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Further insights into calcium sulfoaluminate cement expansion

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There is still an ongoing debate on the mechanisms of expansion of calcium sulfoaluminate (CSA) cements, which can be either favourable, for example, in shrinkage compensating construction materials, or deleterious in cases of excessive expansion. In order to expand on previous studies, CSA cements with molar ratios (M) of calcium sulfate/ye'elimite of 0.1, 1, 1.5 and 2 were investigated from 30 min to 182 d. All systems showed expansion, and expansion was found to increase with increasing gypsum content. The sample with $M=2$ showed a high expansion and severe cracking after 1 d of hydration. Based on the pore solution chemistry, crystallisation pressures were calculated, which revealed that not only ettringite, but also the other hydrate phases present (aluminium hydroxide (AH_3), strätlingite, calcium aluminate decahydrate (CAH_{10}), monosulfate) may contribute to the total crystallisation pressure. The percolation pore radii obtained by mercury intrusion porosimetry were used to calculate hydrostatic tensile stresses. It was found that in all investigated systems the hydrostatic tensile stresses exceeded the 1 d tensile strength, which is in line with the fact that all samples showed expansion.

Notation

A_y, B_y	P, T -dependent coefficients
a_i	ion-size parameter
b_y	semi-empirical parameter (~ 0.123 for potassium hydroxide electrolyte at 25°C)
I	effective molal ionic strength
K_{sp}	solubility product of phase
P	crystallisation pressure
P_c	maximum crystallisation pressure
P_{Hg}	mercury pressure
R	universal gas constant
r_c	radius of crystal
r_p	pore radius
T	absolute temperature
V_m	molar volume of phase
z_i	charge of species i
γ_{cl}	interfacial free energy between crystal and liquid
γ_{Hg}	surface tension
δ	water layer separating growing crystal and pore wall
θ_{Hg}	contact angle
σ_{cyl}	hydrostatic tensile stress for cylindrical geometry
ϕ	volume fraction of crystallising phase

Introduction

Portland cement (PC) production accounts for approximately 5% of anthropogenic carbon dioxide (CO_2) emissions because of its large production quantity and the manufacturing process. Calcium sulfoaluminate (CSA) cements are being researched as potentially more sustainable options that can be added to cement manufacturers' portfolios. CSA cement is regarded as a

sustainable cement because it improves upon ordinary PC manufacture in five ways: (a) CSA cement's main early strength-gaining phase is ye'elimite ($\text{C}_4\text{A}_3\bar{\text{S}}$), which contains only 27.6 wt% calcium oxide (CaO) compared to PC's main phase, alite (C_3S), which contains 73.7% calcium oxide; (b) CSA cement can be manufactured at ~ 150 – 200°C lower temperature than PC; (c) CSA clinker is more friable than PC clinker, making it easier to grind; (d) CSA clinker is blended with relatively high amounts of calcium sulfate to produce CSA cement (Glasser and Zhang, 2001; Mehta, 1980); and (e) CSA can be blended with calcium carbonates or siliceous pozzolans, altering CSA paste's hydration, microstructure and/or other properties (Garcia-Mate *et al.*, 2013; Hargis *et al.*, 2014; Ioannou *et al.*, 2014, 2015; Martin *et al.*, 2015; Pelletier-Chaignat *et al.*, 2012; Zivica, 2000) (cement oxide notation utilised: A = aluminium oxide (Al_2O_3), F = iron (III) oxide (Fe_2O_3), T = titanium dioxide (TiO_2), S = silicon dioxide (SiO_2), $\bar{\text{S}}$ = sulfur trioxide (SO_3), M = magnesium oxide (MgO), C = calcium oxide, $\bar{\text{C}}$ = carbon dioxide, N = sodium oxide (Na_2O), K = potassium oxide (K_2O) and H = water (H_2O)).

In addition to its environmental benefits CSA cement can be utilised either alone or as an addition to PC to produce shrinkage-compensating, self-stressing, high-early-strength and rapid-setting cements (Beretka *et al.*, 1996; Bernardo *et al.*, 2006, 2007; Buzzi *et al.*, 2010; Chen *et al.*, 2012; Cohen and Richards, 1982; Gastaldi *et al.*, 2011). To produce shrinkage-compensating and self-stressing CSA cements, the cement paste must expand. The right timing for expansion is crucial. Expansion without deleterious cracking is most easily achieved

during early ages of hydration and strength gain; however, if expansion occurs after the paste has hardened and densified its microstructure sufficiently, then cracking is likely to occur. The use of CSA cement to produce expansive cements dates back to work by A. Klein in the 1960s (Klein *et al.*, 1961). CSA-based cement's expansive nature quickly sparked a debate about the mechanism of expansion, with two competing schools of thought: crystal growth theory and swelling theory (Cohen, 1983). Swelling theory attributes expansion to the adsorption of water and swelling characteristics of 'ettringite gel,' whereas crystal growth theory attributes expansion to the growth of ettringite crystals on the expansive particles or from the solution resulting in a crystallisation pressure. The two theories may seem very different, but considering that the uptake of water is also a fundamental part of the crystallisation process of ettringite, the practical implication of both historically different schools of thought are rather similar.

Discussions and research on the thermodynamics of crystallisation in stone and cementitious materials have furthered the understanding of how the growth of crystals converts chemical potential into crystallisation pressure, which can exert mechanical force on the microstructure resulting in macroscopic strains (Flatt, 2002; Flatt and Scherer, 2008; Scherer, 1999, 2004; Steiger, 2005a, 2005b, 2006; Xie and Beaudoin, 1992). As Flatt, Scherer and Steiger have presented the thermodynamic calculations thoroughly, only the findings most relevant to the topic of expansion in CSA cements will be discussed briefly here. Their calculations show that crystallisation pressure increases with increasing supersaturation of the pore fluid with respect to the crystallising phase and size of the crystal growing in a confining pore separated by a 1–2 nm water layer.

Thermodynamic calculations initially were utilised to show how salts crystallising could generate stresses in pores of stone or concrete (Flatt, 2002; Scherer, 2004; Steiger, 2005a, 2005b), but were soon also utilised to explain the expansion caused by delayed ettringite formation (DEF) (Flatt and Scherer, 2008). Sant *et al.* (2011) utilised the concept of crystallisation pressure to explain how shrinkage-reducing admixtures elevate the supersaturation of portlandite in the pore solution at early ages, leading to a corresponding expansion. Bizzozero *et al.* (2014) investigated the effect of increasing calcium sulfate content on CSA and calcium aluminate cement pastes. Analysing the pore solutions of the pastes at 7 d, they found that there was a threshold of calcium sulfate where the Ca^{2+} concentration increased rapidly, which results in higher saturation indices (SIs) for ettringite and, as a consequence of the higher SI, higher crystallisation pressures for a given pore size and the ability for crystals to exert sufficient pressure over a wider range of the porosity. Chaunsali and Mondal (2015a, 2015b, 2016) investigated PC-CSA blends. They analysed the pore solution of the blends at 1, 3 and 7 d in all three studies and additionally at 21 d in their study where additional

supplementary cementitious materials were included. They too found that early-age expansion was associated with supersaturation with respect to ettringite.

The chemical and physical factors affecting the amount and timing of CSA cement expansion are understood to include: (a) calcium sulfoaluminate and calcium aluminate content (principally ye'elimite content); (b) particle size distribution of the CSA cement; (c) calcium sulfate content; (d) calcium sulfate reactivity; (e) water availability, both in terms of the water/cement ratio (w/c) and curing conditions; and (f) lime and alkali content (Beretka *et al.*, 1996; Chen *et al.*, 2012; Cohen and Richards, 1982; Glasser and Zhang, 2001; Kurdowski and Thiel, 1981; Deng and Tang, 1994; Odler and Colan-Subauste, 1999; Wang *et al.*, 1992). These factors affect the amount, timing and space available for hydration products to form. Considering these factors with regard to crystallisation pressure, it can be observed that increasing reactants that form ettringite should increase the supersaturation with regard to ettringite, as they dissolve and come into solution, and that varying their proportions will affect the microstructure and porosity in which the crystals will grow.

The aim of the present study is to build upon the growing body of evidence that crystallisation pressure is responsible for expansion in CSA cement-based systems by investigating the hydration of a variety of CSA cements with calcium sulfate to ye'elimite molar ratios (M) ranging from 0.1 to 2 and monitoring their expansion from approximately 30 min to 182 d. By monitoring the hydration over a much broader period of time compared to the earlier studies, the present study seeks to further understand CSA cement hydration and pore solution development and bring additional insights regarding how crystallisation pressure is affecting CSA cement expansion.

Materials and methods

Materials

A high ye'elimite CSA clinker was blended with gypsum to produce CSA cements with molar ratios of calcium sulfate/ye'elimite of 0.1, 1, 1.5 and 2. Table 1 gives the CSA clinker and gypsum's oxide compositions, as determined by X-ray fluorescence (XRF) and presents the density, Blaine fineness and phase quantification determined by quantitative X-ray diffraction (XRD) for all cementitious components utilised.

Methods

Pastes

Cement pastes were prepared using the ratios in Table 2. For purposes of calculating w/c , cement was considered as CSA clinker plus gypsum. A retarder was not utilised in this study because all samples were able to be cast without one; also, not using a retarder avoids adding further ions to the pore solution, which could complicate analysis of the results,

Table 1. CSA clinker and gypsum's chemical composition, density and fineness

CSA clinker			Gypsum		
Silicon dioxide (SiO ₂)	9.52	0.32	C ₄ A ₃ $\bar{S}$	64.4	—
Aluminium oxide (Al ₂ O ₃)	31.51	0.05	C ₂ S	7.7	—
Iron (III) oxide (Fe ₂ O ₃)	1.31	0.04	C ₉ S ₃ $\bar{S}_3 \cdot CaF_2$	6.4	—
Calcium oxide (CaO)	40.14	33.87	M	3.1	—
Magnesium oxide (MgO)	4.17	0.39	C ₃ MS ₂	6.9	—
Sulfur trioxide (SO ₃)	10.07	44.25	C ₇ MS ₄	5.6	—
Sodium oxide (Na ₂ O)	0.49	0.06	CT	1.7	—
Potassium oxide (K ₂ O)	0.47	0.04	C ₂ AS	2.9	—
Titanium dioxide (TiO ₂)	0.41	0.016	C $\bar{C}$	—	1.1
Phosphorus pentoxide (P ₂ O ₅)	0.12	0.006	C $\bar{S}$	1.3	2.4
Manganese oxide (MnO)	0.17	0.003	C $\bar{S}$ H _{0.5}	—	0.8
Chromium (III) oxide (Cr ₂ O ₃)	0.07	0.002	C $\bar{S}$ H ₂	—	95.4
Loss on ignition (LOI)	0.61	21.02	S	—	0.3
Sum	99.06	99.95	Sum	100.0	100.0
			Blaine: cm ² /g	4750	4430
			Density: g/cm ³	2.85	2.31

Table 2. Paste formulations for 1000 cm³

Mix	M0.1			M1		M1.5		M2	
w/c ^a	0.8			0.8		0.8		0.8	
M	0.1			1		1.5		2	
Material	Density: g/cm ³	Mass: g	Vol.: cm ³	Mass: g	Vol.: cm ³	Mass: g	Vol.: cm ³	Mass: g	Vol.: cm ³
CSA clinker	2.85	868.9	304.9	734.8	257.8	676.8	237.5	627.2	220.1
Gypsum	2.31	0	0	125.2	54.2	179.3	77.6	225.6	97.7
Water	1	695.1	695.1	688.0	688.0	684.9	684.9	682.3	682.3

^aIf adjusted for the calcium sulfate's chemically bound water, the w/c equals 0.83, 0.84 and 0.85 for M1, M1.5 and M2, respectively

because chemical admixtures have been shown to affect chemical species' oversaturation levels in the pore solution and crystallisation pressure (Sant *et al.*, 2011). Pastes were mixed for 2 min by an overhead mixer, revolving the paddle at a rate of 140 r/min with a planetary motion of approximately 62 r/min. The pastes were then transferred to 500 ml polyethylene bottles, taking care to remove as much air as possible while capping the bottles. The bottles were slowly rotated to avoid segregation until final setting, approximately 2 h. The pastes were stored in the sealed bottles at 20°C and 95% relative humidity (RH) through 24 h of hydration, then demoulded, and the top and bottom of the moulded pastes were cut off to create cylinders (100 mm × 77 mm dia.). All cylinders were then placed in sealed 1 l plastic cylinders with 500 ml of deionised water, which fully submersed the paste cylinders in water while trying to minimise the amount of water surrounding the pastes and interaction with the atmosphere.

Dimensional stability

For dimensional stability tests in water, stainless steel plugs were affixed to the ends of the paste cylinders using water and chemically resistant epoxy immediately after demoulding and

before placing the cylinders in water to cure beyond 1 d of hydration. Length measurements were taken at 1.08 (reference measurement immediately after attaching stainless steel plugs), 1.25, 2, 3, 4, 7, 10, 14, 21, 29, 43, 56, 175 and 182 d of hydration. The length measurements were taken on two cylinders for each mix and then the results were averaged. The error is estimated to be ±0.05 mm/m, which was determined from the maximum length change difference between any two cylinders for all length measurements.

To study the dimensional stability of the pastes immediately after setting, autogenous strain tests were performed according ASTM C 1698 (ASTM, 2009; Wyrzykowski *et al.*, 2016). Pastes were placed in corrugated tubes utilising vibration. The tubes were then rotated for 30 min during the period when trial samples experienced bleeding, but had not yet experienced initial set. The plastic pastes were then placed into a temperature-controlled silicone oil bath at 20 ± 0.1°C. The length changes were recorded after initial shrinkage terminated (probably in the plastic state) and final setting was achieved, approximately 120–160 min of hydration. The length change was measured for 7 d.

Tensile strength

Paste cylinders were prepared as previously described and demoulded after 24 h of curing. The top and bottom of the specimens were cut off and polished afterwards. Steel discs were glued to the upper and lower ends of the cylinders by means of a rapid-hardening epoxy resin. The steel discs were attached to a tensile loading machine and the tensile strength was measured using a loading rate of 0.05 MPa/s.

X-ray diffraction and thermogravimetric analysis

Hydration was stopped on cylinders at 0.5, 1, 7, 14, 28, 56 and 182 d of hydration by slicing a 5 mm thick section from the centre of a cylinder, then crushing in isopropanol in an agate mortar for 5 min, followed by soaking in isopropanol for an additional 10 min. The isopropanol was then filtered off, and the pastes were soaked in di-ethyl ether for 5 min. The ether was then filtered off, and the pastes were dried for 20 min at 40°C. The pastes were then studied using thermogravimetric analysis (TGA) and XRD. TGA was conducted on a Mettler Toledo TGA/SDTA 851e from 30 to 980°C using 50 ± 2 mg, a 20°C/min heating rate and nitrogen as the protective gas. The relative error is estimated at 5%, which produces an absolute error of ±2% at 980°C.

The XRD was conducted using a PANalytical X'Pert Pro diffractometer equipped with an X'Celerator detector. The incident beam was Co K_α radiation (0.1789 nm) with a 1/2° and 1° divergence and anti-scatter slit, respectively. A 2θ range of 5–65° was scanned continuously over 2 h. Samples were prepared by back loading. An internal standard of 20% calcium fluoride (CaF₂) was utilised. The Rietveld analysis was performed using PANalytical Highscore Plus 3.0.5 software. The background was fit manually using a cubic spline with base points at the same 2θ positions for all patterns. Scale factors, lattice parameters, pattern shift and specimen displacement were refined. Multiple polymorphs for belite and ye'elimite were considered (Le Saout *et al.*, 2011). Ye'elimite was quantified using both an orthorhombic and cubic structure, which improved the pattern fit but did not significantly change the quantification (Alvarez-Pinazo *et al.*, 2012; Calos *et al.*, 1995; Hargis *et al.*, 2014), and the beta polymorph of C₂S was found to provide the best fit.

Pore solution analysis

Pore solutions were expressed using the steel die method (Barneyback and Diamond, 1981) and immediately filtered using 0.45 µm nylon filters. For ion chromatography analysis, one part of the solution was immediately diluted to 1:10, 1:100 and 1:1000 with deionised water (18.2 MΩ). The total concentrations of the sodium, potassium, calcium, chloride, sulfate, aluminate and silicate ions were determined using ion chromatography (Dionex ICS 3000 with columns: IonPac CS12A, AS22 and CS5A). The other part was used for pH measurements. The hydroxide concentrations were determined with a combined pH electrode on the filtered and undiluted

solutions. The pH electrode was calibrated against potassium hydroxide solutions of known concentrations.

Utilising the ion concentrations from the expressed pore solutions, saturation indices for the hydration products were calculated using the Gibbs free energy minimisation software, GEMS-PSI (Kulik *et al.*, 2013; Wagner *et al.*, 2012). Any pH adjustments necessary to match the experimental data were made by reducing sodium hydroxide (NaOH) or hydrochloric acid (HCl) as necessary. Any adjustments made were kept to a minimum because the ion activity products (IAPs) of many hydration products are sensitive to changes in the concentration of hydroxide ions (OH⁻). The IAP of ettringite is equal to {Ca²⁺}⁶{Al(OH)₄⁻}²{OH⁻}⁴{SO₄²⁻}³{H₂O}²⁶, so any change to the hydroxide ion concentration gets raised to the fourth power and can have large effects on the calculated SI.

'GEMS' is a broad-purpose geochemical modelling code which computes the equilibrium phase assemblage and speciation in a complex chemical system from its total bulk elemental composition. The thermodynamic data for aqueous species and solids were taken from the PSI-GEMS thermodynamic database with the PSI-Nagra database (Hummel *et al.*, 2002). For cement minerals, the cement-specific CEMData14 database (Lothenbach *et al.*, 2008, 2012; Matschei *et al.*, 2007) was used. A summary of the thermodynamic database is also available at Empa (2018), where the thermodynamic database in the GEMS format can be freely downloaded. The activity coefficients of the aqueous species γ_i were computed with the built-in extended Debye–Hückel equation with common ion-size parameter a_i of 0.367 nm for potassium hydroxide solutions and common third parameter b_y according to Equation 1

$$1. \quad \log \gamma_i = \frac{-A_y z_i^2 \sqrt{I}}{1 + B_y a_i \sqrt{I}} + b_y I$$

where z_i denotes the charge of species i ; I is the effective molal ionic strength; b_y is a semi-empirical parameter (~0.123 for potassium hydroxide electrolyte at 25°C); and A_y and B_y are P , T -dependent coefficients. This activity correction is applicable up to approximately 1 M ionic strength (Merkel and Planer-Friederich, 2008).

Depending on the equilibration time and temperature, aluminium hydroxide (AH₃) forms with different degrees of crystallinity, which results in different solubility products (Lothenbach *et al.*, 2012). During the first hours of hydration, an amorphous AH₃ with a $\log K_{s0}$ (Al(OH)₃⁰ + OH⁻ ↔ Al(OH)₄⁻) of ~0 forms, which only transforms during months to years to microcrystalline AH₃ with a solubility product of -0.67 at ambient temperature. Crystalline gibbsite ($\log K_{s0} = -1.12$) is even more stable, but forms only at higher temperatures or very long equilibration times. Thus AH₃ solubility was varied as a function of time based on the data

reported in Lothenbach *et al.* (2012), see Figure 1. The data from Capmas and Ménétrier-Sorrentino (1989) (3 to 9 min) and Pokrovskii and Helgeson (1995) (gibbsite) were omitted from the equation fit because their exact times could not be determined but are shown for reference. The water content of AH_3 and its resulting molar volume were not varied in this study because of uncertainty about the amount of bound water and the timing of the change in bound water over time (Cuesta *et al.*, 2017a; Jansen *et al.*, 2017).

In addition to calculating the saturation indices, thermodynamic modelling was utilised to calculate the phase assemblages at 0.5, 1, 7, 14, 28, 56 and 182 d of hydration. The consumption of anhydrous phases as determined from the Rietveld analysis of the XRD data was fit using a four-parameter logistic non-linear regression model and was then input into GEMS to provide the kinetic restraint on the anhydrous phase consumption (Chitvoranund *et al.*, 2017). GEMS was then used to calculate the hydration phase assemblage at 20°C and atmospheric pressure. The experimental temperature affects ion solubility and reaction kinetics, so conducting experiments and modelling at different temperatures can cause different results.

The mercury intrusion porosimetry (MIP) tests were performed on Pascal 140/440 (Thermo Fisher Scientific Inc.) instruments. The MIP mortar samples were dried in the same manner as the XRD samples. Approximately 1 g of mortar was first intruded to a mercury pressure, P_{Hg} , of 395 kPa on the Pascal 140, then the sample was moved to the Pascal 440 and intruded to 200 MPa. A cylindrical pore model and the Washburn equation (Equation 2) using a contact angle, $\theta_{Hg} = 140^\circ$, and a surface tension, $\gamma_{Hg} = 0.48$ N/m, were assumed for intrusion to calculate the pore radius, r_p (Kaufmann, 2010).

$$2. \quad r_p = \frac{2\gamma_{Hg} \cos \theta_{Hg}}{P_{Hg}}$$

Figure 1. Solubility of AH_3 as a function of time

Results

Physical stability

Long-term mass change

Figure 2 presents the mass gain for the CSA cement paste cylinders whose length changes are presented later in Figure 4. Similar to the length change results, the CSA cement pastes with added gypsum gained mass at a faster rate with increasing calcium sulfate content, and their rates of mass gain declined with time. As is the case for its length change, M0.1 gained less mass initially compared to the CSA cement pastes with added calcium sulfate, but sustained additional mass gain through 182 d of hydration. Mass gain during water curing increased with increasing gypsum content due to the increased production of hydration products and water absorbed in cracks and microcracks, which will be discussed subsequently.

Early-age length change

The length changes of the cement pastes as measured by ASTM C 1698 are presented in Figure 3. After setting, all pastes initially expand; however, M0.1 begins to contract after 6 h; whereas all pastes with added gypsum continue to expand further. M1 expands to a maximum strain of 2.3 mm/m at 16 h of hydration, after which it slowly contracts. M1.5 expands to a strain of 2.7 mm/m at 14 h of hydration, after which it contracts to 2.3 mm/m at 22 h before continuing to expand to a maximum strain of 2.7 mm/m at 7 d. M2 expands to a maximum strain of 3.6 mm/m at 15 h of hydration, after which it contracts to 2.8 mm/m at 36 h before continuing to expand to 3.5 mm/m at 7 d. The periods of contraction that all the pastes experience are likely to be attributable to chemical shrinkage, since all pastes have sufficient water for hydration and should not be self-desiccating leading to autogenous shrinkage. For the pastes that continue to expand through 7 d (M1.5 and M2), the period of contraction would

Figure 2. Mass change of CSA cement pastes through 182 d of hydration

Figure 3. Early-age length change of CSA cement pastes

represent a stage of hydration where the chemical shrinkage exceeds the strain induced from crystallisation, and the periods of expansion represent the stages of hydration where the strains induced by crystallisation exceed the chemical shrinkage. It is important to note that expansion begins at 2.5, 2.0, 2.2 and 2.7 h for M0.1, M1, M1.5 and M2, respectively. Many dimensional stability tests begin at 1 d of hydration. As a consequence, those studies could be missing 2–3 mm/m of expansion during the first day of hydration, which is often as much as the total expansion reported over months of hydration.

Long-term length change

Figure 4 presents the expansion of paste cylinders demoulded at 1 d of hydration and stored in water thereafter. M2 expanded rapidly and cracked during the initial day of water storage; it continued to show movement through 21 d of hydration. For the pastes with added calcium sulfate, the initial rates of expansion increased with increasing calcium sulfate content. Likewise, all pastes with added calcium sulfate had decreasing rates of expansion with time. In contrast, M0.1 expanded more slowly initially, but sustained a greater rate of expansion through the 182 d of testing.

Hydration

Equations I–IV give the CSA hydration reactions for ye'elimite and belite (C_2S) relevant to this study. Equations I and II give the hydration reactions for ye'elimite without and with added calcium sulfate to form AH_3 and monosulfate or ettringite, respectively. Equation III gives the formation of strätlingite from belite and AH_3 . Equation IV gives the metastable formation of ettringite, CAH_{10} and AH_3 from ye'elimite.

Figure 4. (a) Zoomed-in section of expansion through 29 d of hydration; (b) expansion of CSA cement pastes through 182 d of hydration

Figure 5 presents the XRD patterns for the CSA cement pastes from 0.5 to 182 d of hydration. Some trends from the qualitative XRD can be observed. All CSA cement pastes' XRD patterns included the appearance of diffuse peaks at the position of gibbsite's main peaks, indicating the presence of poorly crystalline AH_3 (outside the range shown). Second, ettringite content increased with increasing calcium sulfate content, as expected. Third, CAH_{10} formed as a metastable

Figure 5. XRD patterns for: (a) M0-1; (b) M1; (c) M1-5; (d) M2 (Ett, ettringite; Ms, monosulfate; Str, strätlingite; Gyp, gypsum; Ye, ye'elimite; Flu, fluorite)

hydration product in the systems with the least calcium sulfate, M0-1 and M1. Fourth, the amount of strätlingite formed increased with decreasing calcium sulfate content, which is consistent with prior research (Jeong *et al.*, 2018). M2 produced, in addition to AH₃, only ettringite as a crystalline hydration product, but very little or no strätlingite, in contrast to the systems with less calcium sulfate.

Figure 6 presents the results from the Rietveld refinements performed on the XRD patterns in Figure 5. The quantity of ettringite produced increased with increasing gypsum content.

The majority of the ettringite produced formed in the first 12 h of hydration. M0-1 and M1 continued to produce additional ettringite through 182 d, and M1-5 and M2 have formed their maximum amount of ettringite by 56 d. M0-1 formed the most crystalline monosulfate, and M1 formed the second most, as expected; however, M1-5 did not form a significant quantity of crystalline monosulfate through 182 d. Monosulfate can form as part of AFm solid solutions; the presence of different anions lowers the crystallinity and thus limits the ability to quantify it by way of XRD, but the trends observed are as expected.

Figure 6. Quantification of XRD patterns by way of Rietveld refinement. Note: ordinate scale changes between plots

Increasing gypsum content accelerated the reaction of ye'elimite, which is consistent with prior studies (Winnefeld and Barlag, 2010). By 7 d of hydration, M0-1 and M2 had 2.1 and 0.3 g ye'elimite remaining, respectively. All systems have depleted the majority of their ye'elimite by 7 d of hydration, so additional ettringite or monosulfate production past that age is most likely in part due to crystallisation from amorphous hydration products, which peaked in quantity between 7 and 14 d and declined thereafter. In other words, amorphous hydration products which formed during the very rapid hydration of ye'elimite, when the kinetics of ye'elimite dissolution may have exceeded the kinetics of ettringite and monosulfate formation, later dissolved and recrystallised as more ordered and thermodynamically stable phases with lower solubility products than their amorphous precursors.

Increasing gypsum decreased the amount of strätlingite produced and delayed its starting point of formation. The cause of the change is three-fold. First, in the presence of sufficient gypsum, ettringite formation is thermodynamically favoured,

which suppresses the formation of AFm phases such as monosulfate or strätlingite (Winnefeld and Lothenbach, 2016). Second, increasing gypsum content accelerates CSA cement hydration, which causes the paste microstructure to densify more extensively, which inhibits ion mobility and belite dissolution. Third, increasing gypsum reduces the amount of belite in the CSA cement by diluting the clinker content. The slight increase in the belite quantified between the anhydrous and the 12 h patterns is most likely attributed to peak overlap between belite and hydration products, resulting in a belite quantification that is overestimated by approximately 2 g/100 g anhydrous cement in all hydrated systems. Fluorellestadite ($\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3\text{F}_2$) slowly dissolves with time, providing ionic species that can be bound by AFm and AFt phases. Of specific note, the release of sulfate ions will promote the formation of ettringite, which has been shown in prior studies to contribute to expansion.

Figure 7 presents the thermodynamic modelling of CSA cement hydration utilising the quantitative XRD (QXRD)

Figure 7. Thermodynamic modelling of CSA cement hydration over time: (a) M0.1; (b) M1; (c) M1.5; (d) M2

results presented in Figure 6 as the kinetic input. M0.1 is calculated to produce the most strätlingite, which is consistent with the XRD results. CAH_{10} is not predicted to form, as it is thermodynamically not stable (Winnefeld and Lothenbach, 2016). M0.1 is also calculated to produce an increasing amount of ettringite with time due to the small amount of anhydrite in the clinker, but more importantly due to the dissolution of fluorellestadite releasing sulfate ions. With increasing added gypsum, more ettringite is produced and less monosulfate is produced. In the M2 system, there is a transient formation of monosulfate around 1 d of hydration due to the ye'elimite dissolution out-pacing the calcium sulfate supply.

Pore solution analysis

The pH and ion concentrations from the pore solutions expressed are given in Table 3. At early ages calcium and sulfate

concentrations increased with increasing gypsum content. Contrarily, aluminate and silicate ions decreased with increasing gypsum content due to the increased Ca^{2+} concentration. The higher sulfate concentrations in the presence of ettringite result in lower hydroxide concentrations and thus pH values than in the samples with lower sulfate concentration in the presence of both ettringite and monosulfate, so M2 had a lower pH compared to the other pastes. Additionally, M2 at 0.5 d was replicated to confirm the relatively low pH of 10.

The SI of a phase is given as the log of the ion activity product (IAP) divided by the solubility product (K_{sp}) in Equation 3. The SIs for the main phases of interest are given in Table 4. SIs which are positive indicate that the pore solution is oversaturated with regard to that species, indicating a driving force to precipitate that species, and SIs that are negative indicate the solution is undersaturated with regard to that species,

Table 3. pH and ion concentrations in pore solutions

	Time: d	pH	Sodium: mmol/l	Potassium: mmol/l	Calcium: mmol/l	Chloride: mmol/l	Sulfate: mmol/l	Silicate: mmol/l	Aluminate: mmol/l	Hydroxide: mmol/l
M0·1	0·5	12·7	339·7	145·3	0·11	67·3	14·9	0·12	239·4	55·0
	1	12·7	373·9	166·7	0·11	84·9	26·5	0·16	316·0	56·0
	7	12·8	173·6	65·4	0·10	43·7	22·1	0·12	49·4	57·2
	14	12·8	139·1	46·0	0·09	35·2	14·1	0·10	25·2	57·2
	28	12·8	136·4	41·8	0·03	31·0	8·3	0·03	21·2	59·3
	56	12·7	102·9	31·5	0·06	25·7	8·0	0·02	10·3	46·8
	182	12·7	84·9	25·6	0·16	15·7	1·8	0·04	10·1	49·0
M1	0·5	12·7	332·6	136·2	0·07	85·3	48·9	0·25	213·6	44·7
	1	12·7	337·2	149·1	0·07	92·5	35·8	0·19	249·9	48·8
	7	12·7	172·7	62·5	0·10	43·8	18·3	0·12	72·9	51·4
	14	12·7	130·5	46·5	0·09	31·3	13·0	0·10	46·4	47·9
	28	12·7	100·9	35·6	0·04	19·5	5·9	0·06	42·9	45·2
	56	12·7	101·7	34·1	0·05	21·1	9·9	0·08	29·5	50·1
	182	12·8	89·6	34·0	0·08	15·4	4·8	0·09	21·8	57·5
M1·5	0·5	12·2	336·0	142·6	0·18	93·7	109·7	0·20	25·2	16·6
	1	12·3	333·3	141·2	0·17	106·9	116·1	0·13	129·3	18·5
	7	12·5	186·6	63·3	0·12	60·7	41·1	0·14	78·0	31·3
	14	12·6	143·6	46·7	0·11	41·9	17·3	0·10	69·4	36·0
	28	12·5	93·3	32·5	0·06	22·6	6·9	0·07	57·6	32·1
	56	12·6	89·7	30·4	0·07	20·0	7·4	0·09	41·4	36·8
	182	12·7	83·0	30·1	0·09	15·9	6·6	0·13	19·2	49·0
M2	0·5	10·0 ^a	289·5	116·1	9·2	83·6	174·1	0·00	10·6	0·1
	1	11·1	323·8	119·2	3·90	103·2	184·2	0·02	9·0	1·3
	7	10·6	135·8	41·2	5·83	38·5	92·8	0·01	2·1	0·4
	14	11·4	92·1	30·0	1·47	26·1	59·5	0·04	4·5	2·6
	28	11·9	79·5	24·6	0·24	21·0	34·7	0·06	11·3	8·8
	56	12·1	65·7	20·3	0·18	19·3	25·9	0·08	9·2	12·4
	182	11·9	69·2	21·9	0·27	18·3	17·9	0·07	1·2	7·9

^aRepetition of the measurements resulted in pH 9·6

and the species should not form or dissolve until equilibrium is restored.

$$3. \quad SI = \log_{10} \left(\frac{IAP}{K_{sp}} \right)$$

In the system with the highest gypsum addition (M2), gypsum remained near saturation during the first weeks, consistent with its presence observed by XRD. All systems had positive SI for ettringite through 14 d of hydration, and for the pastes with added gypsum the oversaturation increased with added gypsum content. M0·1 was the only paste to have significant levels of oversaturation with regard to monosulfate; again in agreement with the presence of monosulfate observed in these samples (Figures 5 and 6). Oversaturation with regards to AH₃ generally increased with increasing added gypsum and became more persistent into later ages. Note: during the first hours to days generally very soluble amorphous AH₃ is formed, which slowly becomes more ordered, which is accompanied by a decrease in solubility (Lothenbach *et al.*, 2012). Gibbsite, the crystalline form of AH₃, forms extremely slowly at ambient conditions. Thus, the decrease of the solubility of AH₃ with

time was considered in the calculations as detailed in the earlier section entitled ‘X-ray diffraction and thermogravimetric analysis’. CAH₁₀ was supersaturated most markedly at early ages in M0·1 and M1, at ages which precede its transient appearance in the XRD patterns. In M0·1, strätlingite showed the highest degree of oversaturation at early ages. In the pastes with added gypsum, the SI of strätlingite tended to decrease with increasing additional gypsum, which is consistent with the dilution of belite, denser paste microstructures inhibiting belite dissolution, and the reduced stability of AFm phases in the presence of gypsum as discussed in the section entitled ‘Hydration’.

Stress from crystallisation

The maximum crystallisation pressure, P_c , that can be developed due to a given oversaturation of a phase can be calculated according to Equation 4, where the universal gas constant, $R = 8.314 \text{ J/(mol} \cdot \text{K)}$, absolute temperature, $T = 293.15 \text{ K}$, V_m is the phase’s molar volume and K_{sp} is the phase’s solubility product.

$$4. \quad P_c = \frac{RT}{V_m} \ln \frac{IAP}{K_{sp}}$$

Table 4. Saturation indices

	Time: d	Ettringite	Monosulfate	AH ₃ ^a	CAH ₁₀	Strätlingite	Gypsum	C-S-H
M0-1	0.5	1.9	1.4	0.2	1.2	2.3	-3.0	-2.5
	1	2.1	1.0	0.7	1.4	2.5	-2.8	-2.4
	7	1.5	0.1	0.0	-0.1	1.6	-2.6	-1.9
	14	0.3	-0.7	-0.2	-0.7	0.9	-2.8	-1.9
	28	-2.5	-2.4	-0.3	-1.2	-0.4	-3.4	-2.6
	56	-1.4	-2.0	-0.4	-1.5	-0.5	-3.0	-2.5
M1	182	-0.5	-0.8	-0.3	-1.0	0.7	-3.2	-1.9
	0.5	1.1	-0.1	0.5	0.9	2.2	-2.7	-2.1
	1	0.9	-0.1	0.6	1.0	2.1	-2.8	-2.3
	7	1.4	0.1	0.2	0.3	1.9	-2.7	-1.9
	14	0.5	-0.6	0.1	-0.1	1.5	-2.8	-1.9
	28	-2.5	-2.4	0.2	-0.5	0.6	-3.4	-2.2
M1-5	56	-1.1	-1.7	0.1	-0.6	0.8	-3.0	-2.0
	182	-0.9	-1.4	0.0	-0.7	0.9	-3.1	-1.8
	0.5	1.7	-1.0	-0.2	-0.6	1.2	-1.9	-1.5
	1	1.4	-1.2	1.0	0.8	2.0	-2.0	-1.9
	7	1.0	-1.1	0.7	0.4	1.9	-2.3	-1.7
	14	1.1	-0.5	0.5	0.4	1.9	-2.5	-1.8
M2	28	-1.5	-2.1	0.7	0.1	1.3	-3.0	-2.0
	56	-0.9	-1.7	0.4	-0.2	1.3	-3.0	-1.8
	182	-0.6	-1.4	0.1	-0.8	1.0	-2.9	-1.6
	0.5	1.6	-4.9	1.9	0.3	-6.9	-0.1	-9.5
	1	3.1	-2.6	0.9	-0.2	0.6	-0.4	-1.9
	7	2.7	-3.4	0.7	-1.1	-0.6	-0.3	-2.2
	14	1.0	-3.9	0.8	-0.9	0.0	-0.9	-1.8
	28	-0.5	-3.6	0.7	-0.8	0.2	-1.8	-1.8
	56	-0.8	-3.5	0.5	-1.1	0.2	-1.9	-1.7
	182	0.3	-2.5	-0.8	-2.6	-0.8	-1.9	-1.6

^aA decrease of AH₃ solubility with time is considered as detailed in the section entitled 'X-ray diffraction and thermogravimetric analysis'

The maximum crystallisation pressure does not account for the geometry or size of the pore or crystal, but provides an upper bound on crystallisation pressure that would be produced from the growth of relatively large crystals. The calculated maximum crystallisation pressures are presented in Figure 8. Interestingly, AH₃ is calculated to produce the highest crystallisation pressures in all systems and produces the highest crystallisation pressure calculated in this study, 337 MPa, in M2 at 0.5 d. The high crystallisation pressures calculated for AH₃ are a result of its relatively high SI and its low molar volume, $V_m = 32 \text{ cm}^3/\text{mol}$. Strätlingite and CAH₁₀ produce higher crystallisation pressures in the pastes with less added gypsum, which is consistent with the XRD data showing the pastes with less gypsum produced more of those phases. Monosulfate produced its highest crystallisation pressure in the paste without added gypsum between 0.5 and 7 d and tended to produce very low or zero crystallisation pressure in the pastes with added gypsum. Ettringite produced positive crystallisation pressure in all systems through 14 d; however, the calculated crystallisation pressure was often lower than the crystallisation pressures calculated for AH₃, strätlingite and CAH₁₀, despite ettringite having some of the highest SI. Ettringite's relatively lower crystallisation pressure is due to its modest oversaturation and its large molar volume, $V_m = 707 \text{ cm}^3/\text{mol}$. However, the volume of the crystallising phase and the geometry of the

pore in which the crystallisation is occurring affect the amount of force that the crystallising phase can exert on the surrounding paste. The role that spatial effects play in the forces that can be generated from phases crystallising will be discussed subsequently.

The hydrostatic tensile stress, σ_{cyl} , generated from crystallisation can be calculated for cylindrical pore geometries according to Equation 5 (Chaunsali and Mondal, 2015b), where P is the crystallisation pressure and ϕ is the volume fraction of crystallising phase. Inputting P_c from Equation 4 for P gives an upper bound on the hydrostatic tensile stress.

$$5. \quad \sigma_{\text{cyl}} = P \frac{2}{3} \left(\frac{\phi}{1 - \phi} \right)$$

Figure 9 presents the maximum hydrostatic tensile stress assuming cylindrical pores calculated using the phase volumes determined by thermodynamic modelling utilising the QXRD data to account for the hydration reaction kinetics combined with the SI determined from the expressed pore solutions. The phase volumes from thermodynamic modelling were selected over the phase volumes from QXRD to overcome the poor quantification of AFm phases, which form solid solutions, and

Figure 8. Maximum crystallisation pressures, P_c , calculated in the CSA cement pastes: (a) M0-1; (b) M1; (c) M1-5; (d) M2

AH_3 , which is poorly crystalline at early ages of hydration. As was the case with the maximum crystallisation pressure, AH_3 tended to produce the highest hydrostatic tensile stresses in all of the pastes. In M0-1, AH_3 is calculated to produce the greatest tensile stress (8.4 MPa) at 1 d, followed by monosulfate (3.9 MPa) at 0.5 d and strätlingite at 182 d (0.8 MPa). In M1 and M1-5, ettringite produced the second highest hydrostatic tensile stresses and strätlingite continued to produce relatively lower hydrostatic tensile stresses, which tended to increase modestly with time to a maximum of ~ 0.5 MPa at 182 d. In M2, the trend of ettringite producing increasing hydrostatic tensile stresses with increasing amounts of gypsum continued with a maximum of 11.6 MPa at 7 d. All pastes have phases producing maximum hydrostatic tensile stresses which exceed the measured 1 d tensile strengths of the pastes, which are 0.7, 0.9, 1.1 and 1.2 MPa for M0-1, M1, M1-5 and M2, respectively. Accordingly, all pastes cured in water experienced expansion in this study.

As crystals become smaller, their curvature and solubility increases, and when calculating the pressure that they can exert during crystallisation, their interfacial free energy must be

taken into account. The net crystallisation pressure, ΔP , that a growing crystal can exert on the pore wall is given in Equation 6 for cylindrical pores, where γ_{cl} is the interfacial free energy between the crystal and the liquid; r_p is the pore radius; and δ is the water layer separating the growing crystal and the pore wall. The radius of the crystal r_c equals $r_p - \delta$. In this study, δ is assumed to equal 2 nm and γ_{cl} is assumed to be 0.1 J/m^2 , which is consistent with assumptions made in prior studies (Flatt and Scherer, 2008; Scherer, 2004).

$$6. \quad \Delta P = \frac{RT}{V_m} \ln \frac{IAP}{K_{sp}} - \gamma_{cl} \frac{1}{r_p - \delta} = \frac{RT}{V_m} \ln \frac{IAP}{K_{sp}} - \gamma_{cl} \frac{1}{r_c}$$

Setting Equation 6 to zero and solving for r_p produces Equation 7 and gives the minimum pore radius (assuming cylindrical geometry) in which a crystal can grow given the ionic concentration of the pore fluid at that time.

$$7. \quad r_p = \frac{V_m \gamma_{cl}}{RT} \left(\ln \frac{IAP}{K_{sp}} \right)^{-1} + \delta$$

Figure 9. Maximum hydrostatic tensile stresses calculated in CSA cement pastes: (a) M0-1; (b) M1; (c) M1-5; (d) M2. The 1 d tensile strength for each paste is the gray dashed horizontal line

Crystals will tend to form in free space where they do not need to exert expansive forces. Accordingly, the geometry of the pores and the diffusion of ions in the pore solution play an important role in the ability of a hydrated cement paste to develop crystallisation pressure. At a given crystallisation pressure or oversaturation only pores with at least the minimum pore radius, r_p , can be filled, while smaller pores cannot be filled because more oversaturation would be needed. The pressure exerted can be estimated from the difference between the percolation pore radius from MIP measurements and from the minimum pore radius needed for the growth of the oversaturated solid (Bizzozero *et al.*, 2014), according to Equation 6. If the percolation pore radius in the hydrated cement, r_p , is smaller than the minimum pore radius needed for the growth of the oversaturated solid, no damage is expected as no solid can form; damage can be expected if the pore size is larger than the minimum pore radius but less than the percolation pore radius because pores above that value are considered large pores, such as entrapped air voids, where crystals may grow freely without exerting pressure on the pore walls.

Mercury intrusion porimetry was utilised to estimate values for radii of the pore network. MIP has some known limitations, which are that the intrusion pressure measures the volume of pores with that pore entrance (not the actual pore volume with that radius), pores are not perfect cylinders or spheres (which affects the pore radius calculation for a given pressure) and MIP may induce damage during testing, thereby altering the porosity. Figure 10 shows the cumulative pore volume for M2 at 7, 14 and 28 d and shows the determination of the percolation pore radius for M2 at 7 d. The intersection of the two tangents was utilised to define the percolation pore radius. This was done to be consistent with prior research by Bizzozero *et al.* (2014). As can be seen from Figure 10, the hydration of CSA cement continued to refine the porosity of the cement paste through 28 d, reducing both the total pore volume and pore radii.

Table 5 gives the percolation pore radii determined from MIP for all pastes and minimum pore radius in which crystals of each phase can grow between at 7, 14 and 28 d of hydration.

Figure 10. Cumulative pore volume for M2 at 7, 14 and 28 d, showing determination of the percolation pore radius for M2 at 7 d

Comparing the percolation pore radii at 7 d, M0·1 and M2 have higher values for their percolation pore radii compared to M1 and M1·5 for different reasons. Added calcium sulfate accelerates the hydration of ye'elimite and formation of ettringite, which reduces the porosity, which explains the decrease in the percolation pore radius from M0·1 to M1. However, added gypsum also leads to additional expansion, which is

accompanied by cracking, which explains why the percolation pore radius increases from M1·5 to M2. As hydration proceeds and the rate of expansion declines, M2 has a reduction in total porosity and the percolation pore radius. Table 5 also shows that, when the SI for a phase is higher, it can grow into smaller pores. For instance, in M2 at 7 d when the SI of ettringite is 2·7, ettringite crystals can grow into pores with radii as small as 7 nm, but at 14 d when the SI of ettringite is 1·0, ettringite can grow into pores with radii as small as 15 nm. By 28 d, the SI for ettringite was negative for all pastes, indicating further growth of ettringite is not expected at that age. AH_3 can grow into the smallest pores (3 nm) of any of the phases calculated in this study due to its small molar volume. In M1 at 7 d, the minimum pore radius for monosulfate growth (45 nm) exceeds the percolation pore radius (17 nm), indicating that under the given oversaturation for monosulfate at that time, monosulfate is not expected to form in the percolated porosity where it can exert pressure.

The role of porosity and crystal size on the net pressures that crystals can exert on pore walls was determined using ΔP from Equation 6 in Equation 5 for P , utilising MIP data for pore size distributions and thermodynamically calculated phase assemblages and SI. The calculated net hydrostatic tensile stresses were a volume weighted average based on the porosity between the percolation and minimum pore radii. Comparing

Table 5. Percolation pore radius from MIP, minimum pore radius from Equation 7, and net hydrostatic tensile stress utilising Equations 5 and 6 with MIP porosity data

	Time: d	Minimum pore radius: nm				Hydrostatic tensile stress: MPa			
		M0·1	M1	M1·5	M2	M0·1	M1	M1·5	M2
Ettringite	7	10	11	15	7	0·1	0·5	0·2	9
	14	42	28	14	15	0·02	^a	^a	3
	28	^b	^b	^b	^b	^b	^a	^a	^b
Monosulfate	7	41	45	^b	^b	0·4	^c	^b	^b
	14	^b	^b	^b	^b	^b	^a	^a	^b
	28	^b	^b	^b	^b	^b	^a	^a	^b
AH_3	7	^b	4	3	3	^b	2	6	6
	14	^b	6	3	3	^b	^a	^a	7
	28	^b	4	3	3	^b	^a	^a	6
CAH_{10}	7	^b	14	11	^b	^b	^a	^a	^b
	14	^b	^b	12	^b	^b	^a	^a	^b
	28	^b	^b	53	^b	^b	^a	^a	^b
Strätlingite	7	4	4	4	^b	0·3	0·3	0·3	^b
	14	6	5	4	^b	0·5	^a	^a	^b
	28	^b	9	5	20	^b	^a	^a	0·07
Percolation pore radius: nm									
	Time: d	M0·1	M1	M1·5	M2				
	7	271	17	17	262				
	14	304	^a	^a	183				
	28	263	^a	^a	143				

^aNot measured

^bNegative SI

^cMinimum pore radius below percolation pore radius

the values for the net hydrostatic tensile stresses in Table 5 to the maximum hydrostatic tensile stresses in Figure 9, the effect of small pores reducing the hydrostatic tensile stresses developed becomes apparent. For instance in M2 at 7 d, ettringite is calculated to have a net and maximum hydrostatic tensile stress of 8.9 and 11.6 MPa, respectively. Likewise, AH_3 is calculated to have a net and maximum hydrostatic tensile stress of 5.8 and 6.1 MPa, respectively, at 7 d in M2.

Discussion

Historically, expansion in CSA cement pastes has always been attributed to ettringite, whether it be crystalline or 'colloidal'. Accordingly, this study also found that CSA cement pastes with higher ettringite production and supersaturation had greater amounts of expansion. However, unlike prior studies, this study also considered other crystalline hydrates like monosulfate, CAH_{10} , AH_3 and strätlingite. The calculations show that at early ages and low added calcium sulfate content (M0.1 at 0.5–1 d), monosulfate could produce a maximum hydrostatic tensile stress of ~ 4 MPa. At later ages and lower added calcium sulfate contents, strätlingite was calculated to produce a maximum hydrostatic tensile stress of ~ 0.5 –1 MPa. Moreover, AH_3 was calculated to produce higher hydrostatic tensile stresses than ettringite more often than not. In M2 at 0.5 d, the maximum hydrostatic tensile stress produced by ettringite and AH_3 was 4.6 and 18.6 MPa, respectively; however, by 7 d in M2 this had reversed and ettringite was calculated to produce a larger maximum hydrostatic tensile stress than AH_3 .

This raises some important questions. First, is ettringite solely responsible for CSA cement expansion, as prior research has considered, or is expansion due to the sum of all the hydrostatic pressures developed by the different crystallising hydrates? For crystal growth theory to be correct, one would assert that any crystallising phase must be considered to have the potential to exert pressure on the surrounding matrix given the correct circumstances. Otherwise, ettringite is given an almost mythical status to create expansion while ignoring other crystalline phases' potential role in the expansion mechanism. Moreover, fundamental scientific data such as the actual interfacial free energies of the various crystalline hydrates need to be determined in order to better understand how crystal size affects different hydrates differently.

In this study, AH_3 was often calculated to generate some of the highest maximum hydrostatic tensile stresses; however, these calculations do not take into consideration the role of the crystal size on decreasing the net hydrostatic tensile stress which can be generated. Moreover, when utilising MIP values for the porosity in which AH_3 can grow, the assumption is that the crystals are growing to a size to fill the pore radius (to within a 2 nm water layer surrounding the crystal), thus enabling AH_3 to exert pressure on the pore walls. However, although AH_3 can form in clusters of several microns in size,

recent research has shown through pair distribution function (PDF) analysis that the actual crystallites are approximately 3 nm in diameter (Cuesta *et al.*, 2017b). If $r_c = 1.5$ nm ($r_p = 3.5$ nm) is utilised with Equations 5 and 6 for AH_3 in M2 at 7 d, then the net hydrostatic tensile stress calculated is 2.7 MPa (compared to 5.8 MPa using porosity from MIP). However, that stress would only develop in pores of that radius. In larger pores, nanocrystalline AH_3 would be free to form without exerting pressure on the pore walls, and in smaller pores the net hydrostatic tensile stress would be reduced below 2.7 MPa due to the increasing role of small crystal size reducing the net pressure that AH_3 can exert. As a consequence of AH_3 being nanocrystalline and having a small pore range where it can exert pressure, its role in expansion is expected to be dramatically reduced compared to what would be calculated using MIP data and upper bound assumptions for hydrostatic tensile stress and crystallisation pressure.

Certain factors were found to strongly affect the hydrostatic tensile stresses calculated. (a) Using a spherical geometry instead of cylindrical increases the hydrostatic tensile stresses calculated by 50%. (b) The pore solution, porosity and phase assemblage change with time; at less than 6 months of hydration when their values are changing rapidly, calculating the hydrostatic tensile stress developed at a particular point in time utilising values from a different time would create large errors. (c) The distribution of pore radii utilised when considering the interfacial free energy at the crystal–liquid interface can affect the hydrostatic tensile stresses calculated by $\sim 25\%$, depending on whether a simple average or a weighted average is utilised.

Future research should try to determine the interfacial free energies for the various hydration products in CSA cements, which may also help to explain why some hydrates exert more pressure than others. Finally, future improved or new techniques (such as phase resolved tomography or ptychography) may resolve where hydration products are depositing over time, which would greatly enhance understanding of the expansion mechanism in CSA cement pastes.

Conclusions

This study expanded on prior studies investigating the expansion mechanism of CSA cement pastes. Four different molar ratios of gypsum to ye'elimite ranging from 0.1 to 2 were utilised and the expansion, mass gain, phase assemblage and pore solution were monitored at intervals over 182 d. The results of the study can be summarised as follows.

- Mass gain. Mass gain during water curing increased with increasing gypsum content due to the increased production of hydration products and water absorbed in cracks and microcracks.
- Expansion. Expansion of CSA cement pastes increased with increasing gypsum in tests with both externally

supplied water and without. When cured in water, the CSA cement paste with a molar ratio of 2:1 gypsum to ye'elimite had a much faster rate and magnitude of expansion; accordingly, it cracked severely after 1 d of water curing.

- (c) Hydration. As the gypsum content in the CSA cement pastes increased, ettringite production increased and monosulfate, CAH_{10} and strätlingite production decreased due to both a dilution of the clinker phases and, more predominantly, a faster rate of ettringite production densifying the paste microstructure, limiting the further reaction of anhydrous clinker phases.
- (d) Pore solution. Increasing gypsum content raised the calcium and sulfate ion concentrations at early ages, but lowered the aluminate and silicate ion concentrations. Ettringite buffers the pore solution at a lower pH value than monosulfate, so the CSA cement paste with a stoichiometric amount of gypsum for ettringite production had a lower pH of 10.0 at 0.5 d and 12.1 at 56 d, compared to a pH of 12.7 at both ages for the CSA cement, which had a molar ratio of 1:1 gypsum to ye'elimite, which would also produce monosulfate in addition to ettringite. All CSA cement pastes had a positive SI for ettringite through 14 d and pastes with added gypsum had positive SI for AH_3 through 56 d. The CSA cement paste without added gypsum had a positive SI for monosulfate through 7 d, CAH_{10} through 1 d and strätlingite through 14 d. The CSA cement pastes with 1:1 and 1:1.5 molar ratios of gypsum to ye'elimite had positive SI for CAH_{10} at different times through 28 d and positive SI for strätlingite through 182 d. Positive SI for crystallising phases can be converted into crystallisation pressure.
- (e) Crystallisation pressure. AH_3 , strätlingite, CAH_{10} , monosulfate and ettringite were all calculated to produce significant crystallisation pressures. AH_3 was consistently calculated to produce some of the highest crystallisation pressures (up to 337 MPa). Crystallisation pressures for strätlingite, CAH_{10} and monosulfate increased with decreasing gypsum content. All CSA cement pastes were calculated to produce positive crystallisation pressures for ettringite, with the CSA cement paste highest in gypsum content producing the greatest crystallisation pressure for ettringite.
- (f) Hydrostatic tensile stress. When calculating the hydrostatic tensile stresses, strätlingite and CAH_{10} produced much lower stresses compared to their maximum possible crystallisation pressures due to their low volumes. Contrarily, in the pastes with added gypsum, AH_3 and ettringite produce the highest hydrostatic tensile stress, which increase with added gypsum. In the CSA cement paste without added gypsum, monosulfate and AH_3 are calculated to produce the highest hydrostatic tensile stresses, but the hydrostatic tensile stresses produced by strätlingite are calculated to

increase with time as belite hydrates and releases calcium and silicate ions. All CSA cement pastes in this study were calculated to have phases which had hydrostatic tensile stresses that exceeded the 1 d tensile strength of the pastes, and all CSA cement pastes experienced expansion.

- (g) AH_3 . The contribution of AH_3 to the sum hydrostatic tensile stress developed in CSA cement pastes is reduced by its nanocrystalline nature, which reduces the net crystallisation pressures that it can develop and the range of pores where it can effectively exert pressure.

In summary, this study showed that, according to calculations utilised in prior research, all crystalline hydrates such as ettringite, monosulfate, strätlingite, CAH_{10} and AH_3 may contribute to the total crystallisation pressures that are developed in CSA cement pastes and may contribute to the expansion mechanism. Future work should aim to determine the interfacial free energies and spatial distributions of the crystalline hydrates to better understand how each crystalline hydration product may or may not contribute to cement expansion.

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