EFFECT OF CHLORIDE SALTS ON SULFOALUMINATE CEMENT HYDRATION

L. U. D. Tambara Jr (1), J. C. Rocha (1), M. Cheriaf (1), A. Palomo (2) and A. Fernández-Jiménez (2)

(1) Universidade Federal de Santa Catarina - UFSC, Florianópolis, Brazil

(2) Instituto Ciencias de la Construcción Eduardo Torroja - IETcc-CSIC, Madrid, Spain

Abstract

The effect of including 5 % chloride salts (NaCl and $CaCl_2$) on calcium sulfoaluminate cement hydration was studied. The rate of heat release, setting times and mechanical strength were determined in 2 d, 28 d and 90 d cement pastes. The hydration products formed at those ages were identified with XRD and SEM. Hydration reactions were hastened and early age strength heightened with 5 % NaCl. In contrast, 5 % $CaCl_2$ retarded setting times, although it also increased later age compressive strength. The predominant reaction products found in both cases were ettringite and AH_3. Chloraluminates such as Friedel's salt were not observed to form at any of the ages studied. Gypsum precipitation, absent in the reference sample (CSA cement+water), was detected in the presence of chloride salts, however.

Keywords: Chloride, sulfoaluminate cement, hydration, ettringite, X-ray diffraction

1. INTRODUCTION

Calcium sulfoaluminate (CSA) cements are known as eco-friendly materials [1,2] because the sintering temperature required is approximately 200 °C lower than in ordinary portland cement (OPC) and grinding is less energy-intensive [3]. CSA cements also exhibit high early age strength, can offset drying shrinkage and are usable with heavy metals [4].

The predominant phase in CSA is ye'elimite ($C_4A_3\overline{S}$). Others include anhydrite ($C\overline{S}$), belite (C_2S), calcium aluminate (CA), mayenite ($C_{12}A_7$), brownmillerite (C_4AF) and periclase (MgO), to name the most prominent [5]. Depending on the liquid/solid ratio and calcium sulfate content, ye'elimite hydration may induce the formation of calcium monosulfoaluminate (C_4AH_{12}) and gibbsite (AH_3) (Equation 1); ettringite ($C_6A_3H_{32}$), katoite (C_3AH_6) and gibbsite (Equation 2); or ettringite and gibbsite only (Equation 3) [6,7].

$$C_4A_3\breve{S} + 18H \rightarrow C_4A\breve{S}H_{12} + 2AH_3 \qquad \text{(Equation 1)}$$

$$4C_4A_3\breve{S} + 80H \rightarrow C_6A\breve{S}_3H_{32} + C_4A\breve{S}H_{12} + 2C_3AH_6 + 8AH_3 \qquad \text{(Equation 2)}$$

$$C_4A_3\breve{S} + 2\,C\breve{S}H_x + (38 - 2x)H \rightarrow C_6A\breve{S}_3H_{32} + 2\,AH_3 \quad x = 0, 0.5, 2 \qquad \text{(Equation 3)}$$

The effect of $CaCl_2$ and NaCl salts on OPC-based binders has been widely studied [8-13] and shown to accelerate calcium silicate and especially C_3S hydration, shortening initial and final setting and hardening times. Chloride ions, in turn, may react with the calcium monosulfoaluminate (AFm) initially formed in OPC hydration to generate AFm-Cl [9,10]. Alternatively, they may be chemically adsorbed onto C-S-H gel [9-12] or induce the formation of chloroaluminates such as Friedel's [$Ca_4Al_2(Cl)_{1.95}(OH)_{12.05}\cdot 4H_2O$] or Kuzel's [$Ca_4Al_2(Cl)(SO_4)_{0.5}(OH)_{12}\cdot 6H_2O$] salt [12-13].

The effect of such salts on CSA cement hydration has been less thoroughly researched. Ogawa et al. [2], studying the effect of 20 % NaCl on ye'elimite ($C_4A_3\overline{S}$) formation, reported that the degree of reaction of that predominant phase in CSA was lower in the presence of Cl than in its absence (reference cement). They also detected Friedel's salt and observed that the partial replacement of sulfate with chloride ions changed ettringite morphology, rendering it less expansive.

This study explored the effect of including 5 % chloride salts (NaCl and $CaCl_2$) on calcium sulfoaluminate cement hydration. More specifically, it addressed the effect on paste hydration rate, setting times and mechanical strength development. The reaction products were characterised with XRD and SEM.

2. EXPERIMENTAL PROCEDURE

2.1 Sulfoaluminate cement

The chemical and mineralogical composition of the commercial calcium sulfoaluminate (CSA) cement used, ALICEM©, are given in Table 1. XRD-Rietveld **[17]** mineralogical analysis revealed that the cement contained 52.6 % ye'elimite, 22.1 % anhydrite and 19.9 % calcium silicate (C_2S+Bredigite [$Ca_7Mg(SiO_4)_4$]). Particle size distribution was found on a Coulter LS130 laser diffraction analyser with a measuring range of 0.1 µm to 900.0 µm. Cement density was 2.90 g/cm^3, its Blaine fineness 474.6 m^2/kg and its BET specific surface 1373±13 m^2/kg.

Table 1: CSA chemical and physical composition and mineralogical phases

Oxide	**CaO**	**Al_2O_3**	**SO_3**	**SiO_2**	**MgO**	**Fe_2O_3**	**Na_2O**	**Others**	**LoI[1]**
(%)	41.5	23.2	18.4	8.1	3.2	1.1	0.9	1.7	1.5

Phase	**$C_3A_3\overline{S}$**	**$C\overline{S}$**	**C_2S**	**C_3A**	**$Ca_7Mg(SiO_4)_4$**	**MgO**	**$Ca_2Al(AlSiO_7)$**
Content, wt% (R-Bragg)	52.6(4)	22.1(4)	14.9(4)	1.0(2)	5.0(5)	2.8(3)	1.6(5)

[1] Loss on ignition;

2.2 Paste preparation and characterisation

The CSA cement was hydrated with water in the absence or presence of 5 % chloride salts (NaCl and $CaCl_2$). All the pastes were prepared with a liquid/solid ratio of 0.45, by weight, and moulded into specimens cured in a climate chamber at 21±2 °C and >95 % relative humidity until the test date (2 d, 28 d or 90 d). Cubic specimens (1 cm^3) were tested for compressive strength on an Ibertest Autotest 200/100-SW test frame at a load rate of 0.07 kN/s. Twelve specimens per age were tested and the values averaged.

Heat flow and total heat release associated with the hydration reactions were determined with isothermal conduction calorimetry on a TAM AIR calorimeter at a constant 25 °C. For this analysis the pastes were prepared with 10 g of solid and 5 g of liquid. Immediately after mixing for 3 min 7.5 g were placed in the calorimeter. Some of the fragments and the fine powder (<45 µm) were immersed in isopropyl alcohol to detain hydration. The powder was vacuum filtered and dried in a desiccator at 20 °C to a constant weight for microstructural analysis. Setting times were found as described in European standard EN 196-3.

X-ray diffraction was conducted on a Bruker DS Advance diffractometer under the following conditions: Cu kα1 and kα2 radiation with the secondary monochromator enabled; goniometer radius, 217.5 mm. Measurements were recorded at a 6 mm variable divergence slit (hydrated pastes), 2θ angles of 5° to 60°; a step time of 0.5 s; and a step size of 0.02°. Carbon-coated, vacuum dried samples were observed under a Hitachi S-4800 scanning electron microscope with a maximum resolution of 1.4 nm, fitted with a Bruker XRD detector.

3. RESULTS

3.1 Isothermal conduction calorimetry and setting time

Figure 1 shows the calorimetric curves for pastes REF, 5NCl and 5CCl. The REF material exhibited peaks at 1.6 h, 3.4 h and 6.1 h.

The curve for the NaCl-bearing paste (5NCl) had a single peak at 2.1 h with an intensity of 17.3 mW/g or twice as high as the first REF peak. No difference was observed in the induction period between pastes 5NCl and REF (Figure 1a). The former emitted heat more intensely up to 14.5 h, after which the REF values were higher (Figure 1b). Those findings indicated that the initial reaction was slightly earlier with 5 % NaCl, although the effect was mitigated after 14.5 h.

The pastes with $CaCl_2$ exhibited a first peak at 2.7 h with heat flow of 6.3 mW/g and a second weaker peak (2.1 mW/g) at 17.9 h. Paste 5CCl released total heat at a rate similar to REF up to 6.5 h and more thereafter. At 90 h heat release in REF amounted to 305.4 J/g, in 5NCl to 263.3 J/g and 5CCl to 324.8 J/g.

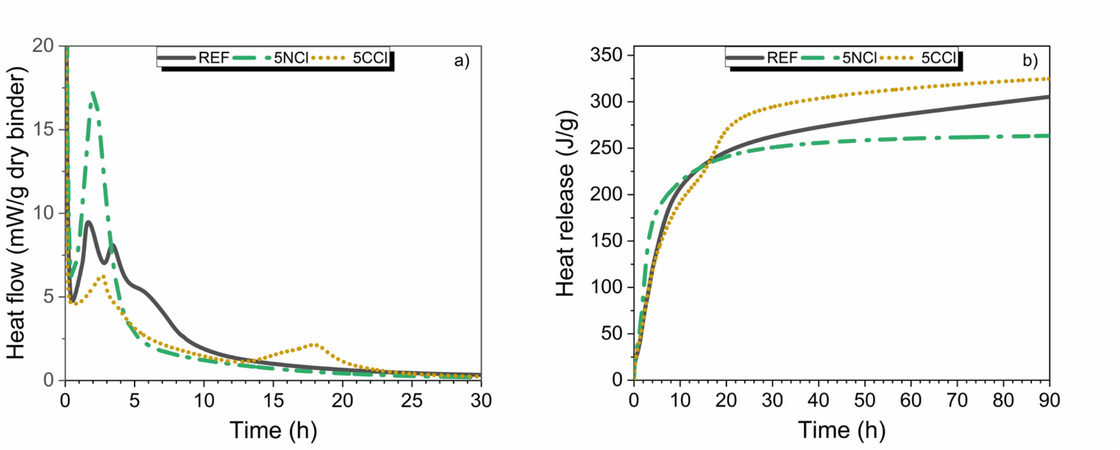

Figure 1: Effect of NaCl and $CaCl_2$ on a) heat flow rate and b) total heat released

As the data given in Table 2 show, initial and final setting times were similar in 5NCl and REF. In contrast, initial setting occurred substantially later in 5CCl, a finding consistent with the longer induction time observed on the calorimetric curves.

Table 2: Initial and final setting times

Sample	Initial setting time (min)	Final setting time (min)
REF	61	161
5NCl	65	150
5CCl	125	170

3.2 Mechanical strength

The 2 d, 28 d and 90 d compressive strength values found for the water-hydrated CSA pastes, with and without chloride salts, are graphed in Figure 2. Although the 5NCl material delivered around 15 % higher 2 d values than REF, the effect reversed at later ages, with strength 8 % lower at 28 d and 16 % lower at 90 d relative to the reference paste. The paste hydrated with water containing calcium chloride (5CCl), in turn, exhibited 2 d and 28 d behaviour similar to REF and higher 90 d strength (63.9 MPa).

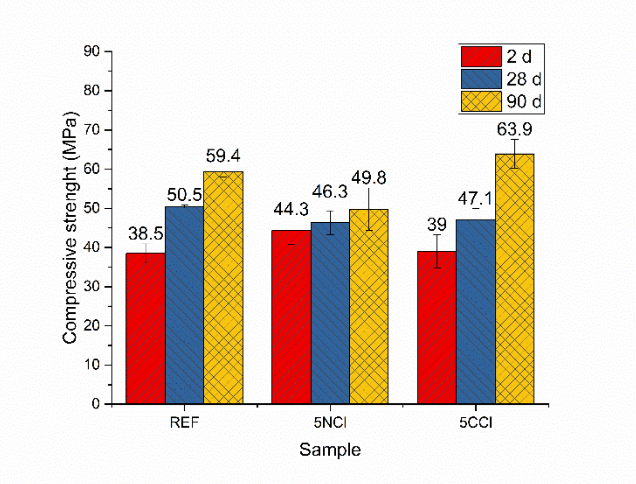

Figure 2: Two-day, 28 d and 90 d compressive strength in CSA pastes hydrated with or without 5 % chlorides

3.3 XRD analysis

The X-ray diffractograms for the anhydrous CSA cement and for the 2 d, 28 d and 90 d REF, 5NCl and 5CCl pastes are reproduced in Figure 3. Diffraction lines for ye'elimite ($C_4A_3\overline{S}$), anhydrite ($C\overline{S}$), ettringite ($C_6A_2\overline{S}_3H_{32}$), AH_3, and calcium carbonate ($CaCO_3$) were generated by all the samples The identification of AH_3 as a series of lines at 2θ values between 18° and 21° was indicative of a semi-amorphous or microcrystalline morphology [18]. Sodium chloride was also detected in the 5NCl samples at all ages.

The intensity of the ye'elimite and anhydrite reflections observed in the anhydrous CSA declined with hydration time. That decline was two-fold steeper for ye'elimite in the 2 d samples bearing chloride salts than in the reference and three-fold after 28 d. Anhydrite intensity also declined more in 5NCl and 5CCl than in REF, especially in the 2 d samples.

Ettringite, which formed as per Equation 3, was the prevalent crystalline hydration product on all the paste XRD patterns Paste 5NCl exhibited lower 2 d ettringite intensity than REF, but higher 28 d and 90 d values than the reference. The AH_3 forming was also observed to be more crystalline in the presence of chloride salts.

The most significant difference in the patterns between the pastes with and without salts was the appearance of gypsum at 28 d and 90 d in the former.

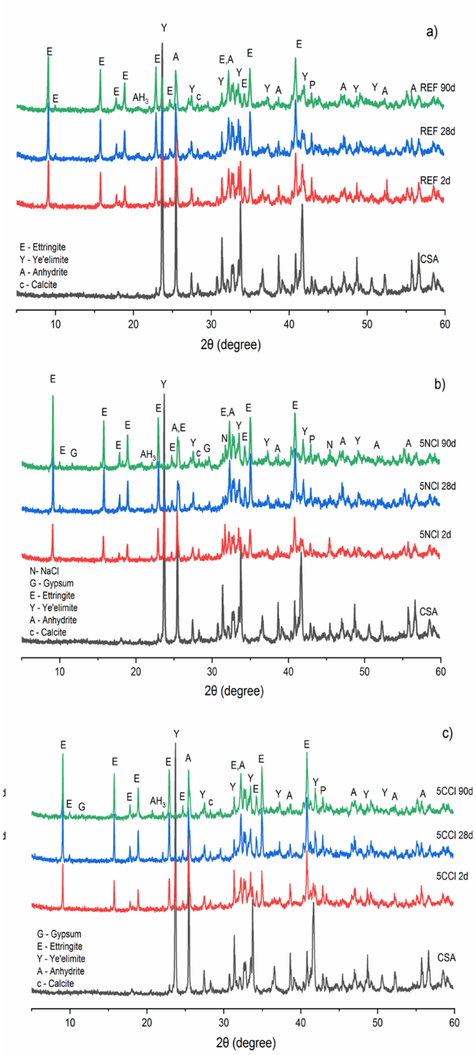

Figure 3: Two-day, 28 d and 90 d diffractograms for a) REF, b) 5NCl and c) 5CCl

3.4 SEM analysis

Micrographs for 28 d REF, 5NCl and 5CCl pastes are reproduced in Figures 4 and 5. The dense REF structure comprised a mix of AH_3 and slender ettringite needles (Figure 4b)). The ettringite phases observed in the chloride salt samples were similar, needle morphology (EDX1 and EDX3), whilst AH_3 was semi-amorphous (EDX4). Ettringite morphology was similar in the salt and non-salt samples, although different in size (Figure 4b). EDX analysis revealed the presence of chloride, although whether it was adsorbed onto the surface or formed part of the hydration products was difficult to discern. Rod-like gypsum crystals were also observed (Figure 5c)).

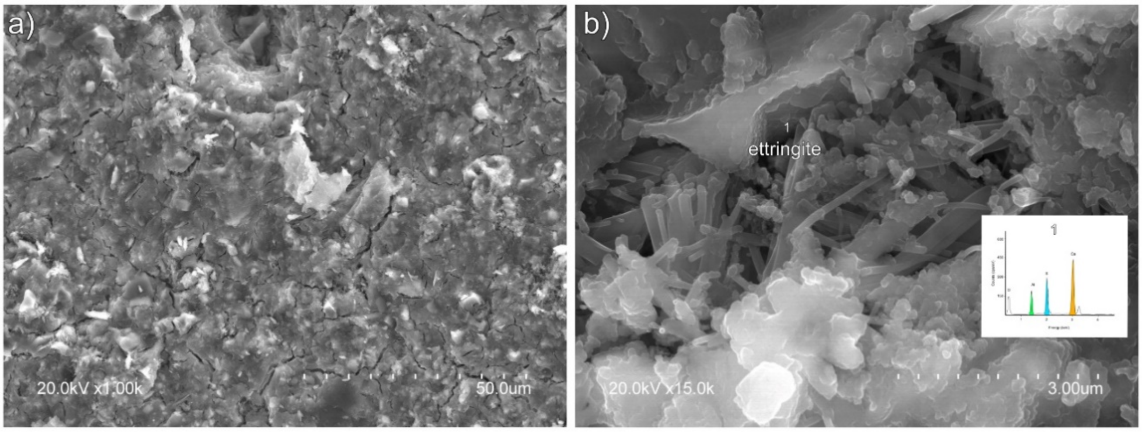

Figure 4: Micrographs and EDX for paste REF

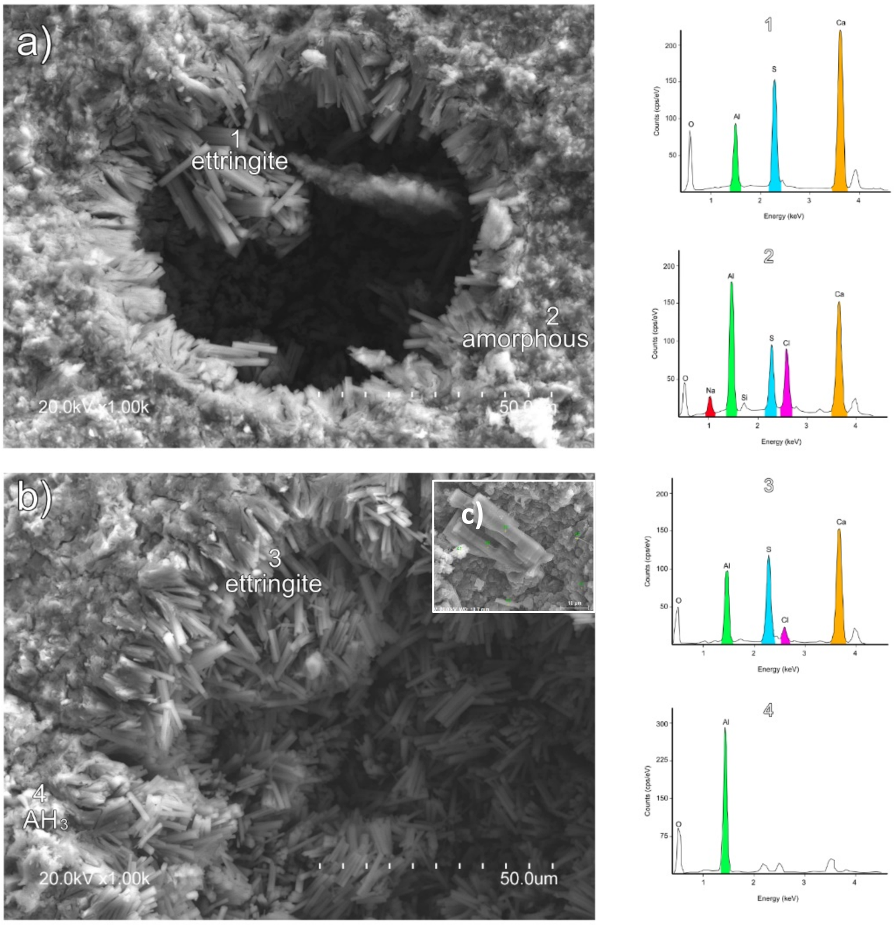

Figure 5: Micrographs and EDX for a) 5NCl and b) 5CCl; (c) gypsum crystals

3. DISCUSSION

Chloride salts shorten setting times in OPC but affect CSA cements differently. At the 5 % concentration studied here, setting times were slightly shorter in the NaCl pastes than in the ones hydrated with water only. In contrast, 5 % $CaCl_2$ retarded setting times, although it also increased later age compressive strength.

At 5 %, NaCl brought initial CSA cement hydration forward slightly, raising initial ye'elimite hydration and initial ettringite precipitation or growth. Ogawa and Roy **[1]** reported accelerated C_4A_3 hydration in an NaCl solution, with saturation taking place in the first few days. Similar behaviour may be attributed to multi-phase CSA cements. The heat release rate curves for 5NCl exhibited a single intense signal associated with the formation of large quantities of initial hydration product, which would explain the higher 2 d strength values. No significant rises in strength were observed in the 28 d or 90 d 5NCl materials, however.

Whilst the XRD findings revealed no AFm-Cl or Friedel's salt -like compounds in the 5 % NaCl pastes, Cl ions were observed in the matrix in the SEM micrographs. Therefore, the possible replacement of SO_4^{2-} with Cl^{1-} ions in AFt hydrate structure cannot be ruled out. In fact, studies currently underway have revealed Friedel's salt formation in pastes bearing 20 % NaCl. A possible working hypothesis is that in the presence of NaCl, Na ions may raise aqueous phase pH slightly. Earlier research [19] showed that pH raises initial ye'elimite dissolution, hastening the reaction (only one intense peak on the calorimetry curves compared to three with water only). That might explain the higher 2 d strength observed here. At 28 d and 90 d, degree of reaction and ettringite content also appeared to be greater with than without the salts (Figure 6), although strength did not rise significantly. That discrepancy was attributed to the possible existence of physical factors related to ettringite needle size and the presence of gypsum. Porosity and dimensional stability studies would be needed to confirm that

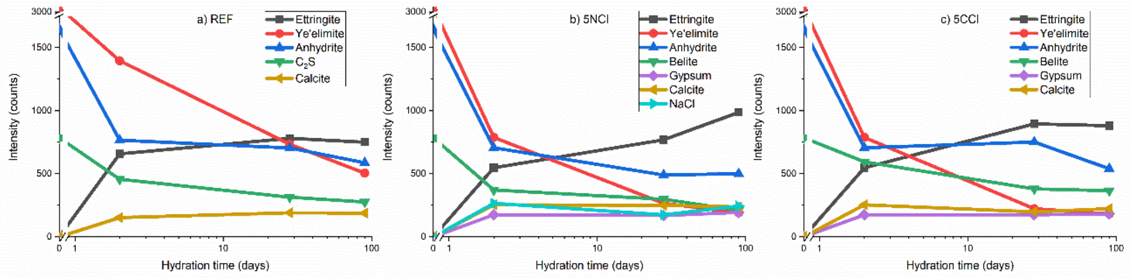

Figure 6: Intensity of the most prominent reflections observed in 2 d, 28 d and 90 d a) water-hydrated, b) 5NCl and c) 5CCl pastes

Initial setting time was retarded by 5 % $CaCl_2$, which also lengthened the induction time on the heat release rate curves. That effect lowered 2 d strength slightly but raised later age values relative to the reference paste. The 2 d XRD patterns showed ye'elimite consumption and ettringite and gypsum formation to be similar in the 5CCl and 5NCl materials, inferring that using one salt or the other has primarily early age implications.

Adding $CaCl_2$ would be expected to lower and adding NaCl to raise pH. $CaCl_2$ detained ye'elimite and other cement clinker phase dissolution, but not the anhydrite reaction. Consequently, gypsum was the sole early age crystalline phase formed. The $CaCl_2$ was consumed (undetected after 2 d). At a sufficiently low 5CCl concentration, ye'elimite would hydrate rapidly, explaining the second peak at 17.9 h and the greater heat of hydration released by this paste at later ages (Figure 1). A more detailed study of early age pastes to verify that hypothesis is currently underway and will be published shortly.

The presence of salts also induced slight variations in ettringite formation and morphology as well as gypsum precipitation, absent in the reference paste. That, in turn, would affect paste microstructure and porosity and consequently their mechanical performance.

4. CONCLUSIONS

This study was conducted as part of a broader research programme on the effect of chloride salts on CSA cement hydration. The preliminary results denote differences in behaviour relative to OPC. At a concentration of 5 %, NaCl hastened hydration, inducing higher initial strength. Conversely, 5 % $CaCl_2$ retarded setting times by up to a full hour and enhanced later age strength development.

In light of the low chloride concentration used in both cases the possible formation of AFm-Cl or Friedel's salt -like phases could not be detected. The presence of chloride salts affected ettringite morphology and formation, however, and induced gypsum formation, not observed in the reference paste. Further studies using higher salt concentrations and earlier age materials will be pursued to acquire a clearer understanding of the effect of chloride salts on CSA cement hydration.

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