $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$  by Fukuda in 1961 [2]. Ye'elimite bearing cement, calcium sulfoaluminate (CSA) cement, was first developed by Alexander Klein in the 1960s [3,4]; consequently, Ye'elimite is often called Klein's compound. CSA cements have been used in China for approximately 40 years where they are referred to as the “third cement series” with Portland cement (PC) and calcium aluminate cements being the first and second cement series respectively [5–7]. Interest in CSA cements waned in Europe and America after their initial development; however, the industry and the research community have a renewed interest in CSA cement due to its many potential environmental and technical benefits.

CSA cement has four major environmental benefits. (1) Ye'elimite has one of the lowest CaO contents of all the major clinker phases, decreasing the amount of  $\text{CO}_2$  released during the calcination of limestone [8]. For instance, compare  $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$  (36.7%) to  $3\text{CaO} \cdot \text{SiO}_2$  (73.7%). (2) CSA clinker can be manufactured at about 150 °C lower than PC clinker, which reduces the amount of fuel necessary in the kiln [9]. (3) CSA clinker is more friable than PC clinker, lowering the energy required to grind [9]. (4) CSA cement can be manufactured from a wide range of industrial by-products including: fly ash, flue gas desulfurization sludge, fluidized bed ash, blast furnace slag, phosphogypsum, incinerated municipal waste, red mud, and anodization muds [10–18].

CSA cements can be manufactured with a variety of properties including: high early strength, rapid setting, shrinkage compensating, or self stressing [19–22]. CSA clinker can also be blended with PC to make Type K cement, which is expansive. The degree of expansion induced by CSA cement can be controlled by varying the  $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$  content, amount of calcium sulfate added, the particle size distribution, lime content, and the water to cement ratio (w/c) [9,23–25]. By varying cement phase proportions and the concrete mix proportions a wide range of properties can be developed including: self stressing, shrinkage compensating, non-expansive, rapid setting, and high early strength [4,9,23–30].

Ye'elimite reacts in the presence of water to form monosulfoaluminate and aluminum hydroxide (Eq. (1)). In the presence of gypsum, Ye'elimite hydrates to form ettringite and aluminum hydroxide (Eq. (2)). Calcium hydroxide accelerates the hydration of Ye'elimite and produces a sulfate/hydroxy solid solution AFm phase at early ages and ettringite at later ages (Eq. (3)) [31,32].



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Portland cement manufacturers have used calcium carbonate (limestone, principally calcite) as filler for decades. Limestone filler reduces the cost, energy demands, and CO<sub>2</sub> emissions associated with cement production. Additionally, fine calcite benefits the cement in many ways, such as increasing early age strength by providing nucleation sites, reacting with calcium aluminates to form monocarboaluminate, and stabilizing ettringite by favoring the formation of monocarboaluminate instead of monosulfoaluminate [33–38].

Calcite has also been shown to affect CSA cement (63% 3CaO·3Al<sub>2</sub>O<sub>3</sub>·CaSO<sub>4</sub>, 8% CaO·Al<sub>2</sub>O<sub>3</sub>, 3% CaO·2Al<sub>2</sub>O<sub>3</sub>, 18% 2CaO·Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub>) hydration and property development in many ways [38]. Fine calcite additions generally reduce the setting time and enhanced early age heat evolution in CSA cement. Second, calcite promotes the formation of hemicarboaluminate and monocarboaluminate over monosulfoaluminate. Finally, calcite additions to CSA cement promote higher compressive strengths at later ages compared to quartz additions, which can be attributed to the calcium carbonate reacting and reducing the porosity.

Previous research used a CSA cement with a mixed phase assemblage [38]. The present study utilized a pure Ye'elimite clinker to simplify the system and further elucidate the chemical reactions that occur. Additionally, the current work sought to enhance the reactivity of calcium carbonate with Ye'elimite, both in the presence and the absence of gypsum, by testing vaterite as well as calcite replacements of Ye'elimite. Vaterite is a less stable form of calcium carbonate in ambient conditions; consequently, we hypothesized that it would be more reactive with Ye'elimite. Recently, the ability to produce vaterite by combining a waste source of calcium with the CO<sub>2</sub> exhaust from power plants has been developed on a commercial scale, so research studying vaterite's incorporation into cementitious systems is now of interest to both academia and industry [39]. In principle, this technology could be adapted to capture the CO<sub>2</sub> from a cement kiln and produce vaterite on site, which could potentially improve cement production's sustainability. The chemical reactions were monitored with X-ray diffraction (XRD) and thermal gravimetric analysis (TGA). Dimensional stability and compressive strength were tested on mortars to understand how the chemical reactions affected the mechanical properties.

## 2. Materials and methods

### 2.1. Materials

Ye'elimite (3CaO·3Al<sub>2</sub>O<sub>3</sub>·CaSO<sub>4</sub>) was synthesized from analytical grade chemicals, namely alumina, calcium carbonate, and calcium sulfate dihydrate which were homogenized in a laboratory mixer. The three compounds were proportioned assuming that (i) CaO, Al<sub>2</sub>O<sub>3</sub> and CaSO<sub>4</sub> react to give only 3CaO·3Al<sub>2</sub>O<sub>3</sub>·CaSO<sub>4</sub> and (ii) solid solution effects were absent. The Ye'elimite-generating mixture was heated in an electric oven for 3 h at 1250 °C; the burnt product was then analyzed using X-ray diffraction (XRD) to study the reacting system behavior in terms of conversion and selectivity toward 3CaO·3Al<sub>2</sub>O<sub>3</sub>·CaSO<sub>4</sub>. XRD results revealed only the presence of Ye'elimite, while reagents and/or secondary phases were absent. The Ye'elimite was then further ground in an alumina shatter box until it passed a 45 μm sieve. XRD also confirmed the calcite (EMD) and gypsum (J.T. Baker) to be pure, and the vaterite (Calera) was found to be 92% vaterite and 8% calcite.

The particle size distributions of all reagents used to produce pastes and mortars were measured in an isopropyl alcohol suspension using a Horiba Partica LA-950® Laser Diffraction Particle Size Distribution Analyzer. Refractive indices of 1.378, 1.525, 1.580, 1.580, and 1.568 were utilized for isopropyl alcohol, gypsum, calcite, vaterite, and Ye'elimite, respectively [40]. The ground Ye'elimite had a D<sub>50</sub> and D<sub>90</sub> of 4.1 and 13.5 μm, respectively. Gypsum, calcite, and vaterite had D<sub>50</sub> of 14.6, 4.5, and 2.0 μm, respectively.

### 2.2. Methods

The study utilized six mixes proportioned by weight where the mass of Ye'elimite was replaced by percentages of gypsum and calcite or vaterite. A naming convention was adopted to quickly identify each sample where C4A3\$ was followed by the first letter of the reagent replacement and its mass percent replacement. For instance, the sample C4A3\$ would be 100% Ye'elimite, and the sample C4A3\$.G15\_C10 would be 75% Ye'elimite, 15% gypsum, and 10% calcite, respectively. The six reagent proportions used in the study were C4A3\$, C4A3\$.G10, C4A3\$.V10, C4A3\$.G15, C4A3\$.G15\_C10, and C4A3\$.G15\_V10.

Mortar specimens were made using a sand to cementitious material ratio of 2.75 and a water to cementitious material ratio (w/c) of 0.5. Mortars were mixed by hand in a polyethylene cup with a metal spatula for 1.5 min on a vibration table. The sand and reagents were premixed to better ensure homogeneity. The mortars were placed into molds in two lifts and tamped with a 2 × 6 mm cross section tamper, then vibrated for 15 s. After molding, the samples were covered with plastic film and placed in a room at 23 °C and 100% R.H. After 24 h, the samples were demolded. For compression tests, the mortar cubes (1.27 cm) were stored at 23 °C and 100% R.H. with a bell shaped dome over them to minimize dripping on the samples and a 1.2 cm plastic grid under them to ensure constant humidity. Ten mortar cubes per mix per target testing date were compressed utilizing a loading rate of 0.34 MPa/s. Compression tests were conducted at 1, 7, 28, and 84 days of hydration. For dimensional stability tests, mortar bars (1 × 1 × 4 cm) were cast simultaneously with the mortar cubes and were prepared utilizing the same procedure. The mortar bars were cast with threaded bars in their ends, so a comparator could be utilized to measure their length change with time. The comparator setup utilized was similar to that used for ASTM C 1293 but had modified ends to accommodate the small threaded rods of the 4 cm long mortar bars. Three mortar bars were prepared for each mix. After 24 h of hydration, the mortar bars were demolded, initial length measurements were taken, and the bars were stored in 50 ml of deionized water in sealed glass jars until subsequent measurements. For set time, the same mortar compositions used in the compression and dimensional stability tests were tested using a modified version of ASTM C 807 [41]. The initial set was taken to be a 10 mm penetration of the needle and the final set was considered to be when the needle no longer left an impression on the mortar surface.

Paste samples for the six mixes were prepared using a w/c of 0.5 and were kept sealed in Eppendorf vials. Reagents were premixed dry and then mixed with water for 1 min in the vial using a metal spatula. After 1 day, 1 ml of water was placed on top of the samples and then the samples were resealed. This was done to ensure adequate water was available for hydration. Hydration was stopped at 1, 7, 28 and 84 days by grinding in an excess of acetone. The acetone was then removed by vacuum. XRD patterns were collected on a PANalytical X'Pert PRO with X'Celerator® position sensitive detector operating at 40 kV with 40 mA using a cobalt target (Co Kα wavelength 1.79 Å) and an iron filter. Scans were collected from 5 to 75° 2θ at a 0.6°/min scan rate. XRD results were quantified using the software X'Pert HighScore Plus®. The scale factors, sample displacement, 2θ shift, and cell parameters were refined for quantification. The crystallographic information files utilized for calcite, ettringite, gibbsite, gypsum, monocarboaluminate, monosulfoaluminate, Ye'elimite, and vaterite were ICSD 18166, 16045, 6162, 151692, 59327, 100138, 80361, and AMCSO 9279. The pastes were also studied with thermogravimetric (TGA) and differential thermal analysis (DTA) from 30 to 1000 °C at a heating rate of 20 °C/min.

Paste samples were tested for heat evolution using an isothermal conduction calorimeter (Thermometric TAM Air®). Four grams of solids and a w/c of 0.8 were utilized to provide an ample signal. Before mixing 30 min. baselines were collected (<10 μW/sample). The reagents were dry mixed, then mixed for 2 min externally. A larger sample mass, a

w/c of 0.8, and external mixing were utilized because internal mixing with 2 g of solids and a w/c of 1 was giving inconsistent results which we believe arose from some difficulties in getting the vaterite to disperse homogeneously and not settle with internal mixing. Hydration was evaluated for 48 h at 23 °C.

### 3. Results and discussion

#### 3.1. Early age hydration

The presence of gypsum, calcite and/or vaterite affected the setting time of the mortars. Table 1 demonstrates that the inclusion of 15% gypsum cut the initial set time approximately in half and the final set time in a third. For all mixes, vaterite reduced the initial set time more than calcite did. This is most probably due to vaterite's smaller particle size compared to calcite; vaterite and calcite's  $D_{50}$  are 2.0 and 4.5  $\mu\text{m}$ , respectively. In the mixes without gypsum, calcite and vaterite delayed the final set; whereas, in the mixes with gypsum, calcite and vaterite accelerated the final set. This would suggest that calcite and vaterite act as better nucleation sites for ettringite than monosulfoaluminate. Both with and without gypsum, the final setting times for the mixes with calcite were slightly lower than those for the mixes with vaterite, which is a reversal from the initial set trend.

Isothermal conduction calorimetry (Fig. 1) showed that calcium carbonates caused the maximal rate of heat evolution to occur earlier than for the mixes without calcium carbonates, which is consistent with prior research [38]. Vaterite had a stronger effect than calcite, and this acceleratory effect on heat evolution was more pronounced in the mixes without gypsum. This is consistent with calcium carbonates reducing the initial setting times.

#### 3.2. Mechanical properties

At 1 day, including 15% gypsum in the mix significantly increased the compressive strength of the mortars both with and without calcium carbonates (Table 2). A 10% replacement of Ye'elimite with calcite or vaterite increased the 1 day strength of the mortars containing gypsum. Vaterite had a more pronounced effect on the 1 day compressive strength than calcite, which can most likely be attributed to vaterite's smaller particle size making it a better nucleation site. The mortars without gypsum experienced decreases in 1 day strength with calcite and vaterite replacements; the decrease was less pronounced for C4A3\$\_V10\$ than for C4A3\$\_C10\$. Calcium carbonate additions increasing the strength of the mortars containing gypsum and decreasing the strength of the mortars without gypsum is consistent with the set time results and again would suggest that calcium carbonate acts as a better nucleation site for ettringite than monosulfoaluminate. At 1 day, C4A3\$\_\$ achieved its maximum strength; however, C4A3\$\_V10\$ continued to gain strength through 28 days then lost 7% of its strength at 84 days. Additionally, C4A3\$\_C10\$ had a slower rate of strength gain than C4A3\$\_V10\$ and continued to gain strength through 84 days. C4A3\$\_V10\$ achieved its maximum strength of 45 MPa at 28 days, and C4A3\$\_C10\$ achieved its maximum strength of 46 MPa at 84 days. The timing of these maximal strengths will be further explained by XRD and DTA later. For the mixes with gypsum, the discussion turns from increases in strength to reductions in compressive strength losses. All mixes

**Table 1**  
Set times for Ye'elimite with varying replacements.

Sample	Initial set (min)	Final set (min)
C4A3\$_\$	34	126
C4A3\$_C10\$	29	148
C4A3\$_V10\$	25	150
C4A3\$_G15\$	18	42
C4A3\$_G15_C10\$	14	34
C4A3\$_G15_V10\$	13	37

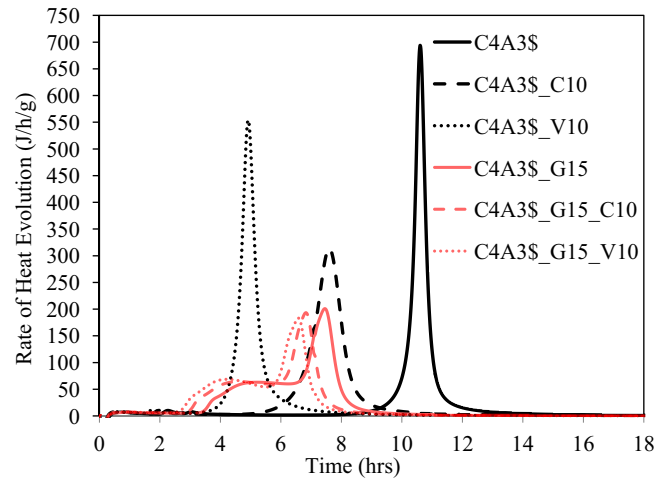


Fig. 1. Rate of heat evolution for Ye'elimite with varying replacements.

with gypsum lost strength after 1 day. Between 1 and 84 days, C4A3\$\_G15\$, C4A3\$\_G15\_C10\$, and C4A3\$\_G15\_V10\$ lost 37, 20, and 13% of their strengths, respectively. The differences in strength losses can in part be explained by the results of the dimensional stability tests.

Ye'elimite replacements with 10% calcium carbonates reduced the amount of expansion through 84 days in both the mixes with and without gypsum (Fig. 2). For C4A3\$\_G15\_C10\$ and C4A3\$\_G15\_V10\$, the expansion was reduced approximately six fold compared to C4A3\$\_G15\$. C4A3\$\_G15\$ expanded significantly more than C4A3\$\_\$, which is consistent with prior research that shows expansion in CSA cements generally increases with increasing calcium sulfate contents [9,23,42]. However, it is interesting to note that the pure Ye'elimite mortar without any gypsum or calcium carbonates expanded 0.9% by 84 days of hydration. XRD results (Table 3) will later show that this mortar would contain little ettringite, which is the phase normally assigned blame for deleterious expansion. The expansion of a Ye'elimite mortar without additional ettringite production or without any of the fine, "colloidal" ettringite found during hydration in the presence of hydroxides [43], strongly supports the confined volumetric expansion theory of expansion for CSA cements [44,45]; however, the ability for AFm and AFt phases to accommodate variable water contents could certainly play a role in expansion due to the uptake of externally supplied water resulting in a volume increase. In section 9 of "Stress from crystallization of salt," Scherer [45] explains how the continued reaction of an anhydrous clinker core that is confined by hydration products could result in localized volume increases and cracking. When aggregated, these micro-volume changes would result in macro-dimensional changes. We term this method of expansion confined volumetric expansion which can also be used to describe the pressures and expansion developed by crystals growing in small pores [45].

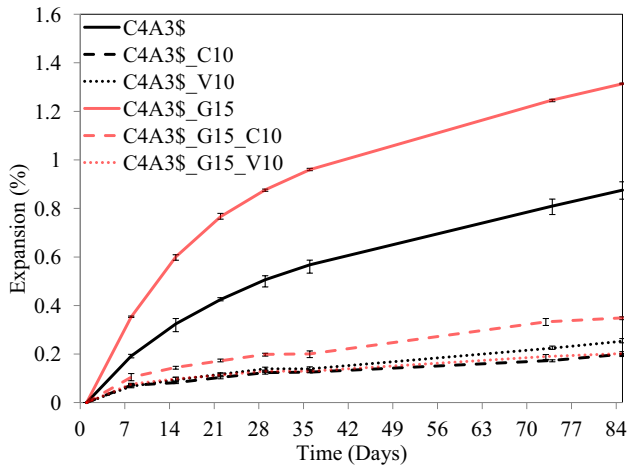
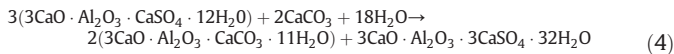
#### 3.3. Chemical reactions

Fig. 3 shows a highlighted region of the XRD plots showing the monosulfoaluminate reduction and ettringite and monocarboaluminate production for C4A3\$\_C10\$ and C4A3\$\_V10\$ with time. Likewise from the figure it is clear that the kinetics of the monocarboaluminate producing reaction was faster for vaterite than that for calcite. Table 3 provides a summary of the quantitative XRD results. All pastes contain anhydrous Ye'elimite at 1 day, which is necessary for the confined volumetric expansion theory. Additionally, the pastes containing gypsum retain it through 7 days of hydration. Although stoichiometrically the gypsum should have been consumed before 7 days, it most probably persists due to the system becoming diffusion limited. As expected in the pastes without gypsum, Ye'elimite initially reacts to form monosulfoaluminate

**Table 2**  
Compressive strength development of mortar cubes with time. Standard deviation is given in parenthesis.

Time (days)	C4A3\$ strength (MPa)	C4A3\$_{C10}\$ strength (MPa)	C4A3\$_{V10}\$ strength (MPa)	C4A3\$_{G15}\$ strength (MPa)	C4A3\$_{G15\_C10}\$ strength (MPa)	C4A3\$_{G15\_V10}\$ strength (MPa)
1	41 (1)	33 (5)	38 (5)	52 (5)	55 (4)	60 (8)
7	39 (5)	39 (5)	39 (5)	49 (6)	47 (7)	51 (9)
28	40 (1)	41 (5)	45 (5)	39 (3)	46 (3)	49 (6)
84	40 (5)	46 (5)	42 (4)	33 (2)	44 (5)	52 (4)

and in the pastes with gypsum, it reacts with gypsum to form ettringite (AFt). The solubility of calcium carbonates is too low to take part significantly in the early age hydration reactions. By 28 days, C4A3\$\_{V10}\$ had reacted 74% of its vaterite and 97% of its monosulfoaluminate to form monocarboaluminate (AFm-CO<sub>3</sub>) and ettringite, according to Eq. (4).



**Fig. 2.** Dimensional stability of Ye'elimites with varying replacements.

**Table 3**  
Quantitative XRD of crystalline paste components.

Paste	Day	Ye'el.	Gyp.	Calc.	Vater.	AFt	AFm	AFm-CO <sub>3</sub>	Gibbs.
C4A3\$	1	28	n/a	n/a	n/a	10	51	0	12
C4A3\$	7	16	n/a	n/a	n/a	10	59	0	15
C4A3\$	28	4	n/a	n/a	n/a	8	71	0	17
C4A3\$	84	3	n/a	n/a	n/a	9	73	0	15
C4A3\$_{C10}\$	1	19	n/a	12	n/a	10	48	0	11
C4A3\$_{C10}\$	7	11	n/a	13	n/a	8	52	3	13
C4A3\$_{C10}\$	28	4	n/a	11	n/a	16	46	9	14
C4A3\$_{C10}\$	84	4	n/a	6	n/a	44	9	27	10
C4A3\$_{V10}\$	1	19	n/a	1	11	9	49	0	12
C4A3\$_{V10}\$	7	12	n/a	1	11	11	47	4	14
C4A3\$_{V10}\$	28	8	n/a	1	3	44	1	30	12
C4A3\$_{V10}\$	84	4	n/a	0	2	47	1	38	8
C4A3\$_{G15}\$	1	31	4	n/a	n/a	54	4	0	7
C4A3\$_{G15}\$	7	25	3	n/a	n/a	57	7	0	7
C4A3\$_{G15}\$	28	8	0	n/a	n/a	61	17	0	14
C4A3\$_{G15}\$	84	2	0	n/a	n/a	64	22	0	12
C4A3\$_{G15\_C10}\$	1	22	3	11	n/a	55	4	0	5
C4A3\$_{G15\_C10}\$	7	18	2	11	n/a	54	6	2	7
C4A3\$_{G15\_C10}\$	28	5	0	10	n/a	66	2	7	10
C4A3\$_{G15\_C10}\$	84	3	0	8	n/a	67	1	13	8
C4A3\$_{G15\_V10}\$	1	27	4	0	8	54	2	0	5
C4A3\$_{G15\_V10}\$	7	21	3	0	9	53	3	4	7
C4A3\$_{G15\_V10}\$	28	6	0	1	6	65	2	13	8
C4A3\$_{G15\_V10}\$	84	2	0	1	5	67	1	17	8

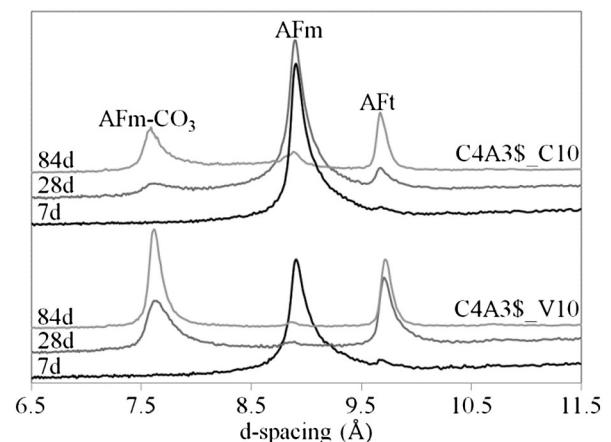
Note: XRD patterns include amorphous material (mainly Al(OH)<sub>3</sub>) and contributions from AFm phases with variable d-spacings due to variable interlayer molecules/ions which are not quantified.

Calcite is a more stable and less soluble form of calcium carbonate than vaterite; hence, it would be expected to react slower with the monosulfoaluminate to form monocarboaluminate, and this is evidenced by C4A3\$\_{C10}\$ forming monocarboaluminate at a slower rate than C4A3\$\_{V10}\$. Additionally, the vaterite utilized in this study had a smaller average particle size and consequently a higher surface area than the calcite utilized, which would also contribute to the enhanced carbonate reactivity. Likewise, C4A3\$\_{C10}\$'s slower rate of monocarboaluminate and ettringite formation corresponded to its slower rate of strength gain. It is interesting that although all the mixes with calcium carbonates produced significant quantities of ettringite, they expanded less than the mixes without calcium carbonate additions that produced much less ettringite over the same time periods. Gypsum in the pastes led to ettringite formation and reduced the amount of monosulfoaluminate formed, thus gypsum reduced the ability of the pastes are reacting the calcium carbonate and form monocarboaluminate.

Thermal analysis confirms the trends established by XRD. The DTA results (Fig. 4) show that at 7 days of hydration the hydrated phases for C4A3\$, C4A3\$\_{C10}\$ and C4A3\$\_{V10}\$ were monosulfoaluminate and aluminum hydroxide, and calcium carbonate was still mainly unreacted. At 28 days of hydration, C4A3\$\_{V10}\$ had reacted more of its calcium carbonate and monosulfoaluminate and produced more ettringite and monocarboaluminate than C4A3\$\_{C10}\$. Finally, the absence of hemicarboaluminate in all samples can probably be attributed to the low hydroxide concentration present in our system.

#### 4. Conclusions

In Ye'elmites pastes, the reaction of calcium carbonate with monosulfoaluminate to produce monocarboaluminate and ettringite was successfully demonstrated. The reaction was approximately three times faster for vaterite than that for calcite because of vaterite's lower stability, higher solubility, and higher surface area. Vaterite and calcite showed a significant reaction by 28 and 84 days, respectively. Gypsum promoted the early age formation of ettringite at the expense of monosulfoaluminate, limiting calcium carbonate's ability to react.



**Fig. 3.** XRD results highlighting monocarboaluminate and ettringite formation with time for mixes without gypsum.

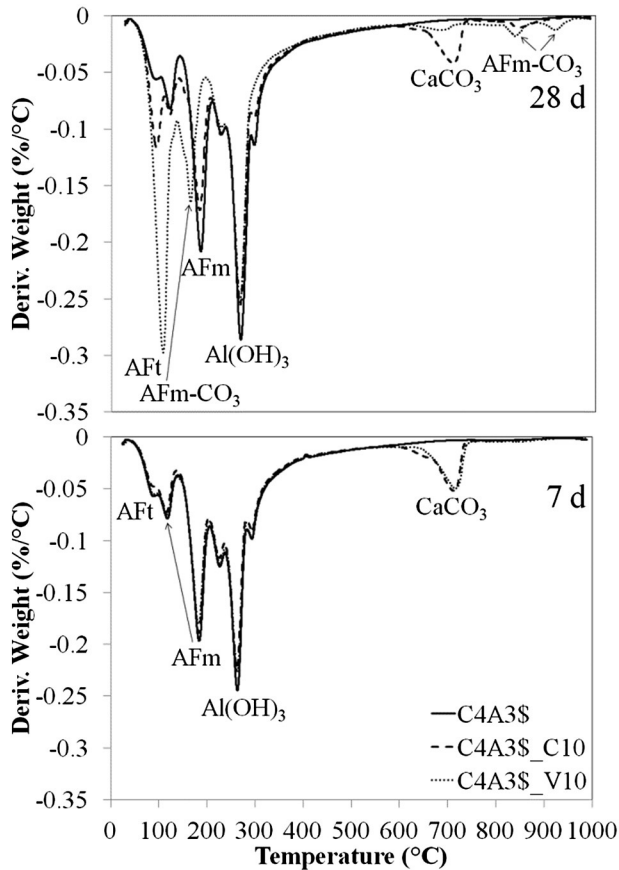


Fig. 4. DTA results for specimens without gypsum at 7 and 28 days.

Vaterite and calcite also benefited the mortar's mechanical properties. In the mortars without gypsum, both calcium carbonates reduced mortar expansion and increased the mortar's compressive strength. The timing of the increase in strength corresponded to when the calcium carbonate reacted. In the samples with gypsum, both calcium carbonates reduced expansion and decreased the strength loss rate related to expansion. Vaterite was more effective than calcite in mitigating the compressive strength loss. The mortar without gypsum or calcium carbonate also expanded significantly despite a low ettringite content (~5%). This strongly supports the confined volumetric expansion theory where an anhydrous Ye'elimite core (i) continues to react with water after being surrounded by a confining matrix causing localized volume increases and (ii) promotes a macro-expansion.

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### References

- [1] T.A. Ragozina, Reaction of calcium sulphate with aluminate at 1200 °C, *Zh. Prikl. Khim.* 30 (1957) 1682–1684.
- [2] N. Fukuda, On the constitution of sulfo-aluminous clinker, *Bull. Chem. Soc. Jpn.* 34 (1961) 138–139.
- [3] G.C. Bye, *Portland Cement*, 2nd Ed Thomas Telford, London, 1999, 206.
- [4] A. Klein, Calciumaluminosulfate and expansive cements containing same, US Patent No. 3, 155, 526, 1963, 4 pp.
- [5] Y. Wang, M. Su, The third cement series in China, *World Cem.* 25 (8) (1997) 6–10.
- [6] Y.M. Wang, M.Z. Su, L. Zhang, *Sulphoaluminate Cement*, Peking University Press, Peking, China, 1990.
- [7] L. Zhang, M. Su, Y. Wang, Development of the use of sulfo- and ferroaluminate cements in China, *Adv. Cem. Res.* 11 (1999) 15–21.
- [8] P.K. Mehta, Investigation on energy-saving cements, *World Cem. Technol.* 11 (1980) 167–177.
- [9] F.P. Glasser, L. Zhang, High-performance cement matrices based on calcium sulfoaluminate–belite compositions, *Cem. Concr. Res.* 31 (2001) 1881–1886.
- [10] I.A. Chen, M.C.G. Juenger, Incorporation of coal combustion residuals into calcium sulfoaluminate–belite cement clinkers, *Cem. Concr. Res.* 34 (2012) 893–902.
- [11] S. Sahu, J. Majling, Preparation of sulphoaluminate belite cement from fly ash, *Cem. Concr. Res.* 24 (1999) 1065–1072.
- [12] P. Arjunan, M.R. Silsbee, D.M. Roy, Sulfoaluminate–belite cement from low calcium fly ash and sulfur-rich and other industrial by-products, *Cem. Concr. Res.* 29 (1999) 1305–1311.
- [13] K. Wu, H. Shi, X. Guo, Utilization of municipal solid waste incineration fly ash for sulfoaluminate cement clinker production, *Waste Manag.* 31 (2011) 2001–2008.
- [14] J. Beretka, B. de Vito, L. Santoro, N. Sherman, G.L. Valenti, Hydraulic behavior of calcium sulfoaluminate-based cements derived from industrial process wastes, *Cem. Concr. Res.* 23 (1993) 1205–1214.
- [15] M. Singh, S.N. Upadhyay, P.M. Prasad, Preparation of special cements from red mud, *Waste Manag.* 16 (1996) 665–670.
- [16] G. Bernardo, M. Marroccoli, F. Montagnaro, G.L. Valenti, Use of fluidized bed combustion wastes for the synthesis of low energy cements, *Proc. 11th Int. Congr. Chem. Cem.*, vol. III, Durban, South Africa, 2003, 2003, pp. 1227–1236.
- [17] M. Marroccoli, F. Montagnaro, M. Nobili, A. Telesca, G.L. Valenti, Synthesis, hydration properties and environmentally friendly features of calcium sulfoaluminate cements, *Proc. 12th Int. Congr. Chem. Cem.*, Montréal, Canada, 2007, Paper W3-11.2, 2007.
- [18] M.L. Pace, A. Telesca, M. Marroccoli, G.L. Valenti, Use of industrial byproducts as alumina sources for the synthesis of calcium sulfoaluminate cements, *Environ. Sci. Technol.* 45 (2011) 6124–6128.
- [19] G. Bernardo, A. Telesca, G.L. Valenti, A porosimetric study of calcium sulfoaluminate cement pastes cured at early ages, *Cem. Concr. Res.* 36 (2006) 1042–1047.
- [20] G. Bernardo, L. Buzzi, F. Canonico, M. Paris, A. Telesca, G.L. Valenti, Microstructural investigations on hydrated high-performance cements based on calcium sulfoaluminate, *Proc. 12th Int. Congr. Chem. Cem.*, Montreal, Canada, 2007, Paper W3-11.4, 2007.
- [21] D. Gastaldi, F. Canonico, L. Capelli, M. Bianchi, M.L. Pace, A. Telesca, G.L. Valenti, Hydraulic behaviour of calcium sulfoaluminate cement alone and in mixture with Portland cement, *Proc. 13th Int. Congr. Chem. Cem.*, Madrid, Spain, 2011, Paper 412, 2011.
- [22] L. Buzzi, F. Canonico, A. Telesca, G.L. Valenti, High-performance and low-CO<sub>2</sub> cements based on calcium sulfoaluminate, *ZKG Int.* 5 (2010) 39–45.
- [23] I.A. Chen, C.W. Hargis, M.C.G. Juenger, Understanding expansion in calcium sulfoaluminate–belite cements, *Cem. Concr. Res.* 42 (2012) 51–60.
- [24] M. Cohen, C. Richards, Effects of the particle sizes of expansive clinker on strength-expansion characteristics of type K expansive cements, *Cem. Concr. Res.* 12 (1982) 717–725.
- [25] J. Beretka, M. Marroccoli, N. Sherman, G.L. Valenti, The influence of C<sub>4</sub>A<sub>3</sub>S̄ content and w/s ratio on the performance of calcium sulfoaluminate-based cements, *Cem. Concr. Res.* 26 (1996) 1673–1681.
- [26] P.K. Mehta, P.J.M. Monteiro, *Hydraulic cements, Concrete Microstructure, Properties, and Materials*, 3rd ed., McGraw-Hill, New York, 2006, pp. 238–239.
- [27] I. Odler, *Cements containing calcium sulfoaluminate*, *Special Inorganic Cements*, 3rd ed., FN Spon, London, 2000, pp. 69–87.
- [28] L. Pelletier, F. Winnefeld, B. Lothenbach, The ternary system Portland cement–calcium sulfoaluminate clinker–anhydrite: hydration mechanism and mortar properties, *Cem. Concr. Compos.* 32 (2010) 497–507.
- [29] M.C.G. Juenger, F. Winnefeld, J.L. Provis, J.H. Ideker, Advances in alternative cementitious binders, *Cem. Concr. Res.* 41 (12) (2011) 1232–1243.
- [30] L. Wang, F.P. Glasser, Hydration of calcium sulfoaluminate cements, *Adv. Cem. Res.* 8 (1996) 127–134.
- [31] F. Winnefeld, S. Barlag, Influence of calcium sulfate and calcium hydroxide on the hydration of calcium sulfoaluminate clinker, *ZKG Int.* 12 (2009) 42–53.
- [32] C.W. Hargis, A.P. Kirchheim, P.J.M. Monteiro, E.M. Gartner, Early age hydration of calcium sulfoaluminate (synthetic Ye'elimite, C<sub>4</sub>A<sub>3</sub>S̄) in the presence of gypsum and varying amounts of calcium hydroxide, *Cem. Concr. Res.* 48 (2013) 105–115.
- [33] T. Matschei, B. Lothenbach, F.P. Glasser, The role of calcium carbonate in cement hydration, *Cem. Concr. Res.* 37 (2007) 551–558.
- [34] P. Lawrence, M. Cyr, E. Ringot, Mineral admixtures in mortars – effect of inert materials on short-term hydration, *Cem. Concr. Res.* 33 (12) (2003) 1939–1947.
- [35] M. Cyr, P. Lawrence, E. Ringot, Mineral admixtures in mortars – quantification of the physical effects of inert materials on short-term hydration, *Cem. Concr. Res.* 35 (2005) 719–730.
- [36] P. Lawrence, M. Cyr, E. Ringot, Mineral admixtures in mortars – effect of type, amount and fineness of fine admixtures on compressive strength, *Cem. Concr. Res.* 35 (2005) 1092–1105.
- [37] M. Cyr, P. Lawrence, E. Ringot, Efficiency of mineral admixtures in mortars: quantification of the physical and chemical effects of fine admixtures in relation with compressive strength, *Cem. Concr. Res.* 36 (2006) 264–277.
- [38] L. Pelletier-Chaignat, F. Winnefeld, B. Lothenbach, C.J. Müller, Beneficial use of limestone filler with calcium sulfoaluminate cement, *Constr. Build. Mater.* 26 (2012) 619–627.
- [39] D. Biello, Cement from CO<sub>2</sub>: a concrete cure for global warming, *Sci. Am.* (Aug. 7, 2008) 1–3 (<http://www.scientificamerican.com/article.cfm?id=cement-from-carbon-dioxide&sc=rss>, retrieved Mar. 29, 2013).
- [40] F.C. Hawthorne, et al., New mineral names, *Am. Mineral.* 72 (1987) 222–230.
- [41] ASTM C807-08, Standard Specification for Time of Setting of Hydraulic Cement Mortar by Modified Vicat Needle, ASTM International, West Conshohocken, PA, 2008. (3 pp.).

- [42] W. Yanmou, S. Muzhen, Y. Renhe, L. Baoyuan, A quantitative study of paste microstructures and hydration characters of sulphoaluminate cement, *Proced. of the 9th Int. Congr. on the Chem. of Cem.*, New Delhi, India, 1992, 1992.
- [43] P.K. Mehta, Effect of lime on hydration of pastes containing gypsum and calcium aluminates or calcium sulfoaluminate, *J. Am. Ceram. Soc.* 56 (6) (1973) 315–319.
- [44] M.D. Cohen, Theories of expansion in sulfoaluminate – type expansive cements: schools of thought, *Cem. Concr. Res.* 13 (1983) 809–818.
- [45] G.W. Scherer, Stress from crystallization of salt, *Cem. Concr. Res.* 34 (2004) 1613–1624.