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Advances in Sustainable Cements

By

Craig Wyatt Hargis

A dissertation submitted in partial satisfaction of the

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in

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University of California, Berkeley

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Professor Paulo J.M. Monteiro, Chair
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Abstract

Advances in Sustainable Cements

by

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Doctor of Philosophy in Civil and Environmental Engineering

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Concrete is crucial for infrastructure development and is the most widely used construction material in the world by mass. Concrete's use will only continue to increase as rapidly developing countries like India and China invest in their infrastructure and developed countries like the United States have to repair an aging infrastructure. However, the concrete industry accounts for 7-8% of the anthropogenic CO_2 emissions worldwide and the production of portland cement account for 5% of the anthropogenic CO_2 emissions. Anyone trying to improve the sustainability of concrete would do well to try and lower cement's environmental impact. Calcium sulfoaluminate cement is promoted as a sustainable alternative to portland cement because of its lower energy demand and CO_2 emissions during production. However, calcium sulfoaluminate cement is not as well studied as portland cement and it could potentially be made even more sustainable if more fundamental knowledge was known about it. For instance the expansive mechanism for calcium sulfoaluminate cement which can cause deleterious cracking and shortened life spans for structures is still debated and not fully understood.

This study utilized a wide variety of analytical, microscopy, and physical techniques to study calcium sulfoaluminate cement and its hydration reactions in order to more fundamentally understand the hydration reactions taking place and to determine calcium sulfoaluminate's elastic properties. High pressure X-ray diffraction was performed at the Advanced Light Source in the Lawrence Berkeley National Laboratory to determine calcium sulfoaluminate's bulk modulus and crystal structure. In-situ hydration reactions were followed using transmission X-ray microscopy at the Advanced Light Source. The hydration reactions were also monitored ex-situ with scanning electron microscopy, X-ray diffraction, and thermogravimetric analysis. The mechanical properties of the cement were studied with compression tests and dimensional stability bars.

The best fitting crystal structure for calcium sulfoaluminate was determined to be orthorhombic and its bulk modulus was calculated to be 69(6) GPa. Calcium sulfoaluminate was found to produce stellated structures during its hydration in dilute suspensions and it is hypothesized that the mechanical interlocking of adjacent stellated structures could contribute significantly to the strength of calcium sulfoaluminate cements. Calcium hydroxide was found to promote the formation of a poorly crystalline solid solution (SO_4^{2-}/OH^-) AFm on the surface of the hydrating calcium sulfoaluminate grains. This coating delays the formation of ettringite and is believed to play an important role in the expansion mechanism of calcium sulfoaluminate cement. Although calcium carbonate's low solubility prevent them from taking part in the early-age hydration reactions, calcite and vaterite did react with monosulfate to yield ettringite and monocarboaluminate. Vaterite was found to be approximately three times faster at converting monosulfate than calcite. Strength increases correlated in timing to the conversion of

monosulfate to ettringite and monocarboaluminate. Both calcite and vaterite were shown to decrease the set times of calcium sulfoaluminate cement and decrease the magnitude of expansion. Incorporating calcium carbonates into calcium sulfoaluminate cements appears to be very promising from both an environmental and performance standpoint. Particularly, if a cement plant could capture its CO_2 emissions and utilize them to make vaterite, the sustainability of the cement could be greatly advanced.

To my parents, Elaine and Terry Hargis, who always encouraged me to pursue my goals.

&

To my Wife, Jean Kim-Hargis, and daughter, Victoria Valentine Hargis, you are my moon and stars that light up my path.

Contents

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Symbols

AFm   monosulfate
AFt   ettringite
CSA   calcium sulfoaluminate
DTA   differential thermal analysis
EDS   energy dispersive spectroscopy
GGBFS   ground granulated blast furnace slag
HAC   high alumina cement
HCP   hydrated cement paste
ICSD   Inorganic Crystal Structure Database
PC   portland cement
SCM   supplementary cementing material
SE   secondary electron
SEM   scanning electron microscope
TEM   transmission electron microscopy
TGA   thermogravimetric analysis
XRD   X-ray diffraction

AH_3 $Al_2O_3 \cdot 3H_2O$
CA $CaO \cdot Al_2O_3$
CA_2 $CaO \cdot 2Al_2O_3$
C_3A $3CaO \cdot Al_2O_3$
$C_{12}A_7$ $12CaO \cdot 7Al_2O_3$
C_2AS $2CaO \cdot Al_2O_3 \cdot SiO_2$
C_4AF $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$
$C_4A_3\$$ $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$
CH $Ca(OH)_2$
$C\$$ $CaSO_4$
$C\$H_2$ $CaSO_4 \cdot 2H_2O$
C_3S $3CaO \cdot SiO_2$
C_2S $2CaO \cdot SiO_2$

CHAPTER 1: INTRODUCTION

1.1 Need for Sustainable Cement

The earth continues to come under constantly heavier pressure from human activity as a result of global population increases and industrialization in developing countries. Some of the threats to the environment include: (1) eutrophication of streams, lakes, and oceans due to run off of fertilizers and livestock manure, (2) acid rain, (3) poor air quality due to factory and vehicle emissions, (4) deforestation, (5) depletion of fisheries, (6) collapse of coral reefs, (7) climate change, (8) acidification of the oceans, (9) holes in the ozone layer, (10) species extinction and (11) depletion of natural resources. As long as this list is, it is by no means exhaustive, and the problems facing the earth will continue to grow until the global community adopts the concepts of sustainable development.

With the current CO_2 concentration in the atmosphere being 398.58 ppm [1] up from the preindustrial revolution value of 260-270 ppm [2] and projected to be above 800 ppm by the end of the century without major changes causing deviations from current trends [3], all people and industry need to reflect on their current behavior and activities to see where they can make improvements and help reverse this trend. For civil engineers and society, the cement industry is crucial to construction and infrastructure development. Concrete is the most widely used construction material in the world by mass, and cement production accounts for approximately 5% of the anthropogenic CO_2 emissions, which is a sizable environmental footprint for a single industry [4, 5].

Concrete is composed of approximately 12% portland cement (PC), 8% water, and 80% aggregate [6]. Each tonne of PC produced consumes 4 GJ of energy and causes the release of approximately one tonne of CO_2 into the atmosphere. Carbon dioxide is released from the PC kiln because of the combustion of the fuel burned to keep the kiln at approximately 1450 °C and due to the calcination (decomposition) of limestone in the kiln, see Eqn. 1.
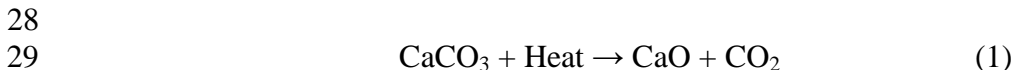
$$CaCO_3 + Heat \rightarrow CaO + CO_2 \qquad (1)$$

In addition to the energy demand and CO_2 emissions associated with PC manufacturing, the production of PC requires mining of non renewable natural resources, clay and limestone. The result of these mining operations is generally a vast pit, which is generally partially abated by flooding with water making an artificial lake and landscaping any exposed scares. Additionally while the mine is in production, noise from blasting and heavy machinery, transient dust, and kiln emissions which can contain heavy metals are environmental problems for the surrounding communities. After the PC is manufactured it is transported to ready mix facilities, distribution centers, and retail stores which adds to its environmental impact. Once at the mixing facility, PC is combined with aggregate, supplementary cementing materials (SCM), water and chemical admixtures to produce concrete. The components added to cement to make concrete also have environmental impacts associated with them. The aggregate has to be mined and transported, resulting in quarry scars, emissions, and nonrenewable resource depletion. Mix water is usually

43 taken from municipal drinking supplies and consequently has a substantial trade off cost and
44 energy cost associated with it. The true cost of the concrete industry on the environment is a
45 result of its scale. In 2010, the global concrete industry consumed approximately 3.7 billion
46 tonnes PC, 27 billion tonnes of aggregate, and 2.7 billion tonnes of mixing water [6]. In total,
47 the concrete industry including aggregate mining, materials transportation, and instillation
48 accounts for 7-8% of the anthropogenic CO_2 emissions.

50 Concrete does have some environmental benefits as well. For instance, many SCMs are
51 industrial byproducts that can be recycled into concrete preventing them from being dumped
52 into landfills or detention ponds where they can leach toxic heavy metals into the ground water.
53 Two examples of industrial byproducts that are used as SCMs are fly ash and ground granulated
54 blast furnace slag (GGBFS) which are byproducts of coal fired powered plants and steel
55 production, respectively. Additionally the hydration reactions of PC have been shown to
56 stabilize toxic heavy metals enabling the safe disposal of many toxic wastes [7].

58 PC is made from clay and limestone which upon firing combine to form new cementing phases.
59 The principal cementing phases in PC (given in cement chemistry) are alite (C_3S), belite (C_2S),
60 aluminate (C_3A) and ferrite (C_4AF). Cement chemistry utilizes a shorthand oxide notation (C =
61 CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, \$ = SO_3, H = H_2O). The hydration of C_3S provides PC
62 with the majority of its early strength gain. Unfortunately of the primary cementing phases, C_3S
63 requires the highest firing temperature and releases the most CO_2 during formation, so replacing
64 C_3S with an alternative phase that requires less energy and releases less CO_2 provides the
65 opportunity to make a more sustainable cement.

67 Calcium sulfoaluminate (CSA) cement is promoted as a sustainable alternative to PC because of
68 its lower energy demand and CO_2 emissions during production. Accordingly, academic and
69 industry research in CSA cement has experienced a renaissance because of its performance
70 advantages in special applications and its four main potential environmental and monetary
71 benefits. First, all phases in CSA cement can form and are stable at a temperature of
72 approximately 1250°C, which is about 100-200°C lower than PC clinker [8, 9]. The lower
73 formation temperature also lowers the energy requirement and CO_2 emissions from fossil fuel
74 burning. This saves money on fuel and could lead to additional savings if CO2 is treated as a
75 pollutant and emitters are charged in the future. Second, CSA cement principally utilizes
76 $C_4A_3\$^1$ (Ye'elimite), instead of C_3S, as the primary early-age strength gaining phase and utilizes
77 C_2S to develop additional long-term strength. Of the major cement phases, $C_4A_3\$$ has one of the
78 lowest CaO contents. To illustrate the wide variation in CaO content in cement phases, the CaO
79 content by weight of several cement phases are listed: C_3S 73.7%, C_2S 65.1%, C_3A 62.2%,
80 C_4AF 46.2%, $C_4A_3\$$ 36.7%. $C_4A_3\$$'s low CaO contents makes it an attractive option for
81 developing a sustainable cement. The lower CaO content equates to a lower $CaCO_3$ demand in
82 the kiln, which results in less CO_2 emissions during calcination (Eqn. 1). Third, CSA clinker is
83 more friable than PC, due to high porosity; therefore, it requires less energy to grind [8].
84 Finally, CSA clinker can be manufactured from a wide variety of industrial byproducts
85 including: fly ash, flue gas desulfurization sludge, fluidized bed ash, blast furnace slag,

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[1]Cement chemistry notation used (C=CaO, Ŝ=SO_3, A=Al_2O_3, F=Fe_2O_3, S=SiO_2, & H=H_2O)

86 phosphogypsum, incinerated municipal waste, red mud, and anodization muds [10-18].

1.2 CSA Cement Development and $C_4A_3\$$ Crystal Structure

88 CSA cement was first developed in the 1960s at the University of California at Berkeley by
89 Alexander Klein; consequently, $C_4A_3\$$ is often called Klein's compound [19-21]. CSA cements
90 have been used in China for approximately 40 years where they are referred to as the "third
91 cement series" with PC and calcium aluminate cements being the first and second cement series,
92 respectively [22-25]. Interest in CSA cements waned in Europe and the Americas after their
93 initial development; however, industry and the research community has renewed interested in
94 $C_4A_3\$$ bearing clinkers due to its many potential environmental and property benefits.

96 CSA clinker generally contains a high proportion of $C_4A_3\$$, which can be accompanied by a
97 wide variety of other phases (C_3S, C_2S, C_4AF, $C\$$, CA, and $C_{12}A_7$) depending on the kiln feed
98 and operating conditions [26]. CSA clinker can be used to make cements with a variety of
99 properties including: high early strength, rapid setting, shrinkage compensating, or self stressing.
100 CSA clinker can also be blended with PC to make Type K cement, which is expansive. The
101 amount of expansion induced by CSA cement can be controlled by varying the water to cement
102 ratio (w/c), amount of calcium sulfate added, the particle size distribution, lime content, and the
103 $C_4A_3\$$ content [8, 27-29]. By varying cement phase proportions and the concrete mix
104 proportions a wide range of properties can be developed including: self stressing, shrinkage
105 compensating, non-expansive, rapid setting, and high early strength [8, 19, 20, 26-32].

107 Although preliminary models for the structure of $C_4A_3\$$ have been developed, there is ongoing
108 research in this area due to the complexity of the structure. At the current time, it is unclear if
109 $C_4A_3\$$ is cubic [33, 34], orthorhombic [35], or tetragonal [36, 37], although there is a generally
110 well agreed upon cubic subcell with space group $I\bar{4}3m$. In the following paragraphs, the work
111 that has been done to determine the structure of $C_4A_3\$$ will be discussed chronologically.

113 The synthesis of CSA was first reported by Ragozina in 1957 [38]. Ragozina prepared the
114 compound by heating tricalcium aluminate (C_3A) with gypsum ($C\$H_2$) at 1200°C; the
115 composition was reported as 1.6-3.6(CA)·C$. In 1958 during the course of producing expansive
116 cements, Klein and Troxell reported composition estimates of $C_5A_2\$$ and $C_9A_4\$_3$ [39]. They
117 produced their samples by firing CH or $CaCO_3$, $C\$H_2$, and bauxite or aluminum sulfate at
118 1350°C. In 1961, Fukuda correctly identified the composition of $C_4A_3\$$ after firing bauxite,
119 lime, and $C\$H_2$ at 1350°C [40].

121 In 1962, Halstead and Moore suggested the cubic space group $I4_132$ for $C_4A_3\$$, based on
122 systematic absences in their powder patterns [33]. They determined the refractive index to be
123 1.57 and the density to be 2.61 g/cm^3. Additionally, they observe that all reflections that cannot
124 be indexed on a body-centered cubic cell (a = 9.195) are weak, and the strong reflections are
125 consistent with the space group $I\bar{4}3m$. These observations suggested that $C_4A_3\$$ is an end
126 member of the sodalite ($Na_8[Al_6Si_6O_{24}]Cl_2$), noselite ($Na_8[Al_6Si_6O_{24}]SO_4$), hauynite ($[Na,Ca]_{4-}$
127 $_8[Al_6Si_6\{O,S\}_{24}[SO_4,Cl]_{1-2}$) series with all the Na^+ replaced by Ca^{2+} and the Si^{4+} replaced by
128 Al^{3+}.

3

129
130 Sodalites have the general formula $M_8(T_{12}O_{24})X_2$, where M is a relatively low charge caged
131 cation (Na^+, K^+, Ca^{2+}, Sr^{2+}, etc...), T (usually Si^{4+} or Al^{3+}) is a cation, tetrahedrally coordinated
132 with oxygen to form the framework, and X is the caged anion (either a single atom anion such as
133 Cl^- or a tetrahedrally shaped oxyanion XO_4^{2-}) [41]. In $C_4A_3\$$, the chemical formula denoting the
134 aluminate sodalite structure is $Ca_8(Al_{12}O_{24})(SO_4)_2$. The excess charge of the framework,
135 $(Al_{12}O_{24})^{12-}$, is charge balanced by the caged Ca^{2+} and SO_4^{2-}. Based on a pseudo-cubic cell of
136 approx. 9 Å, the Al tetrahedra form 4 member rings in the <100> direction (Figure 1a) and 6
137 member rings in the <111> direction through corner sharing (Figure 1b). Figure 1 shows how
138 Al-O bonds form the framework, Ca^{2+} tends to take up positions near the center of the 6-member
139 rings, and the SO_4^{2-} tetrahedron resides in the center of the cage. Dangling and Ca-O bonds are
140 omitted for clarity.
141

a)   b)

142
143 Figure 1: Perspective view of the pseudo-cubic sodalite cage. a) 4 member ring in the <100>
144 direction and b) 6 member ring in the <111> direction. Al (red), Ca (purple), O (blue), and S
145 (orange).

146 In 1965, Kondo ascribed the cubic space group I23 to $C_4A_3\$$ [42]; however, Fischer et al. [43]
147 state, "[T]he coordinates as given there conform completely to space group $I\bar{4}3m$." In 1972,
148 Saalfeld and Depmeier produced a crystal structure for the subcell based on the cubic space
149 group $I\bar{4}3m$ [34], and they, like Halstead and Moore, explain the superstructure and weak
150 reflections by using the space group $I4_132$. Additionally, they proposed that the sulfate groups
151 rotate approximately 90° in alternating positions and the Ca^{2+} occupy 2 different positions among
152 the equipoints x,x,x and $\bar{x},\bar{x},\bar{x}$.
153
154 In 1991, Feng et al. [44] produced a single crystal of $C_4A_3\$$ by first firing calcite, alumina, and
155 $C\$H_2$ at 1350°C for 2 hours and then combining the resultant $C_4A_3\$$ with lead chloride in a ratio
156 of 5:100. The mixture was then heated at 850°C for 24 hours and 950°C for 48 hours. This
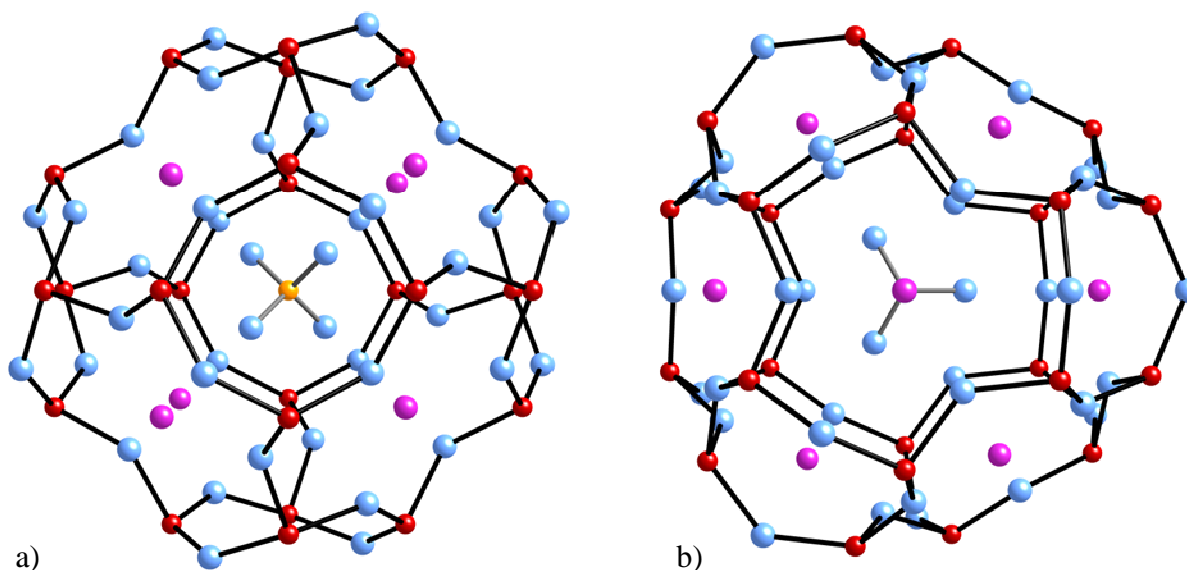
4

157 seems like an unusually low temperature to produce a single crystal even with a flux since most
158 prior research produced $C_4A_3\$$ at approximately 1350°C. Feng et al. chose the same cubic space
159 group, $I\bar{4}3m$, as Saalfeld and Depmeier, but some atomic positions and calcium occupancy
160 factors differ. Feng et al. also reported two cubic, an orthorhombic, and a tetragonal
161 superstructure in their data.
162
163 Between 1990 and 1991, Wang et al. [45-48] published a series of transmission electron
164 microscopy (TEM) studies on $C_4A_3\$$ with much of their data interpretation being based on the
165 cubic crystal structure proposed by Feng et al. [44] who were coauthors of the TEM studies. The
166 studies propose explanations for multiple superstructures (orthorhombic, tetragonal, monoclinic,
167 and rhombohedral) by ordering the occupancy of the calcium atoms and performing image
168 simulations to test their hypotheses. They do not test the hypothesis of ordering the sulfate
169 groups in different orientations as proposed by Saalfeld and Depmeier [34] to explain the
170 superstructures. Wang et al. [46] showed a TEM image of $C_4A_3\$$ and mark a superstructure with
171 spacings of 1.4 nm, but the dark bands measured could be Moiré patterns [49]. They also
172 claimed to have found a new cubic phase with a lattice parameter of about 15 Å; they state,
173 "[Q]ualitative estimation of EDAX on this phase shows it has nearly the same composition as the
174 matrix." Tricalcium aluminate (C_3A) can be an impurity phase when attempting to synthesis
175 pure $C_4A_3\$$; likewise, C_3A can be cubic and has a lattice parameter of 15.263(3) Å [50]. Last,
176 Wang et al. [48] presented multiple cases of twinning in $C_4A_3\$$.
177
178 In 1992, two tetragonal structures were proposed for $C_4A_3\$$, independently; however, they have
179 essentially the same lattice parameters of a = 13.031 Å and c = 9.163 Å [36, 37]. Peixing et al.
180 [36] used infrared spectroscopy to determine the tetrahedral coordination of aluminum and sulfur
181 and utilized electron diffraction to place $C_4A_3\$$ in the tetragonal crystal system. They determined
182 the space group to be $P\bar{4}c2$ and gave a full set of atomic positions. Their Fig. 4 shows ordering
183 of the caged sulfate ions, which breaks down the cubic symmetry. Krstanović et al. [37] give
184 possible space groups of $P4_1$ or $P4_122$ but do not give atomic positions.
185
186 In 1995, Calos et al. [35] published an orthorhombic crystal structure using space group Pcc2
187 and lattice parameters a = 13.028(3), b = 13.037(3), and c = 9.161(2). They utilized infrared
188 spectroscopy, aluminum magic angle solid state nuclear magnetic resonance spectroscopy,
189 electron diffraction, and neutron diffraction to give evidence on the crystal structure. Moreover,
190 they utilized Depmeier's probable symmetry breakdowns from the space group $I\bar{4}3m$ (which
191 describes the maximal symmetry of a collapsed aluminate sodalite cage) through the maximal
192 subgroups that result from symmetry reductions to select Pcc2 [51]. Likewise, the various
193 distortions that aluminate sodalites can undergo in order to accommodate various caged ions
194 were considered including: partial collapse and tilting of the alumina framework tetrahedra,
195 tetragonal orientation of the caged XO_4^{2-} anion, twinning (which Calos et al. did observe with
196 electron diffraction, as did Wang et. al [48]), and modulation of the structures [41]. Fischer et al.
197 [43] cast doubt on the orthorhombic space group Pcc2 proposed by Calos et al. [35] stating
198 "refinements with such large estimated standard deviations are unlikely to prove clearly
199 deviations from higher symmetry."
200
201 In 1996 utilizing X-ray powder diffraction data, Ikeda et al. [52] performed a structure

202 refinement of $C_4A_3\$$ utilizing space group I23. They found an abnormally low density of 2.53
203 g/cm^3 (compare to 2.61 g/cm^3 [33]) and attributed the lower density to oxygen vacancies. Their
204 structural refinement resulted in the oxygen atoms in the Wyckoff positions 24f and 8c to have
205 occupancy values of 0.80 and 0.79, respectively; however, they do not offset the anion
206 deficiencies with cation deficiencies. Consequently, each of their unit cells has an excess
207 positive charge of 12.96. This result does not make physical sense and highlights the pitfalls
208 present in refinements.
209
210 Álvarez-Pinazo et al. [53], during their recent work using Rietveld quantitative phase analysis on
211 various CSA cements, state, "It is worth to highlight the importance of having accurate structural
212 descriptions for every phase in the cements to be analyzed." Their work used two of the three
213 $C_4A_3\$$ crystal structures in the Inorganic Crystal Structure Database (ICSD), the cubic $I\bar{4}3m$
214 from Saalfeld et al. [34] and the orthorhombic Pcc2 of Calos et al. [35]. It is important to note
215 that the information in the ICSD for the space group c given by Saalfeld et al. is for the subcell,
216 and Saalfeld et al. actually propose the space group $I4_132$ to explain the entire structure, which is
217 the same space group selected by Halstead et al. [33] which is not in the ICSD. Additionally, the
218 crystal structure from Saalfeld and Depmeier [34] in the ICSD is from 1972, and W. Depmeier
219 performed many studies that furthered the understanding of aluminate sodalites' structures after
220 that initial work. Álvarez-Pinazo et al. [53] found that in their BCSAF_B2 sample (CSA cement
221 with iron and 2% boron oxide) the $C_4A_3\$$ phase was cubic, and "[They] speculate that this might
222 be due to the simultaneous presence of Na, Fe, and Si." In the rest of their samples they found
223 that peak intensities in the XRD patterns could be attributed to a combination of cubic and
224 orthorhombic intensities. From a review on aluminate sodalites' crystal structures, it is
225 improbable that a pure $C_4A_3\$$ would have a cubic structure at ambient temperature and pressure,
226 but with substitutions of larger caged ions for Ca^{2+} or SO_4^{2-} to expand the framework to a non-
227 collapsed state or with substitutions of smaller framework cations such as B^{3+} or Si^{4+} for Al^{3+} the
228 cubic symmetry could be restored. Ion substitutions are highly likely to occur in CSA clinker
229 produced from impure starting materials like what is found in commercial clinker production.
230 Additional resources for $C_4A_3\$$ synthesis and the structure of aluminate sodalites include [54-
231 59].
232
233 A note on synthesizing $C_4A_3\$$. Many of the studies reviewed utilized $CaCO_3$, AH$_3$, or C\$H$_2$ to
234 synthesize $C_4A_3\$$; however, hydrated or carbonated reagents will release H_2O or CO_2 when
235 heated, leaving behind porosity and hindering the sintering reaction; therefore, reagents should
236 be pre-fired before using them to synthesize $C_4A_3\$$. Likewise, sulfate can volatilize during
237 firing, encouraging the formation of impurity phases such as C_3A. When possible, it would be
238 beneficial to either control the SO_x vapor pressure or use sealed containers to reduce the amount
239 of SO_x escaping. Reducing conditions should be avoided in the furnace as Brenchley and Weller
240 [60] showed that reducing conditions will convert the caged SO_4^{2-} tetrahedra to S^{2-} and restore
241 the cubic symmetry to $I\bar{4}3m$. Depmeier [41] gives some guidelines on how to grow adequately
242 large single crystals of aluminate sodalites utilizing a Bi_2O_3 flux; however, this technique proved
243 unsuccessful for $C_4A_3\$$ [W. Depmeier, Personal Communication, 11/27/2012]. Potential
244 candidates for an alternative flux include $Bi_2(SO_4)_3$, $VOSO_4$, or rare earth sulfates. A single
245 crystal XRD experiment of $C_4A_3\$$ is needed to confirm and/or determine the crystal structure, or
246 range of crystal structures, depending on the synthesis conditions and starting materials as

6

247 highlighted by Álvarez-Pinazo et al. [53].

249 Despite great effort put into the determination of $C_4A_3\$$'s crystal structure by both
250 crystallographers and material scientists, the correct crystal structure for $C_4A_3\$$ has probably yet
251 to be determined. The uncertainty in the structure arises from nuances in the structure potentially
252 brought about by partial collapse and tilting of the alumina framework tetrahedra, tetragonal
253 orientation of the caged XO_4^{2-} anion, twinning, and modulation of the structures. These factors
254 affect the symmetries present in the crystal structure and hence affect the space group
255 determination. Although all of $C_4A_3\$$'s symmetries are not known, the basic framework and
256 general positions of the charge balancing cations are fairly well understood as evidenced by the
257 agreement by the majority of the proposed crystal structures. The present research will further
258 elucidate which of the currently proposed crystal structures best fits experimental data.

259 ## 1.3 CSA Cement Properties

260 ### 1.3.1 Hydration of CSA Cement

261 CSA cements contain a significant fraction of synthetic ye'elimite ($C_4A_3\$$). In fact, $C_4A_3\$$ is
262 chemically equivalent to three units of monocalcium aluminate (CA) plus anhydrous calcium
263 sulfate (C\$), and in most applications $C_4A_3\$$ plays roughly the same role in hydration as CA
264 does in high alumina cement (HAC). $C_4A_3\$$ has the advantage, however, that it is more
265 compatible with PC clinker phases at high temperatures and can thus be used to stabilize high-
266 alumina clinker compositions in the presence of calcium silicates under normal clinkering
267 conditions, thus permitting CSA clinkers to be manufactured in conventional rotary-kiln
268 systems as used for PC clinkers, which significantly reduces the manufacturing costs relative to
269 HAC.

271 Depending on the CSA clinker composition, particle size distribution, w/c, and the amount of
272 $C\$H_2$ added, the CSA cement can have similar rheology, workability, set time, dimensional
273 stability, and strength gain to PC, or the CSA cement can be formulated to develop high early
274 strength, or to be shrinkage-compensating or self stressing [26-28, 31, 32].

276 It is well known that the most voluminous early hydration product in most CSA cement
277 formulations with $C\$H_2$ is ettringite ($C_6A\$_3H_{32}$). The hydration reactions of $C_4A_3\$$ with calcium
278 sulfates (C\$ and $C\$H_2$) initiates rapidly and forms ettringite and AH_3, which contribute to the
279 early-age property development in CSA cement. In the absence of excess calcium hydroxide
280 (CH), crystalline ettringite is usually found together with smaller amounts of a largely
281 amorphous hydrated alumina gel (AH_3) [61, 62], see Eqn. 2. If both $C\$H_2$ and CH are present to
282 react with $C_4A_3\$$, then hydration can produce ettringite without also producing AH_3 (Eqn. 3). CH
283 accelerates the hydration of $C_4A_3\$$ and produces a sulfate/hydroxy solid solution AFm phase at
284 early ages and ettringite at later ages (Eqn. 3) [63, 64]. When $C\$H_2$ is absent or depleted, the
285 formation of monosulphate ($C_4A\$H_{12-18}$) becomes the dominant reaction (Eqn. 4). The AH_3
286 produced during hydration can further react with additional CH and $C\$H_2$ to form ettringite
287 (Eqn. 5). Often Fe^{3+} is substituted for Al^{3+} in clinker phases and can play much the same role in
288 hydration as Al^{3+}. Eqn. 6 shows one such reaction for the hydration of C_4AF with $C\$H_2$. The
289 reaction of two other common CSA clinker phases are anhydrite (C\$) hydrating to from $C\$H_2$
290 and C_2S hydrating to form calcium silicate hydrate (C-S-H) which are Eqns. 7 and 8,

291   respectively.

292

293         $C_4A_3\$ + 2C\$H_2 + 34H \rightarrow C_6A\$_3H_{32} + 2AH_3$ (2)
294         $C_4A_3\$ + 8C\$H_2 + 6CH + 74H \rightarrow 3C_6A\$_3H_{32}$ (3)
295         $C_4A_3\$ + 18H \rightarrow C_4A\$H_{12} + 2AH_3$ (4)
296         $AH_3 + 3CH + 3C\$H_2 + 20H \rightarrow C_6A\$_3H_{32}$ (5)
297         $3C_4AF + 12C\$H_2 + 110H \rightarrow 4C_6(A,F)\$_3H_{32} + 2(A,F)H_3$ (6)
298         $C\$ + 2H \rightarrow C\$H_2$ (7)
299         $C_2S + 2H \rightarrow CH + C\text{-}S\text{-}H$ (8)

300

301   PC manufacturers have used calcium carbonate (limestone, principally calcite) as filler for
302   decades. Limestone filler reduces the cost, energy demands, and CO_2 emissions associated with
303   cement production. Additionally, fine calcite benefits the cement in many ways, such as
304   increasing early age strength by providing nucleation sites, reacting with calcium aluminates to
305   form monocarboaluminate, imparting favorable rheological properties for the production of self
306   consolidating concrete, and stabilizing ettringite by favoring the formation of
307   monocarboaluminate instead of monosulfate [65-71]. Increasing the amount of limestone filler,
308   lowers the peak rate of heat evolution and the total heat evolved due to a decrease in the amount
309   of cement reacting [72]. Coarser grained limestone filler tends to delay the occurrence of the
310   main heat evolution peak; whereas, limestone filler that is significantly finer than the cement
311   advances the occurrence of the main heat evolution peak. Durability is directly linked to
312   permeability. Since many researchers have found limestone powder to act as a nucleation site,
313   this would have the effect of disrupting the pore continuity, consequently improving durability.
314   Schmidt found that portland limestone cements had slightly lower permeability than the
315   corresponding PCs [73]. Using mercury intrusion porosimetry, Sellevold et al. found that
316   cements containing a 12% limestone addition had a finer pore structure and slightly less total
317   porosity [74].

318

319   Calcite additions to PC can have some negative effects on PC. With calcite additions over
320   approximately 10% by mass, the strength of the blended cement begins to decline due to
321   dilutionary affects beginning to outweigh the nucleation benefits [75]. The addition of
322   limestone powder to PC can increase drying shrinkage as much as 15% [76]. In the past decade,
323   a lot of research has been done on the thaumasite form of sulfate attack. Unlike the classical
324   form of sulfate attack where hydration products are converted to ettringite and $C\$H_2$ by the
325   ingress of sulfate ions, the thaumasite form of sulfate attack also requires carbonate ions. Due
326   to the higher solubility of carbonate ions at lower temperatures, thaumasite formation occurs
327   much faster at lower temperatures. Typically the carbonate ions came from carbonate bearing
328   aggregates and dissolved CO_2 in the water; however, when limestone powder is added to cement
329   an additional more soluble (due to higher surface area) source of carbonate ions is available.
330   This could make limestone addition to PC in cold environments very detrimental. Indeed,
331   Barker and Hobbs demonstrated that when portland limestone cement (Type I) is exposed to
332   sulfate and maintained at 5°C, ettringite and thaumasite are formed [77].

333

334   Calcite has also been shown to affect CSA cement (63% $C_4A_3\$$, 8% CA, 3% CA_2, 18% C_2AS)
335   hydration and property development in many ways [70]. Fine calcite additions (46.9% of total
336   fines) generally reduce the set time and enhanced early age heat evolution in CSA cement.

8

Second, calcite promotes the formation of hemicarboaluminate and monocarboaluminate over monosulfate. 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.

Many CSA cements give very rapid strength development, and, since ettringite is usually the major hydration phase in the early-age microstructure, the question arises as to how this early strength is generated. The strength of PC systems is generally ascribed to bonding by the C-S-H phase, which like AH_3, is largely amorphous. However, at early ages the AH_3 gel appears very tenuous and seems unlikely to contribute significantly to strength; therefore, bonding and interlocking between ettringite crystals probably makes the major contribution to the strength of the CSA paste. In fact, many quite strong hydraulic cementing systems exist based entirely on crystalline hydrates, for example: $C\$H_2$ plasters, HAC, magnesium phosphate cements, Sorel cements, etc.

1.3.2 Dimensional Stability of CSA Cement

Due to the fast reacting $C_4A_3\$$ and the expansive nature of ettringite, CSA cements can be manufactured with a variety of properties including: high early strength, rapid setting, shrinkage compensating, or self stressing [8]. 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 $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ content, amount of calcium sulfate added, the particle size distribution, lime content, and the w/c [8, 27-29]. 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 [8, 19, 20, 26-32]. In field practices, CSA cements have been used mainly in pre-cast concrete applications and cold environments and have shown good dimensional stability, low permeability, low alkalinity, good durability, and comparable compressive strength to PC [78-81]. However, despite the increasing interests in CSA cement, industrial scale production and usage are mostly limited to China [82].

Since ettringite formation in PC has been linked to expansion and degradation in several forms of sulfate attack including delayed ettringite formation and external sulfate attack [83, 84], the dimensional stability and durability of any particular CSA cement formulation, which relies on ettringite to provide early strength, needs to be extensively studied.

The formation of ettringite from the hydration reactions of $C_4A_3\$$ with calcium sulfates can be expansive [62]. It has been suggested that if most of the ettringite forms before hardening, then non-expansive and rapid hardening CSA cement can be achieved, but significant ettringite formation after hardening can cause expansion and cracking [85]. Specific factors that have been shown to affect expansion in CSA cements have been identified as: $C_4A_3\$$ content, pore structure, w/c, sulfate content, free lime content, alkali hydroxide content, and particle fineness. These factors are discussed in more detail next.

The phase assemblage in CSA clinker has been shown to affect expansion; specifically, higher amounts of $C_4A_3\$$ have been linked to higher expansions. Beretka et al. [29] showed that CSA

9

381 cements containing mainly $C_4A_3\$$, $C_5S_2\$$, and $C\$$ expanded and cracked with $C_4A_3\$$ contents
382 higher than 50% using a w/c of 0.4. These results agree with those of Janotka et al. [86] who
383 found that CSA cement with a low $C_4A_3\$$ content (20.2% $C_4A_3\$$, 50.3% C_2S, 9.7% $C\$$, and
384 19.5% C_4AF) and a w/c of 0.5 had limited expansion (0.25%), although it expanded more than
385 PC mortar (-0.10%).

386

387 The effect of $C_4A_3\$$ content on expansion is mainly dependent on the amount of ettringite that
388 formed after cement hardened according to Equation 2, but the cement pore structure at the time
389 of ettringite formation also plays an important role [85, 87]. The cement pore structure affects
390 the mobility of ions and the amount of space for reaction products to form. It has been
391 suggested that the formation of ettringite confined to the vicinity of aluminum-bearing grains
392 results in large expansions [87]. Therefore, ettringite formation in pastes with denser pore
393 structures could cause more expansion. Bernardo et al. [88] showed that CSA cement that
394 contained a relatively high amount of $C_4A_3\$$ (53.0% $C_4A_3\$$, 13.2% C_2S, 18.6% $C\$$, and 10.3%
395 $C_{12}A_7$) using a w/c of 0.5 hardened rapidly due to the fast formation of ettringite. The initial
396 hydration products quickly reduced the internal pore space. After 6 hours of hydration, the
397 smaller pores (~25 nm) dominated over the capillary pores (~200 nm) and the system developed
398 a bimodal pore structure, which generally correlates to a disconnected pore structure and a
399 denser microstructure. PC, on the other hand, showed a unimodal or continuous pore structure
400 at early ages, which generally correlates to a more porous microstructure. PC only developed a
401 bimodal pore structure after 7 days of hydration, demonstrating the disconnected nature of the
402 pore system as the larger pore volume decreased. These results suggest that the high $C_4A_3\$$
403 cement examined by Bernardo et al. [88] should be expansive. While Bernardo et al. [88] did
404 not measure expansion on their specimens, the high $C_4A_3\$$ cements tested by Beretka et al. [29]
405 earlier would presumably have a similarly dense microstructure and these did expand. On the
406 other side of the spectrum, Janotka et al. [86] found that their low $C_4A_3\$$ content CSA cement
407 (20.2% $C_4A_3\$$, 50.3% C_2S, 9.7% $C\$$, and 19.5% C_4AF) with a w/c of 0.5 had higher porosity
408 and coarser pore structure than PC mortar at 90 days of hydration and both were non-expansive,
409 as discussed earlier.

410

411 The w/c affects the amount of space (porosity) available for hydration product formation and the
412 amount of water available to hydrate the cement phases, both of which can alter expansion in
413 CSA cements. At lower w/c, the cement matrix develops a denser pore structure, which affects
414 the mobility of ions and the amount of space for reaction products to form that could lead to
415 expansive behavior in CSA cements, as discussed in the previous paragraph. Furthermore, at
416 lower w/c, high $C_4A_3\$$-bearing CSA cements can undergo self-desiccation because the
417 formation of ettringite requires large amounts of water according to Equation 2 [8]. Therefore,
418 more cement particles remain unhydrated, even at later ages. Having large amounts of
419 unhydrated cement after setting can lead to expansion if the cement is later exposed to external
420 water from the environment, since unhydrated phases can react to form secondary ettringite.
421 Beretka et al. [29] tested a range of w/c with CSA cements that mainly contained $C_4A_3\$$, $C_5S_2\$$,
422 and $C\$$. It was observed that when using a w/c of 0.4, the CSA cements with $C_4A_3\$$ content
423 higher than 50% expanded and cracked after curing in 100% relative humidity (RH). At w/c of
424 0.4, the initial water content was not enough for the large amount of $C_4A_3\$$ to completely react
425 according to Equation B2. Therefore, the secondary ettringite formed from the unhydrated
426 $C_4A_3\$$ and $C\$$ during curing after the paste hardened combined with the denser pore structure

427   from the low w/c and high $C_4A_3\$$ content (more ettringite formation) resulted in the expansion
428   and cracking at later ages.   However, when using higher w/c of 0.65-0.7, the high $C_4A_3\$$
429   cements remained dimensionally stable during curing in 100% relative humidity because water
430   in the system was sufficient for $C_4A_3\$$ to fully react at early ages and the microstructure is more
431   porous. It should be noted that secondary ettringite formation and associated expansion depends
432   on the curing environment [89]. When curing at low humidity, ettringite formation stops after a
433   few days of hydration due to the loss of free water in the system.
434
435   Dimensional stability of commercial CSA cement has been shown to be dependent on the
436   amount of $C\$H_2$ available in the system, with higher $C\$H_2$ contents linked to higher expansions
437   [8, 90]. Yanmou et al. [90] experienced ~0.15% and ~0.70% expansion with 15% and 35%
438   $C\$H_2$, respectively, with a CSA clinker that contained 58.4% $C_4A_3\$$ and 11.6% C_2S. Glasser
439   and Zhang [8] showed that a different commercial CSA cement (unreported phase assemblage)
440   shrunk slightly at 18% $C\$H_2$ addition, showed zero dimensional change at 22-24% $C\$H_2$
441   addition, and became expansive at 24-25% of $C\$H_2$ addition.
442
443   Type K cements [91] contain CSA cement as an additive to PC and are designed to be
444   expansive. The degree of expansion in Type K cement has been linked to free lime content
445   (CaO in the PC clinker). While investigating Type K cements, Kurdowski and Thiel [92] found
446   that a cement containing 3.9% free lime produced much greater expansion than a low free lime
447   cement (0.8%). When the two pastes were examined in a scanning electron microscope (SEM)
448   at 1 and 7 days of hydration, the free lime accelerated the formation of ettringite but did not
449   appear to affect the size of the ettringite crystals.   In contrast, Mehta [93] found that the
450   hydration of $C_4A_3\$$ in the presence of $C\$H_2$ and free lime resulted in ettringite crystals that were
451   significantly smaller than ettringite crystals formed from the hydration of $C_4A_3\$$ in the presence
452   of $C\$H_2$ only, suggesting a faster ettringite crystal formation rate when free lime is available.
453   The presence of free lime may make the reaction pathway in Equation 3 more favorable than the
454   reaction pathway of Equation 2; consequently, each unit of $C_4A_3\$$ would produce 3 units of
455   ettringite instead of 1. The larger amount of ettringite produced per unit of $C_4A_3\$$ in Equation 3
456   would result in a larger potential for expansion.
457
458   Alkali hydroxides have been shown to increase the dissolution rate of the aluminate phases in
459   PC [94], and Min and Mingshu [87] found that alkali hydroxides increased the expansion in a
460   sulfoaluminate cement, presumably through increasing the dissolution rate of $C_4A_3\$$ and
461   formation of ettringite.
462
463   Cement particles can remain unhydrated through means other than self-desiccation. If the CSA
464   cement contains high quantities of coarser particles, then those larger particles will be slow to
465   hydrate [95]. In Type K cements, the particle size of the $C_4A_3\$$-bearing cement has been shown
466   to affect the amount and timing of the expansion [28]. When finer ground expansive Type K
467   clinker was added to PC, the $C_4A_3\$$ particles reacted faster with calcium sulfates to form
468   ettringite and the cement paste expanded at a high early rate for only a few days. However,
469   when coarser ground expansive Type K clinker was used, the $C_4A_3\$$ particles reacted slower
470   with calcium sulfates to form ettringite and the cement paste expanded at a slower rate for a
471   longer period of time, which led to abnormal behavior. The delayed expansion and strength
472   drop in coarser blends could be attributed to the formation of ettringite crystals on larger grains

473   of $C_4A_3\$$ after the C-S-H matrix had formed, which caused localized mechanical failures in the
474   matrix.
475
476   While previously discussed research identified variables that contribute to CSA cement
477   expansion, each study attributed expansion of the system to individual factors. Oftentimes
478   identifying the cause of expansion was not the goal of the research; consequently, factors
479   affecting expansion were not controlled in these studies. Also, many published studies do not
480   give the phase composition of the CSA cements tested. The results of the study discussed next
481   attempted to elucidate the interdependency of $C_4A_3\$$ content, particle fineness, w/c, and calcium
482   sulfate content and show how CSA cement expansion can be controlled by altering chemical
483   and physical factors in CSA clinker, cement, and pastes [27]. The results provide insights for
484   future usage of CSA cements as potential direct alternatives to PC in specialty applications.
485
486   Three CSA cements synthesized from reagent grade materials with different phase assemblages
487   were examined for dimensional stability in water and sulfate solutions. The reactions were
488   tracked using X-ray diffraction (XRD), and the microstructure development was observed
489   utilizing a SEM. Hydration product development showed that $C_4A_3\$$ and $C\$H_2$ reacted quickly
490   and contributed to the formation of ettringite and amorphous phases (mainly AH_3). Most of the
491     $C_4A_3\$$ and $C\$H_2$ reacted by 7 days of hydration. However, C_2S remained mostly unhydrated at
492   90 days of hydration in all the CSA cements.
493
494   The dimensional stability tests and companion XRD and SEM studies showed that expansion in
495   CSA cement increases with the following: (1) Increasing $C_4A_3\$$ content. As the $C_4A_3\$$ content
496   increases, the amounts of ettringite and amorphous phases (mainly AH_3) that can be formed
497   increase. The large store of "potential" ettringite and amorphous phases (mainly AH_3) that can
498   be formed increases the sensitivity of the cement to other factors that cause expansion. (2)
499   Decreasing w/c. As the w/c decreases, there is less space for the formation of hydration
500   products, including ettringite and amorphous phases (mainly AH_3). The expansive pressure
501   from ettringite increases when space is restricted. Also, since there is less water available for
502   hydration reactions, fewer hydration products can form prior to self-desiccation, which could
503   lead to expansion later when external water is supplied. (3) Increasing $C\$H_2$ content.
504   Increasing the amount of $C\$H_2$ provides the calcium and sulfate ions necessary for the
505   formation of ettringite and amorphous phases (mainly AH_3), increasing the amounts that can be
506   formed and the risk for expansion. (4) Increasing PSD. Coarser cement grains result in the
507   production of reaction rims around the hydrating $C_4A_3\$$ particles, confining the formation of
508   ettringite and amorphous phases (mainly AH_3) to around the surface of the hydrating grains,
509   resulting in localized expansion. Furthermore, since large grains hydrate slowly they can cause
510   expansion for a longer period of time. (5) Increasing sulfate content in the curing environment.
511   As more sulfate ions are available in the curing water, ettringite could form more rapidly and the
512   potential for expansion increases.
513
514   From the dimensional stability results presented in the study [27], the $C_4A_3\$$ content had the
515   most significant effect on CSA cements expansive behavior. However, expansion could be
516   mitigated even in high $C_4A_3\$$ content CSA cements when appropriate measures were taken
517   simultaneously. For example, providing enough initial internal water for the hydration reactions
518   provided more pore space for hydration products to form and prevented self-desiccation, adding

519   less CH_2$ reduced the formation of ettringite and amorphous phases (mainly AH$_3$), eliminating
520   exposure to high sulfate environments prevented free sulfate ions from entering the system that
521   could accelerate the formation of ettringite, and finally the most effective approach, reducing the
522   PSD of the cements prevented localized expansion around coarser C$_4$A$_3$\$ particles. However, it
523   should be noted that increasing the w/c and reducing the CH_2$ content might adversely affect
524   other property development in CSA cements as the higher w/c results in a more porous
525   microstructure and the lower CH_2$ content prevents C$_4$A$_3$\$ from reacting.

527   E.J. Garboczi quantified the stresses, displacements, and cracking around a single spherical
528   aggregate under different expansive conditions [96], and by analogy his results can be applied to
529   CSA cement expansion. To apply his results, one would need to consider the anhydrous C$_4$A$_3$\$
530   core as the aggregate and then his results can be used to understand the microcracks that form
531   around hydrating C$_4$A$_3$\$ cores. First, his results will be presented as applied to aggregates, and
532   then his results will be applied to CSA cement hydration. Garboczi presented three scenarios.
533   (1) Uniform matrix expansion, which includes the deleterious actions of certain kinds of sulfate
534   attack, freeze thaw, and hypothesized for delayed ettringite formation, results in tensile forces
535   that are their greatest at the aggregate-matrix interface. Consequently, the aggregate may break
536   free from the matrix leaving a circumferential gap or crack around the aggregate. In real
537   concrete systems, it is possible that some aggregates don't break free altering the stress field;
538   however, on average with uniform matrix expansion, gaps would be expected to form around
539   the aggregates that are approximately proportional to the radius of the aggregates. (2) A thin
540   expansive shell around the aggregate, which has been proposed as a mechanism for DEF
541   expansion, would also produce tensile radial stresses at the interface, causing the aggregate to
542   debond and form a rim of free space around the aggregate. In this case, however, the gap
543   produced is proportional to the thickness of the expansive rim and not the radius of the
544   aggregate. (3) Expansive aggregate, which could occur during alkali-silica reaction (ASR)
545   when the gel forms inside the aggregate, produces compressive radial stresses in both the
546   aggregate and the matrix, yet it produces tangential stresses that are compressive in the
547   aggregate and tensile in the matrix. As a consequence, radial cracks from the aggregate surface
548   into the matrix are expected. In real concrete systems where the aggregate is not expanding
549   uniformly then tensile stresses will also be produced within the aggregate causing cracking
550   inside the aggregate as well.

552   Figure 2 is a backscattered electron SEM image showing the typical crack patterns in CSA
553   cement and is adapted from Chen et al. [27]. The bright spots are the anhydrous C$_4$A$_3$\$ cores.
554   Several different crack patterns can be observed and are highlighted by arrows of different
555   colors. The red arrows point out cracks that appear to have coalesced into macrocracks based
556   on their length and width compared to the other cracks in the field of view. The green arrows
557   mark cracks that are roughly circumferential or tangential and the blue arrows mark cracks that
558   are roughly radial from the C$_4$A$_3$\$ cores. The yellow arrow points out cracks that are random in
559   nature and are typical of drying cracks that are common with ettringite shrinkage due to the loss
560   of free water. The circumferential/tangential cracks would indicate either bulk matrix expansion
561   or expansive shells around the C$_4$A$_3$\$ cores. Reaction rims can be seen around the C$_4$A$_3$\$ cores
562   that are microns to tens of microns thick. The radial cracking that is evidenced could be a result
563   of either drying shrinkage or from considering the reaction rim around the C$_4$A$_3$\$ cores as a
564   zone that is expanding while new hydration products formed by the core reacting with water fill

565 any gaps that may have otherwise formed between the core and the reaction rim. It is possible
566 the small cracks are the former and the large cracks are the later.
567

568
569 Figure 2: Backscattered electron images for the hydrated high $C_4A_3\$$ content CSA cement from
570 [27]; field width: 1250 μm.
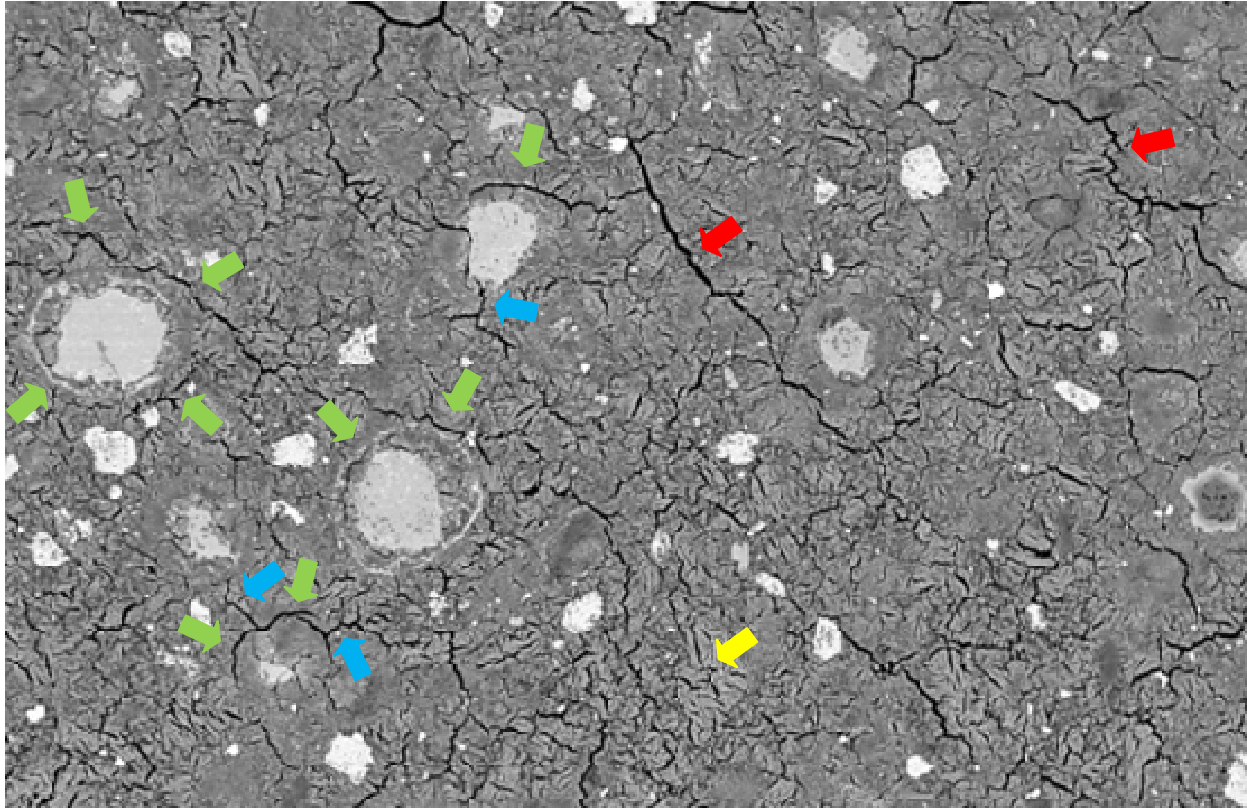
571 There are three predominant theories for the expansion mechanism in CSA cement: (1) crystal
572 growth theory [97], (2) swelling theory [97], (3) confined volumetric expansion theory (a name
573 I propose for the phenomena described by Scherer [98]. Historically, (1) and (3) have at times
574 been combined to varying degrees; however, here they will be separated to account for more
575 recent research, namely that of Scherer [98].
576
577 Crystal growth theory states that expansion is caused by the growth of ettringite crystals on the
578 surface of expansive particles ($C_4A_3\$$) or in the solution. The crystal growth is responsible for
579 the crystallization pressure and consequently the expansive force. The theory as applied by
580 Richards and Helmuth [99] states that the expansive cement is immediately covered by a dense
581 coating of ettringite and that further reaction proceeds topochemically increasing the thickness
582 of the coating layer. When the coating's thickness exceeds the surrounding solution's thickness,
583 then it will push other particles apart resulting in expansion. A micromechanical model was
584 developed to calculate geometrically the final magnitude of expansion. The expansion in the
585 model was dependent on the final thickness of the coating and the number of expansive sites.
586 The more expansive sites the lower the expansion. The chemical composition of the system,
587 w/c and particle size distribution affected the coating thickness and number of expansive sites.
588 Bentur and Ish-Shalom developed a very similar model relying on topochemical reaction but

14

589   instead of using a solid coating they utilized fine intermeshed crystallites of ettringite with pores
590   between the crystallites and instead of using a particle size distribution they utilized a single size
591   of expansive particles [100, 101]. Their model states that expansion initiates at a critical degree
592   of hydration occurring when hydrating spheres begin to come into contact and exert pressure on
593   each other causing expansion. Kalousek and Benton studied seawater attack on cement pastes
594   and concluded that it was ettringite crystals that grew in confined spaces and exerted pressure on
595   the surrounding walls that caused expansion [102]. Scherer showed that the stresses necessary
596   to crack cement paste (in the MPa range) could only be developed by crystals growing in the
597   nanometer pores under high supersaturation conditions [98]. Richards and Helmuth and Bentur
598   and Ish-Shalom's models are essentially geometrical in nature and assigning them the name of
599   crystal growth theory is perhaps unfortunate; since, many of the defenders of the theory simply
600   rely on the volume of the products being larger than the volume of the anhydrous expansive
601   cement and not on crystallization pressures. This concept will be further expanded when
602   discussing confined volumetric expansion a term developed to get away from this unfortunate
603   naming convention.
604
605   Mehta proposed a theory of expansion based on the uptake of water by ettringite which has been
606   called the swelling theory of expansion [103]. The theory relies on a through solution formation
607   of ettringite and that ettringite crystals formed in the presence of CH are gel-like and colloidal in
608   size. The large surface area of the colloidal ettringite adsorbs water causing swelling pressures.
609   In the absence of CH, $C_4A_3\$$ and C$H2 will react to form ettringite that is large crystals have
610   less surface area and thus adsorb less water on their surfaces. To support this theory, Mehta
611   studied the microstructure of the reaction products of $C_4A_3\$$ with $C\$H_2$ both with and without
612   CH [103]. The ettringite crystal formed in the presence of lime were about a ¼ μm wide and 1
613   μm long and without CH they were ½ - 1 μm wide and 6 - 8 μm long. Mehta and Hu, also,
614   observed that the amount of water adsorbed correlated to increased expansion [104].
615
616   The confined volumetric expansion theory (a name proposed in the present work) simply relies
617   on the continued hydration of a confined anhydrous core after the formation of a rigid coating
618   and matrix has confined it [98]. The hydration products have larger volumes than their
619   anhydrous predecessors, so if hydration products are confined to form near the vicinity of the
620   anhydrous cores the localized volume increase will exert pressure on the confining matrix and
621   exert pressures that will eventually exceed the tensile strength of the hydrated cement paste
622   (HCP) matrix resulting in cracking and expansion. Ions would not able to diffuse away into
623   open porosity if there were either (1) little to none open porosity, (2) discontinuous porosity, or
624   (3) the diffusion rate of water to the anhydrous core was more rapid than the diffusion rate of
625   ions away from the anhydrous core. Scherer makes the analogy of a water drop forming a
626   coating of ice and then the core of the water drop continues to freeze exerting pressure on the
627   confining ice around the core [98]. This is the phenomenon that creates the domes on top of the
628   ice in your freezer ice cube trays. The confined volumetric expansion theory relies only on
629   hydration of the confined core to cause a volume increase and expansion and does not rely on
630   crystallization pressure. However, that is not to say that crystallization pressure does not at
631   times contribute to expansion.

1.3.3 Mechanical Properties of CSA Cement

The mechanical properties of CSA cement can be altered by all the same variables that affect its dimensional stability. Those variables are particle size distribution of the cement, curing environment, w/c, clinker phase assemblage, and $C\$H_2$ addition level. In fact, all these same variables affect PC strength development. A finer cement particle size distribution causes faster strength gain because there is more surface area of the cement to react. Providing a proper curing environment benefits any cement that utilizes hydration reactions to gain strength. A proper curing environment can be achieved by either sealing in the moisture already present in the hydrating cement paste with plastic or curing compounds, or even better by providing external water by fogging, ponding, or covering with wet burlap. Without a proper curing environment the cement paste dries out and the chemical reactions that take place with water cease to occur and strength gain halts. A lower w/c increases strength by lowering the capillary porosity. Since porosity cannot carry load reducing it results in a strength gain. However for a given w/c ratio and degree of hydration, CSA cement will have a lower porosity than PC because of the large volume of water consumed forming ettringite and monosulfate. In CSA clinker, raising the $C_4A_3\$$ raises the early-age strength and increasing the C_2S raises the late age strength. Increasing $C\$H_2$ content in the cement generally lowers the strength of the cement [105]; however, $C\$H_2$ accelerates the hydration of CSA cements [106], so at early-ages CSA cements with $C\$H_2$ would be expected to have higher strength. Rapid hardening cement can be made with CSA clinker that has a high $C_4A_3\$$ (up to 70%) and utilizes 10-15% $C\$H_2$ [107]. The same cement could be made expansive (self stressing) by using 20-25% $C\$H_2$; however, unrestrained expansive cements loose strength with time due to cracking, so adequate reinforcement is required. Many different researchers have formulated CSA cements using different formulations, feedstocks, burning conditions, and grinding schemes and the results of their studies are just as varied, yet their results tend to follow the trends previously mentioned. One such study [108] is here highlighted to illustrate how changes in the phase composition of the cement can alter the strength development, see Table 1. Comparing the belite cement to the belite CSA cement, it is clear that increasing the $C_4A_3\$$ content increases the early-age strength, but the reduction in C_2S negatively affects the long-term strength. Additionally, changing from C_2S to C_3S as the accompanying calcium silicate phase increases both early-age and late-age strength in CSA cement. To produce C_3S bearing CSA cement, a CaF_2 mineralizer is necessary to lower the firing temperature necessary to form C_3S below 1300 °C, since above that temperature $C_4A_3\$$ decomposes.

667 Table 1: Comparison of cement composition and strength developement for a variety of
668 cements. Data from [108]

	PC	Belite Cement	Belite CSA	Alite CSA
Clinker Composition (%)				
C_3S	80	0	0	80
C_2S	0	80	60	0
C_3A	10	10	0	0
$C_4A_3\$$	0	0	20	10
C_4AF	10	10	20	10
$C\$H_2$ Addition	3	3	7	5
Compressive Strength (MPa)				
1 d	22	9	21	35
3 d	50	12	27	59
7 d	73	23	29	77
28 d	82	35	33	86
365 d	85	96	78	102

669

1.3.4 Durability of CSA Cement

671 In the field, properly formulated CSA concrete has proven to be durable in regards to many of
672 the chemical and physical attacks that it can undergo during service; however, CSA cement does
673 perform more poorly than PC at times [78]. Like PC, CSA cement is susceptible to carbonation;
674 however, CSA cement formulations that are higher in Fe and calcium silicates tend to perform
675 better [26, 78]. During hydration, calcium silicates liberate CH and reduce the permeability of
676 the HCP which helps slow carbonation. CH helps slow carbonation by reacting with CO_2 to
677 form calcium carbonate which further densifies the paste since a unit of calcium carbonate
678 occupies more volume than a unit of CH. Carbonation of ettringite yields calcium carbonate,
679 $C\$H_2$, and alumina gel, resulting in a loss of strength [81, 109, 110]. Hydrated CSA cement's
680 high ettringite content makes it more susceptible to carbonation and strength loss. Zhang et al.
681 [78] showed strength losses of 2.5-7.1% for a variety of different CSA formulations after 28 d
682 of accelerated carbonation (90% R.H. and 20% CO_2/80% Air).

683
684 Corrosion of steel reinforcing bars is a concern in CSA cement because CSA cements have a
685 lower pH compared to PC; however, in practice CSA reinforced concrete has performed well
686 [78]. The adequate corrosion resistance in CSA concretes has been attributed to its lower
687 permeability compared to PC. Alkali-silica reaction has been shown to be worse in higher pH
688 PC concrete, but due to its inherently lower pH, CSA concrete has not been shown to be
689 susceptible to alkali-silica reaction [78, 107]. Additionally, CSA cement has been shown to be
690 resistant to sulfate attack from seawater [78]. This can be attributed to the higher sulfate content
691 initially present in CSA cements that causes the majority of the $C_4A_3\$$ to hydrate to form

17

692 ettringite leaving little monosulfate available to react with the sulfates from the seawater to form
693 ettringite, and hydrated CSA cement's lower CH compared to PC further reduces the quantity of
694 phases that are susceptible to sulfate attack. Any remaining anhydrous $C_4A_3\$$ would be
695 susceptible to attack and conversion to ettringite, but this can be overcome with grinding the
696 cement to a sufficient degree where little anhydrous $C_4A_3\$$ remains at later ages and by keeping
697 the w/c low enough to produce an impermeable HCP matrix. A durability concern and life-
698 safety issue with CSA cement is fire resistance. Upon heating to 120°C, ettringite loses its
699 bound water and turns amorphous, but its basic structural framework persists to approximately
700 400°C. Above 600°C, the amorphous calcium sulfoaluminate decomposes into $C_4A3_\$$, C\$, and
701 CaO [111]. In a high $C_4A_3\$$ bearing CSA cement, Su et al. [107] observed 15%, 45%, and 70%
702 strength losses upon heating to 100-150°C, 300°C, and 500°C , respectively.

1.4 Research Scope and Motivation

704 The literature review revealed that manufacturing PC consumes a lot of resources and places a
705 heavy burden on the environment through its CO_2 and other emissions and the geographic
706 footprints left behind by the mining operations. This study focuses on an alternative to PC,
707 CSA cement, in an effort to aid in the development and acceptance of a more sustainable
708 alternative to PC. Although CSA cement has been well studied, certain aspects of its hydration
709 and expansion mechanism are still not fully understood. Therefore, this work focused on those
710 aspects of CSA cement and also developed a way to make CSA cement perform better and be
711 more environmentally friendly by incorporating calcium carbonate into the cement blend. The
712 motivation behind the specific topics and how each of these topics is covered in detail is
713 discussed next.

1.4.1 $C_4A_3\$$ Structure Evaluation and Bulk Modulus Determination

715 As computational power of computers continues to grow, modeling of cementitious systems at
716 the microstructure scale will play an ever increasing role in cement and concrete research as
717 well as in the engineering of concrete structures, yet to utilize these models fundamental basic
718 parameters, such as bulk moduli, need to be determined for all the phases in the system.
719 Likewise, the growing interest in CSA cements warrants that more fundamental knowledge be
720 developed about this increasingly important material. A thorough literature review revealed
721 uncertainties about the correct crystal structure for $C_4A_3\$$ and determined that its elastic
722 properties were undetermined. To determine $C_4A_3\$$'s bulk modulus, a high pressure XRD
723 experiment of $C_4A_3\$$ was performed at the U.S. Department of Energy's Advanced Light
724 Source (ALS) at Lawrence Berkeley National Laboratory. The determination of $C_4A_3\$$'s elastic
725 properties is important to perform micromechanical models, particularly to determine the elastic
726 mismatch between the cement grain and the matrix. Enabling micromechanical modeling would
727 allow for previously presented expansion models to be validated or disproved ending a
728 longstanding debate and uncertainty among CSA cement researchers. Furthermore, enabling
729 micromechanical modeling would allow CSA cementitious systems to be formulated and
730 validated on the microscale which would allow more durable, sustainable, and high performance
731 systems to be engineered. $C_4A_3\$$ structure evaluation and bulk modulus determination will be
732 discussed in Chapter 3.

1.4.2 CSA Hydration in the Presence of Gypsum and Calcium Hydroxide

The hydration of CSA cement produces a much higher proportion of crystalline phases than does the hydration of PC; consequently, understanding how poly-crystalline binder systems gain strength is of the utmost importance in understanding how CSA cement develops strength. Although, the subject of bonding in poly-crystalline hydraulic binders has been discussed in some detail with respect to the properties of $C\$H_2$ based binders. How $C_4A_3\$$ hydration to produce crystalline ettringite and monosulfate contributes to strength development is now well understood. For the case of $C\$H_2$ plasters, it was suggested that the $C\$H_2$ crystals formed initially from individual nuclei may bond together in preferred orientations at very early ages when free rotation in the suspension can easily occur [112]. This study sought to determine whether similar preferred orientations may develop in CSA cements and could contribute to strength development. Such preferred crystal orientations are, however, very hard to observe by the conventional techniques of scanning electron microscopy applied to dense hardened cement pastes. This is because, due to the likely high porosity of such hypothetical domains, they may well interpenetrate to a significant degree with other adjacent domains giving the impression of a completely random microstructure. Therefore, the best chance to observe the formation of preferred crystal orientations is probably at very early ages and/or in very dilute suspensions.

In this work, the hydration of $C_4A_3\$$ in dilute suspensions under conditions as close as possible to those expected in CSA cements used for construction applications was studied utilizing wet cells observed by transmission X-ray microscopy at the Advanced Light Source in the Lawrence Berkeley National Laboratory. The reaction products from the dilute suspension were imaged ex-situ as well using scanning electron microscopy to better understand any microstructure domains that might develop and to improve the statistical significance of the findings by allowing a larger number of sites to be observed than is practical at the Advanced Light Source. Previous research has shown that CH both retarded the formation of ettringite and accelerated the rate of heat release during $C_4A_3\$$ hydration. These two phenomena would seem to be at odds with each other, so this study also sought to understand how both could occur simultaneously. The transmission X-ray microscope allows in-situ imaging of the $C_4A_3\$$ hydration reaction and was utilized to provide visual evidence of how this dichotomy might arise and to provide kinetic information about the reaction. Additionally, $C_4A_3\$$ pastes with 15% $C\$H_2$ and varying amounts of CH were investigated with isothermal conduction calorimetry and XRD to better understand CH's effect on the hydration kinetics and hydration products formed. The microstructural and product development during $C_4A_3\$$ hydration in the presence of varying amounts of CH and what implications that has on CSA cement dimensional stability will be discussed in Chapter 4.

1.4.3 CSA Hydration in the Presence of Calcite and Vaterite with Varying Gypsum

Although CSA cements are promoted as a more environmentally friendly alternative to PC, their manufacture still consumes a large quantity of resources and energy. One way to reduce CSA cement's environmental impact is to blend it with calcium carbonate. Prior research showed that calcium carbonate additions also improved many of the hydration characteristics and mechanical properties of the CSA cement as well [70]. The previous research used a CSA cement with a mixed phase assemblage. The present study utilized a pure CSA clinker ($C_4A_3\$$) to simplify the system and further elucidate the chemical reactions that occur. Additionally, the

19

777 current work sought to enhance the reactivity of calcium carbonate with CSA, both in the
778 presence and absence of CH_2$, by testing vaterite as well as calcite replacements of C$_4$A$_3$$.
779 Vaterite is a less stable form of calcium carbonate in ambient conditions; consequently, we
780 hypothesized it would be more reactive with C$_4$A$_3$$. Recently, Calera, a startup company in
781 California, has developed the ability to produce vaterite by combining a waste source of calcium
782 with the CO_2 exhaust from power plants [113]. In principal, this technology could be adapted to
783 capture the CO_2 from a cement kiln and produce vaterite on site, which could potentially
784 improve cement production's sustainability. The chemical reactions were monitored with XRD
785 and thermal gravimetric analysis (TGA). Dimensional stability and compressive strength were
786 tested on mortars to understand how the chemical reactions affected the mechanical properties.
787 C$_4$A$_3$$'s reaction with calcite and vaterite will be discussed in Chapter 5.
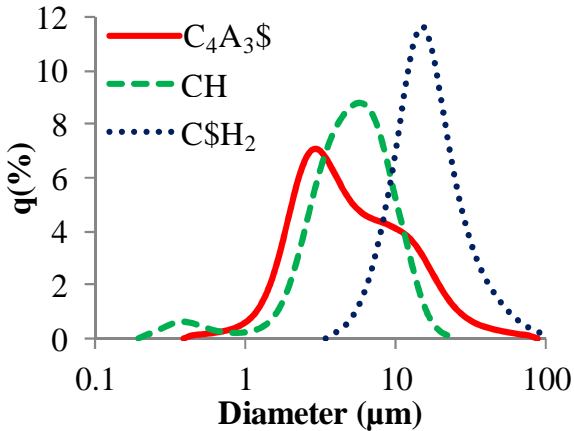
CHAPTER 2: MATERIALS AND METHODS

2.1 Materials

2.1.1 C$_4$A$_3$$ Structure Evaluation and Bulk Modulus Determination

791 C$_4$A$_3$$ was synthesized from a stoichiometric mixture of analytical grade (Fluka) calcite,
792 aluminum oxide, and CH_2$. The materials were homogenized with water, pelletized, then fired
793 in a laboratory kiln at 1,300°C for 4 h. The C$_4$A$_3$$ was ground in an automatic agate mortar
794 grinder mill (Retsch RM100). The ground C$_4$A$_3$$ had a Blaine fineness of 5,520 cm^2/g and a
795 density of 2.60 g/cm^3. The synthesized material was confirmed to be pure by XRD utilizing a
796 Panalytical X'Pert PRO Diffractometer with X'Celerator detector, goniometer radius of 240
797 mm, Cu K$_{\alpha1}$ radiation, step size of 0.017°, a dwell time of 24.765 sec/step, and a fixed
798 divergence slit of 0.25°. Using the extraction method [114], a free calcium oxide of 0.2 mass%
799 was determined.

2.1.2 C$_4$A$_3$$ Hydration in the Presence of Gypsum and Calcium Hydroxide

801 A sample of C$_4$A$_3$$ was obtained from Construction Technology Laboratories, Inc., Skokie, IL,
802 USA. It was synthesized by heating a stoichiometric blend of finely-ground reagent grade
803 alumina, calcium carbonate and calcium sulfate in an electric furnace at 1000-1100°C, followed
804 by quenching in air. After cooling, it was ground in a ceramic mill to pass a 75 µm (#200) mesh
805 sieve. Its particle size distribution was measured in an isopropyl alcohol suspension using a
806 Horiba Partica LA-950$^®$ Laser Diffraction Particle Size Distribution Analyzer. Refractive
807 indices of 1.568, 1.525, and 1.574 were used for C$_4$A$_3$$, CH_2$, and CH, respectively [115]. The
808 C$_4$A$_3$$ had a mean diameter of 6.9 µm with a standard deviation of 7.7 µm and 90% of the
809 particles had an effective diameter less than 15 µm, see Figure 3.
810
811

812
813 Figure 3: Particle size distribution of the $C_4A_3\$$, CH, and $C\$H_2$ used in all experiments.

814 The phase-purity of $C_4A_3\$$ was confirmed by XRD, using a PANalytical XPert Pro[®]
815 diffractometer and by thermogravimetric analysis (TGA) using a TA Instruments[®] TGA, model
816 SDT 2960. Freshly boiled de-ionized water was mixed with reagent grade CH and $C\$H_2$ at
817 room temperature for 24 hours to make the solution used for all X-ray microscopy experiments.
818 The solution was then filtered twice [116]. To avoid carbonation, the solution was prepared and
819 stored in a glove bag filled with nitrogen gas [117]. To avoid silica contamination, which might
820 influence the hydration processes, only polyethylene or Teflon beakers, flasks, and pipettes were
821 used.

822 **2.1.3 $C_4A_3\$$ Hydration in the Presence of Calcite and Vaterite with Varying Gypsum**

823 $C_4A_3\$$ was synthesized from analytical grade chemicals, namely alumina, calcium carbonate,
824 and calcium sulfate dihydrate which were homogenized in a laboratory mixer. The three
825 compounds were proportioned assuming that (i) CaO, Al_2O_3, and $CaSO_4$ react to give only
826 $C_4A_3\$$ and (ii) solid solution effects were absent. The $C_4A_3\$$-generating mixture was heated in
827 an electric oven for 3 hours at 1250°C; the burnt product was then analyzed using XRD to study
828 the reacting system behavior in terms of conversion and selectivity towards $C_4A_3\$$. XRD results
829 revealed only the presence of $C_4A_3\$$, while reagents and/or secondary phases were absent. The
830 $C_4A_3\$$ was then further ground in an alumina shatter box until it passed a 45 micron sieve.
831 XRD also confirmed the calcite and $C\$H_2$ reagents to be pure, and the vaterite (Calera) was
832 found to be 92% vaterite and 8% calcite.

833
834 The particle size distributions of all reagents used to produce pastes and mortars were measured
835 in an isopropyl alcohol suspension using a Horiba Partica LA-950® Laser Diffraction Particle
836 Size Distribution Analyzer. Refractive indices of 1.378, 1.525, 1.580, 1.580, and 1.568 were
837 utilized for isopropyl alcohol, $C\$H_2$, calcite, vaterite, and $C_4A_3\$$, respectively [115]. The ground
838 $C_4A_3\$$ had a D_{50} and D_{90} of 4.1 and 13.5 µm, respectively. $C\$H_2$, calcite, and vaterite had D_{50} of
839 14.6, 4.5, and 2.0 µm, respectively.

840

841 **2.2 Methods**

842 **2.2.1 C$_4$A$_3$$ Structure Evaluation and Bulk Modulus Determination**

843 Using a synchrotron monochromatic X-ray beam, ambient and high pressure XRD experiments
844 were performed on beamline 12.2.2 of the Advanced Light Source of Lawrence Berkeley
845 National Laboratory [118]. The working distance between the sample and detector were
846 calibrated using the National Bureau of Standard's LaB$_6$ powder diffraction standard. A sample
847 to detector distances of 285.4270 mm and 282.6159 mm were utilized for the ambient and high-
848 pressure experiments, respectively. The X-ray wavelengths were 0.6199 and 0.4133 Å for the
849 ambient and high-pressure experiments, respectively. All patterns were collected on a MAR345
850 image plate with a 600 s exposure time.
851

852 The C$_4$A$_3$$ was mixed with a silicone oil pressure medium (polysiloxane chains with methyl and
853 phenyl groups) and ruby [119]. The mixed sample was placed in the hole (180 μm diameter, 75
854 μm thickness) of a steel-gasketed two-screw diamond anvil cell which was used to generate the
855 high pressures and analyzed in axial geometry, see Figure 4. The schematic shows the X-rays
856 (orange arrows) first passing through a diamond anvil, then through mixture of the pressure
857 medium, ruby (red pentagons), and sample (green stars), then passing out of the second diamond
858 anvil before proceeding to the image plate. For each pressure, the sample pressure was allowed
859 to equilibrate for 20 min before collecting the pattern. The pressures ranged from ambient
860 (101.3 KPa) to 4.75 GPa. The ruby fluorescence technique was used offline to determine the
861 pressure [119]. The collected two-dimensional images were radially integrated using the Fit2D
862 program to produce 2 Θ vs. relative intensity plots [120].
863
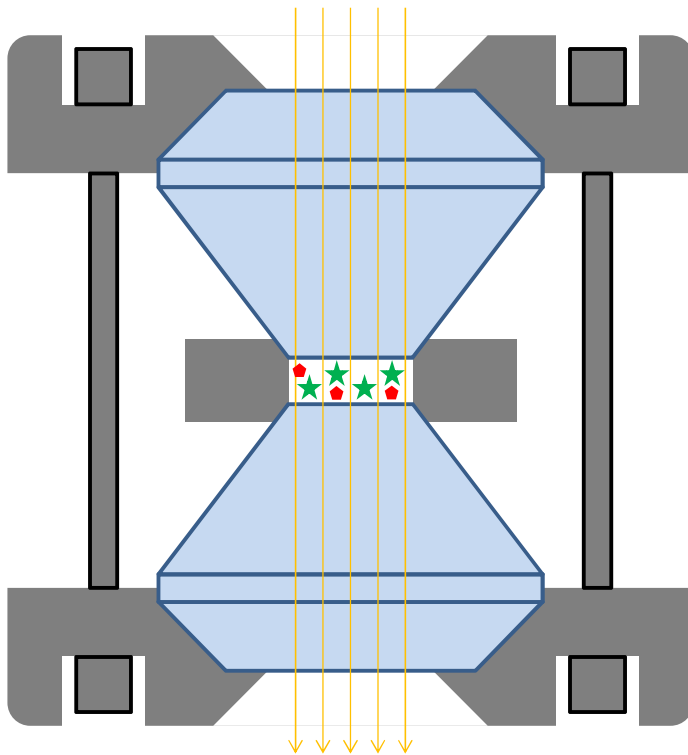
864
865 Figure 4: Two screw diamond anvil cell schematic.

22

866
867 After radially integrating the diffraction patterns, the data was imported into the MAUD
868 program [121]. First, the LaB$_6$ pattern was refined to determine the diffraction instrument's
869 parameters. The first parameters were refined the background, scale, and anisotropic
870 temperature factors. Crystallite size and microstrain was set to 5,000 Å and 1.0E-5,
871 respectively, because the LaB$_6$ standard was known to have large crystallites and low
872 microstrains. Arbitrary texture was selected to provide a full Le Bail fit. Next, the detector
873 distance, center displacement in x and y, and tilting error in x and y were refined. Then, the
874 instrument broadening parameters (peak width, asymmetry, Gaussianity) were refined [122].
875 Wenk et al. [123] have a more detailed account of how to determine the instrument parameters
876 for synchrotron XRD experiments.
877
878 The instrument parameters were then fixed, and the high pressure XRD data was analyzed to
879 determine the lattice parameters. The background, scale, and lattice parameters were refined in
880 the range of 5 - 18° 2Θ. The anisotropic thermal parameters were bound to 1 to avoid refining
881 to unreasonable values. Likewise, the lattice parameter b was constrained to be 1.00069x the
882 lattice parameter a, which was their ratio given by Calos et al. [35]. This was done to avoid the
883 refinement from arbitrarily changing the a or b lattice parameters (depending on which lattice
884 parameter began lower, it would be decreased and the other would be increased without the
885 constraint).

886 **2.2.2 C$_4$A$_3$\$ Hydration in the Presence of Gypsum and Calcium Hydroxide**

887 **2.2.2.1 Soft X-ray Microscopy**

888 Soft X-ray microscopy operating in the water window (between 2.34 and 4.40 nm photon
889 wavelength) combines a high lateral resolution (few tens of nm range) with the ability to
890 penetrate several µm of aqueous solution, which makes it an ideal in-situ technique to study wet
891 nanostructured materials. To allow for sufficient transmission of the soft X-rays a small droplet
892 of the suspension to be examined was placed in the sample holder, where it was squeezed
893 between two silicon nitride windows. Variations in window spacing account for most of the
894 variation in illumination time. The X-ray optical setup of the soft X-ray microscope, XM-1,
895 which is operated at the Advanced Light Source in Berkeley CA is illustrated in Figure 5 and is
896 described in more detail elsewhere [124]. All samples were analyzed three times with multiple
897 sites being observed per sample.
898
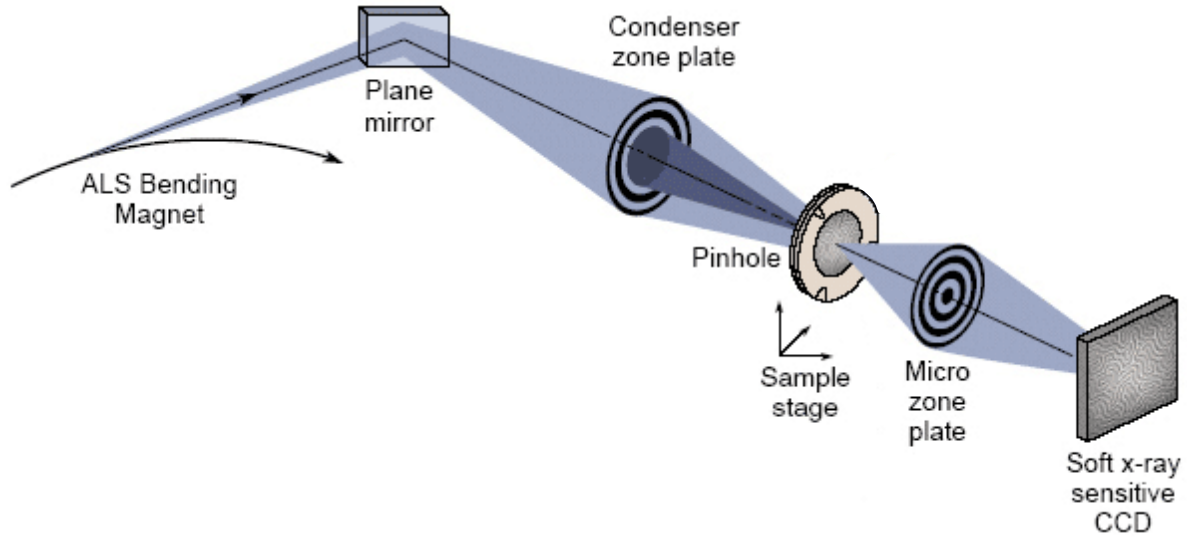
Figure 5: Transmission X-ray microscope schematic from [125].

The amount of time that each site was observed was kept to a minimum (~30-60s to focus) to limit introducing artifacts from the X-ray beam. No artifacts, such as accelerated dissolution of cement or hydration products or the formation of precipitates due to localized heating of the observation site, were observed in any of the experiments presented. Carbonation was not observed in any of the samples presented. The selected images presented in this paper summarize the behavior shown in all samples. Two different suspensions were investigated. Suspension one (S1) was prepared by adding 0.0400±0.0001 g of $C_4A_3\$$ to 2.00 ml of the pre-saturated solution of $C\$H_2$ and CH, hand-mixing for 50 s and then centrifuging in an Eppendorf vial for 15 s to remove most of the particles larger than 5μm in diameter, so the suspension would fit between the windows of the microscope cell. In a second series of suspensions, suspension two (S2) was prepared by adding 0.0040 g solid CH to 0.0400 g of $C_4A_3\$$ to 2.00 ml of the pre-saturated solution of $C\$H_2$ and CH to assure that sufficient excess CH would be present during the early hydration, which essentially guarantees that no AH_3 will form and better simulates the conditions found at early ages in many real CSA cements such as ASTM Type K shrinkage-compensating cement.

2.2.2.2 Scanning Electron Microscopy

The scanning electron microscopy investigations used the same suspensions and mixing protocol as the soft X-ray microscopy investigations. The suspensions were then poured onto sample stubs and allowed to hydrate for 2 hours before being dried in a vacuum desiccator for 24 hours. The samples were then coated in Au or C depending on whether the samples were intended for topographic or spectroscopic investigations. The SEM used was a Zeiss EVO MA10®. Energy dispersive spectrometry (EDS) was conducted utilizing a 15-25 keV accelerating voltage and 1-2 nA beam current. Quantitative stereo microscopy was conducted to make accurate length and angle measurements from the SEM images. Two images were taken of the same site with a 5° tilt angle difference, α, between the 2 images to create a stereo pair, see Figure 6. The electron beam was assumed to be moving parallel to the optic axis (Magnifications>>100x), and eqs. (9)-(12) were utilized to determine the 3D positions of features from the 2D images where M is the

929 magnification, X_L denotes the X position on the left image, and uppercase letters (X_{3d}, Y_{3d}, Z_{3d})
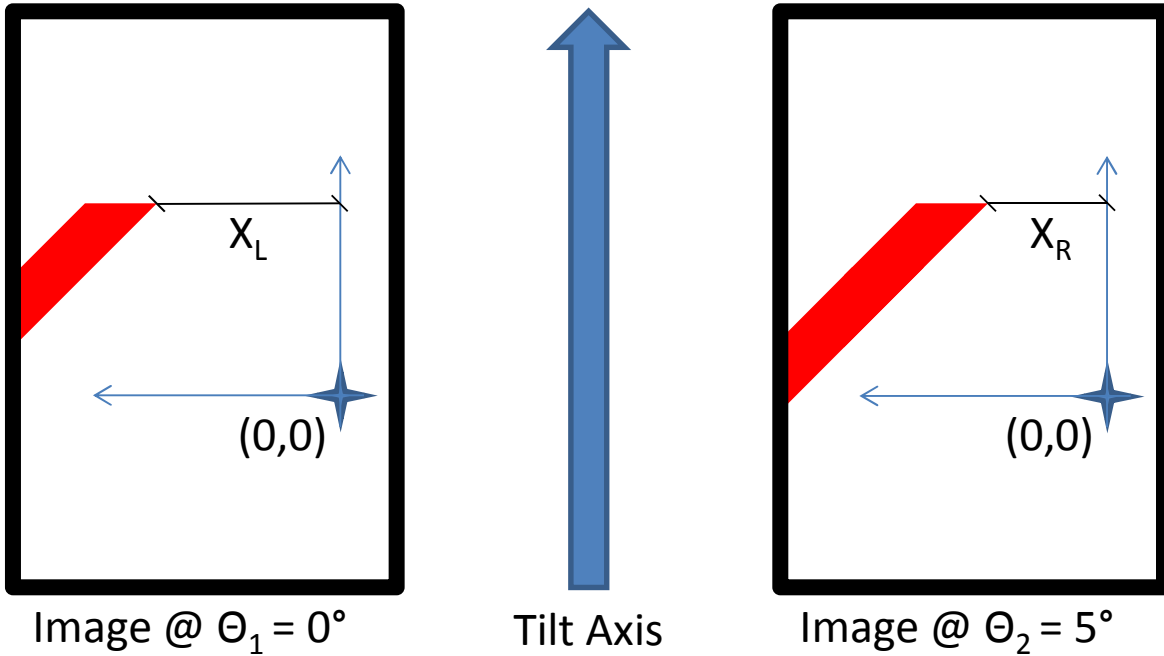930 denote the 3D coordinates [126].
931

932 $$P = X_L - X_R \tag{9}$$
933 $$M*Z_{3d} = P/(2\sin(\alpha/2)) \tag{10}$$
934 $$M*X_{3d} = X_L - P/2 = X_R + P/2 \tag{11}$$
935 $$M*Y_{3d} = Y_L = Y_R \tag{12}$$
936

937
938 Figure 6: Schematic of quantitative stereo SEM setup after [126].

939 **2.2.2.3 In-Situ X-ray Diffraction**

940 In-situ XRD investigations on the suspension without excess CH (S1) were carried at the X-ray
941 powder diffraction (XPD) beamline in the Brazilian Synchrotron Light Laboratory (LNLS) at
942 Campinas, São Paulo, Brazil. The solution was mixed at LNLS then a capillary was filled with
943 the liquid media and analyzed utilizing a X-ray wavelength of 1.5418Å in the angle ranges of 7º
944 to 13º 2θ and 20º to 27º 2θ, to follow the ettringite formation and the $C_4A_3\$$ peaks, respectively.
945 The solution to solids ratio was lowered from 50 to 10 to generate a larger signal from the X-rays
946 diffracting off the crystalline phases. The method was based on Dreele (2006) [127]. The X-ray
947 source is a 1.67 T bending magnet of the LNLS ring operating at 1.37 GeV [128] with a typical
948 initial average current of about 270 mA and 20 h lifetime. The critical energy of the emitted
949 photons is 2.08 keV. The beamline operates in the energy range between 4.5 to 15 keV (2.76 –
950 0.83 Å) with a maximum horizontal acceptance of about 10 mrad. The X-ray optical setup of
951 XPD is described elsewhere [129].

952 **2.2.2.4 Isothermal Conduction Calorimetry**

953 To better understand the effect of CH on $C_4A_3\$$ in the presence of $C\$H_2$, pastes were prepared by
954 mixing $C_4A_3\$$ with mass replacements of 15% $C\$H_2$ and 0, 1, 2, 5, or 10% CH. All $C_4A_3\$$

25

955 pastes were prepared with a water/solids (w/c) of 1, and when used as a comparison, PC pastes
956 were produced from a Type I/II PC using a w/c of 0.5. Table 2 contains the five paste mix
957 proportions. The paste mixes are labeled according to their CH content, such as P0 for the paste
958 mix with 0% CH.   Dry solids were first premixed to promote homogeneity. All pastes were
959 hand mixed with a metal spatula for 2-3 min. All water used was de-ionized and de-aired.
960
961 Table 2: $C_4A_3\$$ paste mix proportions.

	0% CH		1% CH		2% CH		5% CH		10% CH	
	Wt (%)	Mol. Ratio	Wt (%)	Mol. Ratio	Wt (%)	Mol. Ratio	Wt (%)	Mol. Ratio	Wt (%)	Mol. Ratio
$C_4A_3\$$	85	1	84	1	83	1.00	80	1	75	1
CH	0	0.00	1	0.10	2	0.19	5	0.49	10	0.98
$C\$H_2$	15	0.63	15	0.63	15	0.63	15	0.63	15	0.63
C / \$	2.8		2.9		3.0		3.1		3.4	
A / \$	1.8		1.8		1.8		1.8		1.8	

962
963 Pastes were tested for heat evolution using an isothermal conduction calorimeter (Thermometric
964 TAM Air®). Two grams of solids, a w/c of 1, and internal mixing were utilized. The powders
965 were dry mixed.   Then the samples were placed in the calorimeter and allowed to equilibrate for
966 48 hours, a 30 min. baselines were collected (<10μW/sample)   before the mix water was
967 injected, and the pastes were mixed for 2 min. via the injection ampoules. Hydration was
968 evaluated for 9 hours at 23˚C.

969 **2.2.2.5 X-ray Diffraction**

970 $C_4A_3\$$ pastes were prepared in the aforementioned manner in a nitrogen glove box to prevent
971 carbonation and were kept sealed in Eppendorf vials until hydration was stopped by grinding in
972 an excess of acetone. Hydration was stopped at 30 min., 1 h, 2.5 h, 1 d, and 7 d. XRD patterns
973 were collected on a PANalytical X'Pert PRO with X'Celerator® position sensitive detector
974 operating at 40 kV with 40 mA using a cobalt target (Co Kα wavelength 1.79 Å) and an iron
975 filter. Scans were collected from 5–75° 2θ at a 0.6°/min scan rate.

976 **2.2.2.6 Dimensional Stability**

977 $C_4A_3\$$ pastes were prepared in the aforementioned manner and cast into bars (1x1x4 cm) with
978 steel gauge studs in there ends. The polycarbonate molds were filled in two lifts tamping each
979 lift approximately 25 times. After tamping, the excess was screeded off, the molds were
980 covered with polyethylene film and placed in a room at 100% R.H. at 23°C. After 24 hrs, the
981 paste bars were demolded and placed in 100 ml of deionized water. The samples were then
982 measured daily for length changes. After 10 days of hydration the samples were allowed to air
983 dry for 10 days and then were reimmersed in water, in order to determine the effects of a drying
984 and rewetting cycle on the paste bars.

2.2.3 $C_4A_3\$$ Hydration in the Presence of Calcite and Vaterite with Varying Gypsum

The study utilized six mixes proportioned by weight where the mass of $C_4A_3\$$ was replaced by percentages of $C\$H_2$ 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. Note that the sample names are not subscripted to help indicate them as samples and differentiate them from $C_4A_3\$$ as a material. For instance, the sample C4A3$ would be 100% $C_4A_3\$$, and the sample C4A3$_G15_C10 would be 75% $C_4A_3\$$, 15% $C\$H_2$, and 10% calcite respectively. The six reagent proportions used in the study are C4A3$, C4A3$_C10, C4A3$_V10, C4A3$_G15, C4A3$_G15_C10, and C4A3$_G15_V10.

Mortar samples were made using a sand to cementitious material ratio of 2.75 and a water to cementitious material ratio (w/cm) 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 x 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 hrs, the samples were demolded. For compression tests, the mortars cubes (1.27 cm [0.5 in.]) were stored at 23˚C and 100% R.H. with a bell shaped dome over them to minimize dripping on the samples and a plastic 1.2 cm plastic grid under them to ensure constant humidity. Ten mortar cubes per mix per testing date were tested in compression utilizing a loading rate of 0.34 MPa/s (50 psi/s). Compression tests were conducted at 1, 7, 28, and 84 d of hydration. For dimensional stability tests, mortar bars (1x1x4 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. Three mortar bars were prepared for each mix. After 24 hrs 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 C807 [130]. Initial set was taken to be a 10 mm penetration of the needle and final set was considered to be when the needle no longer left an impression on the mortar surface.

Pastes for the six mixes were prepared using a w/cm 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 1d, 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 d 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 5–75° 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 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.

1029   Pastes were tested for heat evolution using an isothermal conduction calorimeter (Thermometric
1030   TAM Air[®]). Four grams of solids and a w/cm of 0.8 were utilized to provide ample signal.
1031   Before mixing 30 min. baselines were collected ($<10\mu W$/sample). The reagents were dry
1032   mixed, then mixed for 2 min. externally. A larger sample mass, a w/cm of 0.8, and external
1033   mixing were utilized because internal mixing with 2 g of solids and a w/cm of 1 was giving
1034   inconsistent results which we believe arose from some difficulties in getting the vaterite to
1035   disperse homogenously and not settle with internal mixing. Hydration was evaluated for 48 hrs
1036   at 23˚C.

1037 CHAPTER 3: $C_4A_3\$$ STRUCTURE EVALUATION AND BULK MODULUS
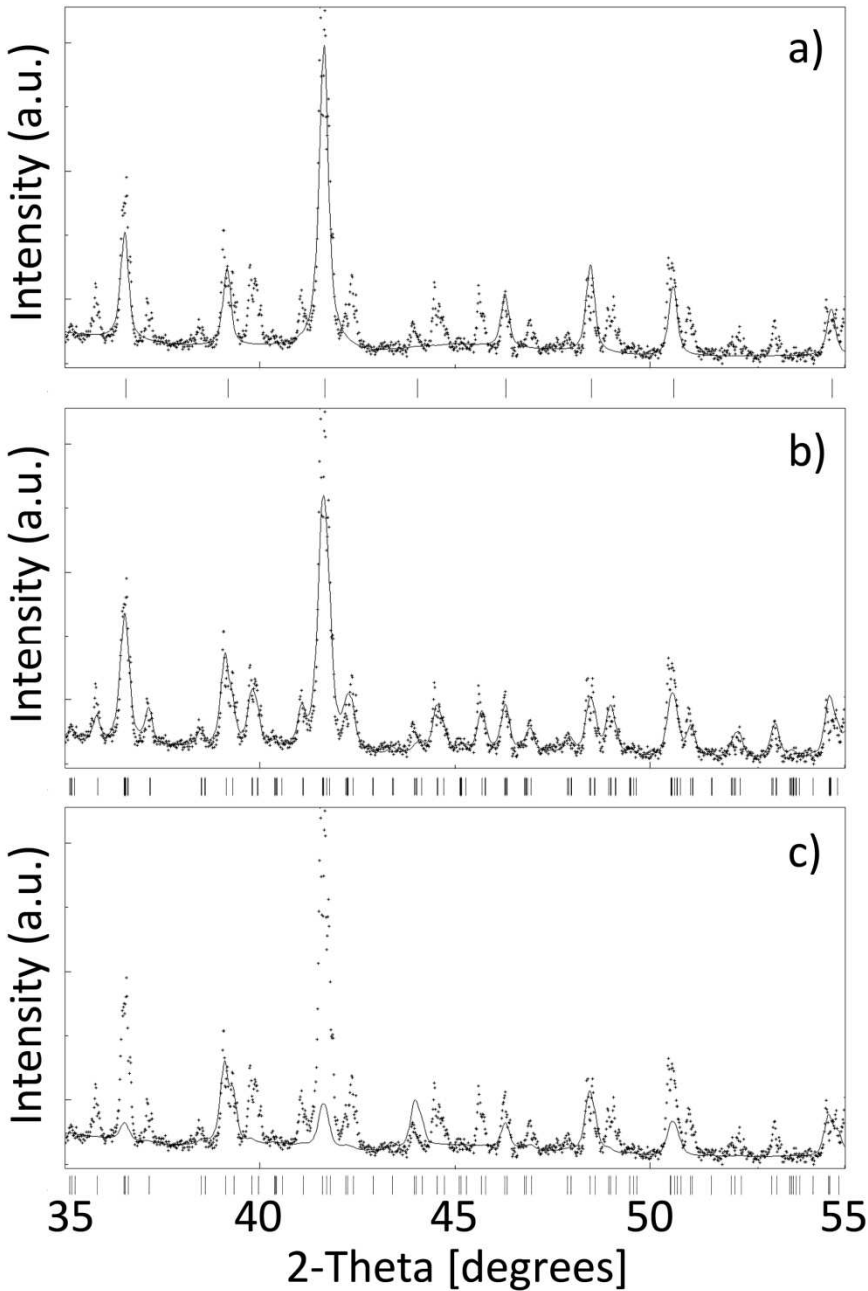## 1038 DETERMINATION

1039 3.1 $C_4A_3\$$ Structure Evaluation

1040   To determine how well the cubic subcell [34], orthorhombic unit-cell [35], and tetragonal unit-
1041   cell [36] (Table 3) describe the synthesized $C_4A_3\$$, Rietveld refinements were performed (Fig.
1042   A2) using the MAUD program [121], and the only parameters refined were the background,
1043   sample displacement, X-ray intensity, and lattice parameters. Only varying these parameters
1044   allows the merit of a few of the published crystal structures to be evaluated. The cubic subcell
1045   with space group $I\bar{4}3m$ was selected instead of the full cubic unit cell because atomic positions
1046   are not given for the space group $I4_132$. Figure 7 illustrates how many of the weaker reflections
1047   (superstructure reflections) are not produced by the cubic subcell crystal structure. Comparing
1048   Figure 7b and Figure 7c, one can see that both the orthorhombic and tetragonal crystal structures
1049   produce reflections at all the observed peaks, but the orthorhombic crystal structure does a much
1050   better job of matching the observed peak intensities. Consequently, the orthorhombic crystal
1051   structure of Calos et al. [35] appears to be the most accurate crystal structure, presently
1052   proposed, for $C_4A_3\$$. This result is not unexpected since Calos et al. considered the probable
1053   symmetry breakdowns from the space group $I\bar{4}3m$ (which describes the maximal symmetry of a
1054   collapsed aluminate sodalite cage) through the maximal subgroups that result from symmetry
1055   reductions to select Pcc2 [51]. Likewise, they took into account the various distortions that
1056   aluminate sodalites can undergo in order to accommodate various caged ions including: partial
1057   collapse and tilting of the alumina framework tetrahedra, tetragonal orientation of the caged
1058 XO_4^{2-} anion, twinning, and modulation of the structures [41].
1059
1060   Table 3: Initial unit-cell parameters for the crystal structures.

| Cubic [34]		Orthorhombic [35]				Tetragonal [36]		
a (Å)	Space Group	a (Å)	b (Å)	c (Å)	Space Group	a (Å)	c (Å)	Space Group
9.20	$I\bar{4}3m$	13.028	13.037	9.161	Pcc2	13.031	9.163	$P\bar{4}c2$

1061

Figure 7: Comparison of calculated peak positions and intensities for a) cubic subcell [34], b) orthorhombic unit-cell [35], and c) tetragonal unit-cell [36].

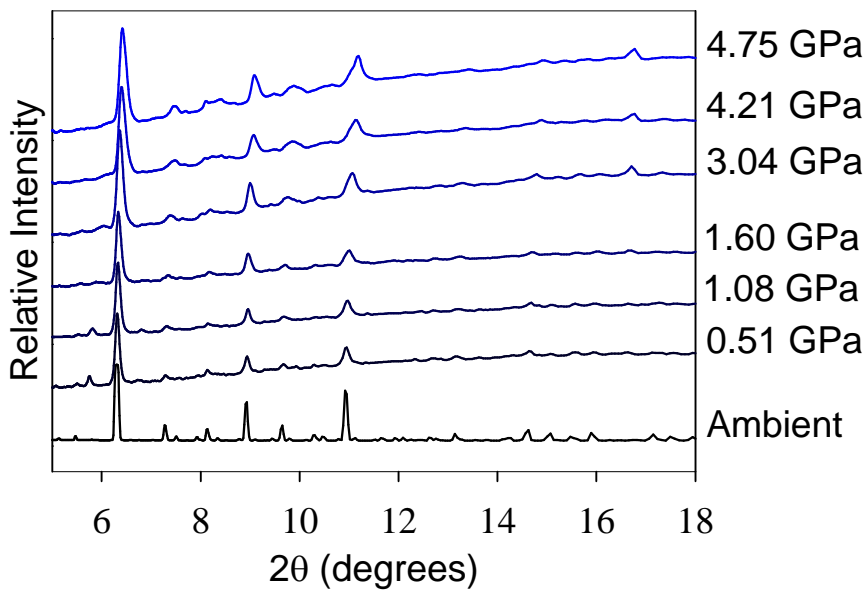## 3.2 C$_4$A$_3$$\bar{S}$ Bulk Modulus Determination

Figure 8 shows the 2D diffraction pattern of C$_4$A$_3$$\bar{S}$ in ambient conditions. After integrating radially, the plot of intensity vs. 2Θ is obtained, Figure 9. Figure 9 shows the diffraction patterns as a function of pressure, and the d-spacings of C$_4$A$_3$$\bar{S}$ decrease (peaks shifting to larger 2Θ) with increasing pressure as expected.
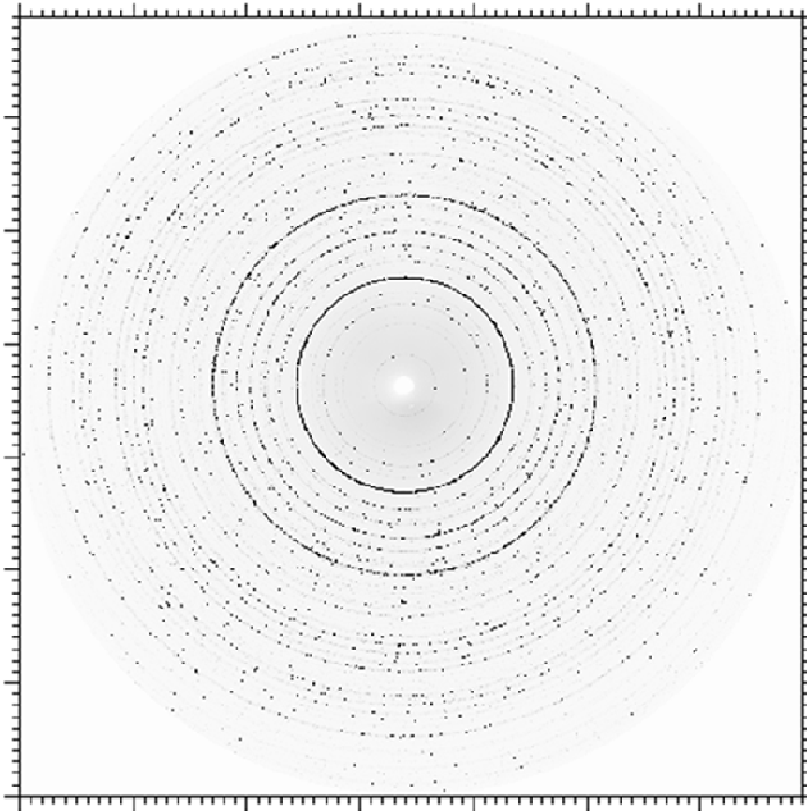
1071
1072   Figure 8: Ambient $C_4A_3\$$ X-ray powder diffraction pattern.

1073
1074   Figure 9: Integrated X-ray powder diffraction pattern for $C_4A_3\$$ from ambient pressure to 4.75
1075   GPa.

1076   Figure 10 shows how the lattice parameters change with pressure. The cubic lattice parameter, a,
1077   appears to have a more uniform contraction than the orthorhombic cell parameters; however, the

30

1078 variability in the orthorhombic cell parameters is most likely a result in the difficulty of fitting
1079 the lattice parameters to a crystal structure that has so many overlapping reflections; however the
1080 variability in the orthorhombic lattice parameters averages out and all crystal structures volumes
1081 show a contraction of approximately 5.5(2)% from 0.51 to 4.75 GPa.
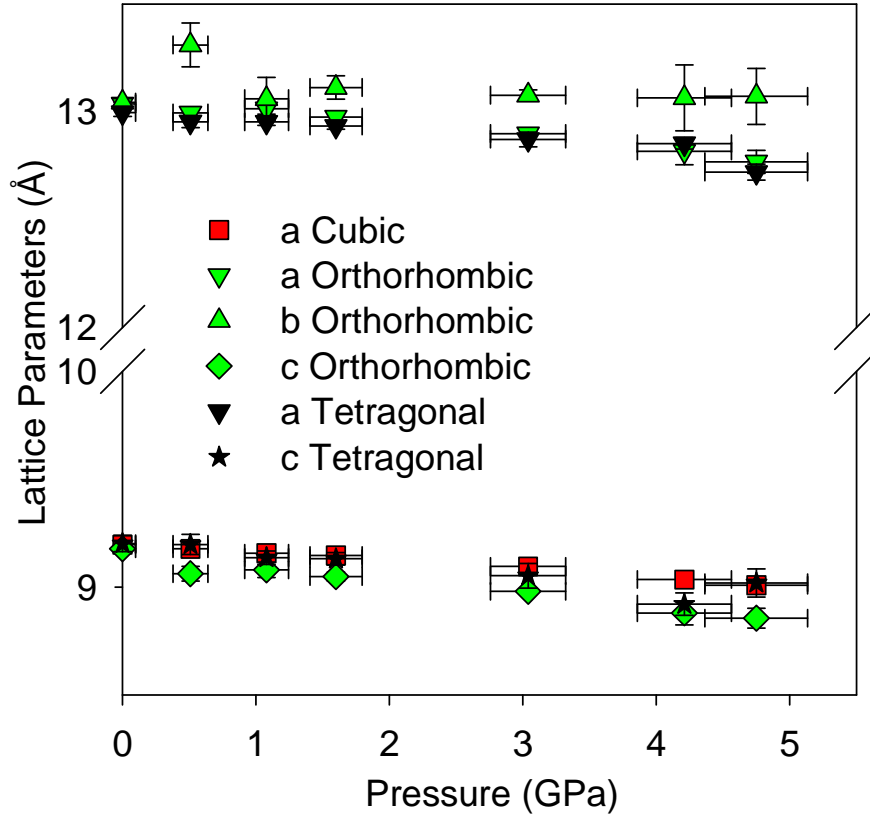
1082
1083 Figure 10: Change in lattice parameters as a function of pressure.

1084 Figure 11 illustrates the pressure dependent behavior of the unit-cell's volume. Additionally, the
1085 Birch-Murnaghan equation of state (B.M. EOS) [131] assuming $K'_0=4$ is plotted, Eqn. 13.
1086 Additionally, the Eulerian strain (Eqn. 14) and normalized pressure (Eqn. 15) can be defined and
1087 used to reorganize the B.M. EOS into the simpler linear form (Eqn. 16).
1088

1089 3rd Order B.M. EOS: $\quad P=1.5K_0\left[\left(V_0/V\right)^{7/3}-\left(V_0/V\right)^{5/3}\right]\left[1+0.75\left(K'_0-4\right)\left\{\left(V_0/V\right)^{2/3}-1\right\}\right]$ $\quad\quad$ (13)

1090 Eulerian Strain: $\quad\quad f=0.5\left[\left(V_0/V\right)^{2/3}-1\right]$ $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ (14)

1091 Normalized Pressure: $\quad F=P/[1.5\{\left(V_0/V\right)^{7/3}-\left(V_0/V\right)^{5/3}\}]$ $\quad\quad\quad\quad\quad\quad$ (15)

1092 Linear form of B.M. EOS: $\quad\quad F(f)=K_0-1.5K_0(4-K'_0)f$ $\quad\quad\quad\quad\quad\quad\quad$ (16)

1093
1094 Due to different conditions in ambient XRD versus in high pressure XRD with the diamond anvil
1095 cell, a g-G plot was used to find $C_4A_3\$$'s initial state cell volume in the diamond anvil cell [132].
1096 Second order B.M. EOS ($K'_0=4$) were fitted with R^2 = 0.986, 0.990, 0.990 for the cubic,
1097 orthorhombic, and tetragonal cases, respectively. There was no sign of rearrangement or

31

1098 abnormal compressibility in the diffraction patterns or in the pressure dependent response of the
1099 volume. The largest propagated error from the refined lattice parameters to the cell volume was
1100 0.01 Å^3.

1101
1102 Figure 11: Pressure dependent unit-cell volume change normalized to the ambient volume.

1103 Figure 12 shows the normalized pressure, F, as a function of the Eulerian Strain, f, see Eqns. 14-
1104 15. From the plot, it is clear that the bulk modulus (where the B.M. EOS intercepts the y-axis) is
1105 69(6) GPa. The propagated error mostly arises from the utilization of the ruby fluorescence
1106 technique to determine the pressure offline. Due to the remaining uncertainty about the crystal
1107 structure of $C_4A_3\$$, the analysis was also performed utilizing the cubic subcell. The difference in
1108 the bulk modulus calculated using the orthorhombic structure or the cubic subcell was less than 1
1109 GPa. The bulk modulus is relatively low due to the open and tilted sodalite framework when
1110 compared to other minerals that have denser packing such as 239(4) GPa for corundum (α-
1111 Al_2O_3) [133]. For a clinker mineral, the atomistic framework and the type of uptaken ion are
1112 important in its compressibility and reactivity [134]. For example, in a unit cell of C_3A, there are
1113 72 cavities consisting of Al_6-O_8 rings filled with a Ca atom and eight empty cavities. Even
1114 though C_3A is quite incompressible {102(6) GPa}, the 8 empty cavities make the whole system
1115 quite reactive with water [134]. Likewise, $C_4A_3\$$'s large crystal structure porosity and relatively
1116 higher internal energy and activity make it relatively unstable and reactive with water [44].
1117 $C_4A_3\$$'s bulk modulus is higher than reported bulk moduli for hydrated cementitious phases,
1118 27(7), 37.8(1), 32(2), and 54(4) GPa for ettringite, CH, hemicarboaluminate, and

32

1119   monocarboaluminate, respectively [135-138].
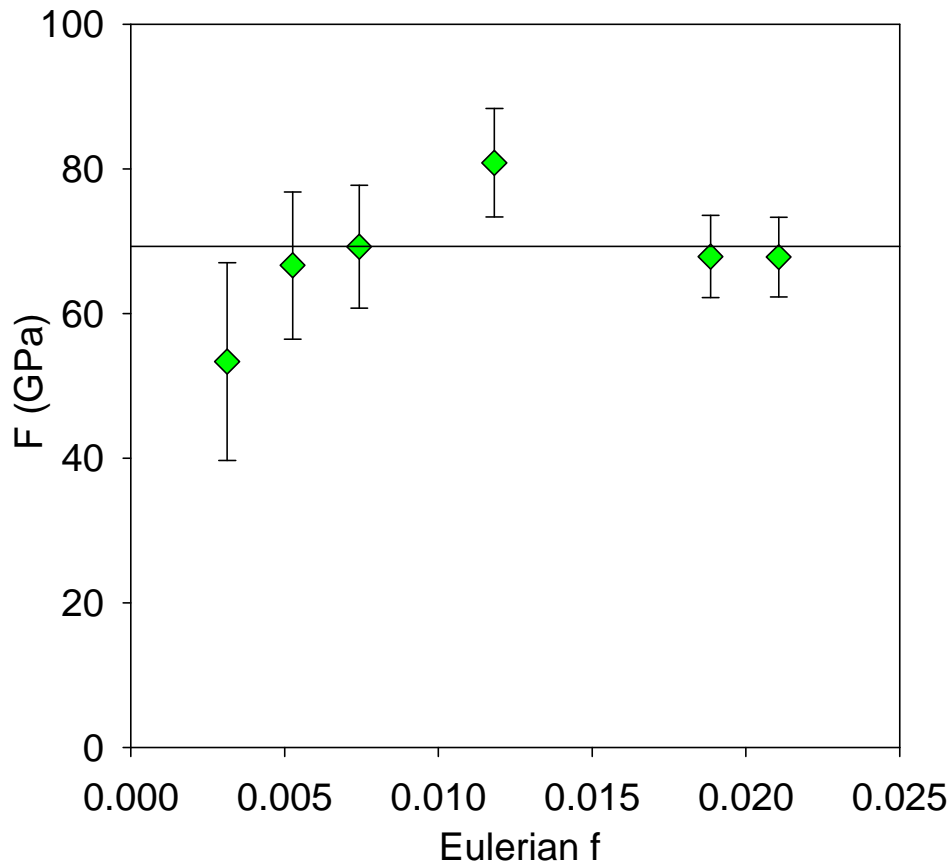
1120
1121   Figure 12: Normalized pressure, F, as a function of Eulerian strain, f, for orthorhombic crystal
1122   structure.

1123 $C_4A_3\$$'s bulk modulus is higher than some other sodalites' bulk moduli of 52(8) GPa for
1124 $Na_8(AlSiO_4)_6Cl_2$ [139] or 43(4) GPa for $Na_8(AlSiO_4)_6(OH)_2 \cdot H_2O$ [140], which have monovalent
1125   caged ions and silicon in the framework. The higher bulk modulus of $C_4A_3\$$ compared to the
1126   other sodalites listed can be in part explained by the higher charged anion and cation of $C_4A_3\$$
1127   compared to the other structures. As explained by Melzer et al. [141], with increasing charge of
1128   the anions and cations, the variation of lattice energy increases which decreases the
1129   compressibility of the lattice.   By comparing the bulk modulus of $C_4A_3\$$ with
1130 $Sr_8(Al_{12}O_{24})(CrO_4)_2$ (72 GPa calculated from [141]), which has the same aluminate cage and
1131   divalent cage ions, the effect that the caged ions' sizes have on the lattice compressibility can be
1132   observed. Ca^{2+} and Sr^{2+} have effective ionic radii of 1.12 Å and 1.26 Å, respectively, for
1133   coordination numbers of 8, and sulfate and chromate ions have bond distances of 1.50 Å and
1134   1.65 Å, respectively [142-144]. As the size of the caged ions increases, the compressibility of
1135   the lattice decreases, this makes sense structurally.

CHAPTER 4: C$_4$A$_3$\$ HYDRATION IN THE PRESENCE OF GYPSUM
AND CALCIUM HYDROXIDE

1138 **4.1 Dilute Suspension Experiments**

1139 **4.1.1 Soft X-ray Microscopy**

1140 Figure 13 shows in-situ soft X-ray images of hydrating C$_4$A$_3$\$ particles suspended in S1. Each of
1141 the three columns in each figure corresponds to a single position in the cell viewed for almost
1142 three hours. The elapsed time after mixing is indicated below each image, so that the evolution
1143 of each sample position can be followed by scanning down the columns. The scale bar in each
1144 image corresponds to 1 µm.
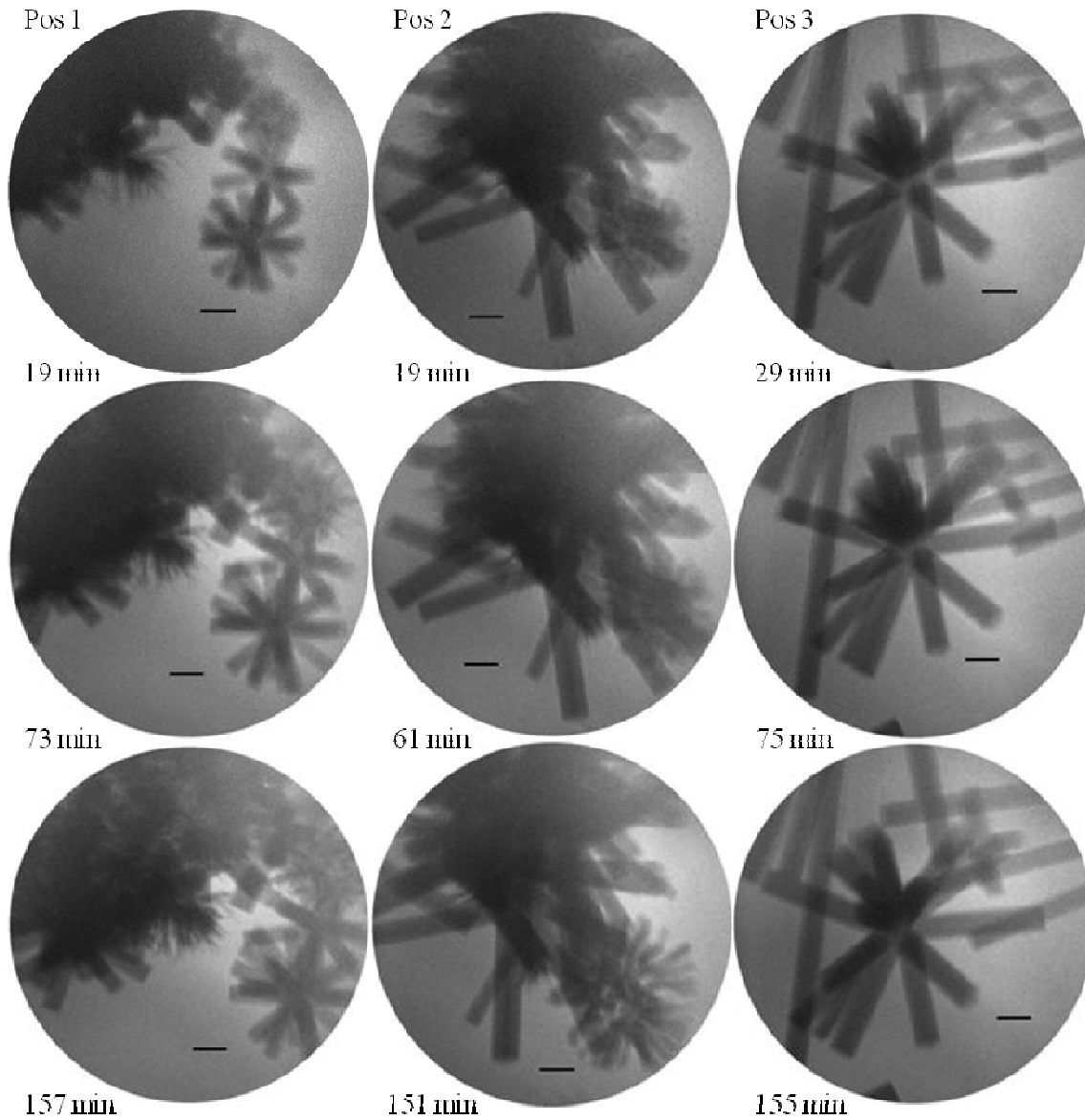
1145
1146 Figure 13: In-situ soft X-ray images of hydrating C$_4$A$_3$\$ particles in a saturated CH-C\$H$_2$
1147 solution, liquid/solid = 50 ml/g. Hydration time is indicated. Scale bar corresponds to 1 µm.

1148 Figure 13 shows that the majority of ettringite formed in this system occurred before the first
1149 images were taken (taken 19-29 minutes after mixing); however, certain sites do show evolution
1150 with time. This suggests that the hydration of small (< 5 µm) $C_4A_3\$$ particles is very rapid and
1151 was almost complete by the time the first image was recorded in the suspension without excess
1152 CH. However, some evolution with time occurs. The upper right hand corner of Position 1 and
1153 lower right hand corner of Position 2 show evidence of an amorphous hydrate evolving into a
1154 stellate (star-shaped) ettringite cluster. Most of the images in Figure 13 are dominated by large
1155 acicular crystals, typically of the order of 0.5µm in width and ranging from about 2µm to over
1156 10µm in length. Based on what is already known about $C_4A_3\$$ hydration and the morphology of
1157 the usual reaction products, there can be little doubt that this acicular phase is ettringite;
1158 however, this will be confirmed later in the discussion. What is somewhat more unusual,
1159 however, is the crystal habit of the ettringite clusters that are observed. Most of them are stellate
1160 polycrystalline clusters that give the appearance of having grown out from a single central point.
1161 Accordingly, the clusters on the bottom right hand side of the column representing Position 1 do
1162 show growth from the first image to the final image which confirms that the acicular crystals are
1163 lengthening by growing outwards from the center of the "star". It thus appears likely that this
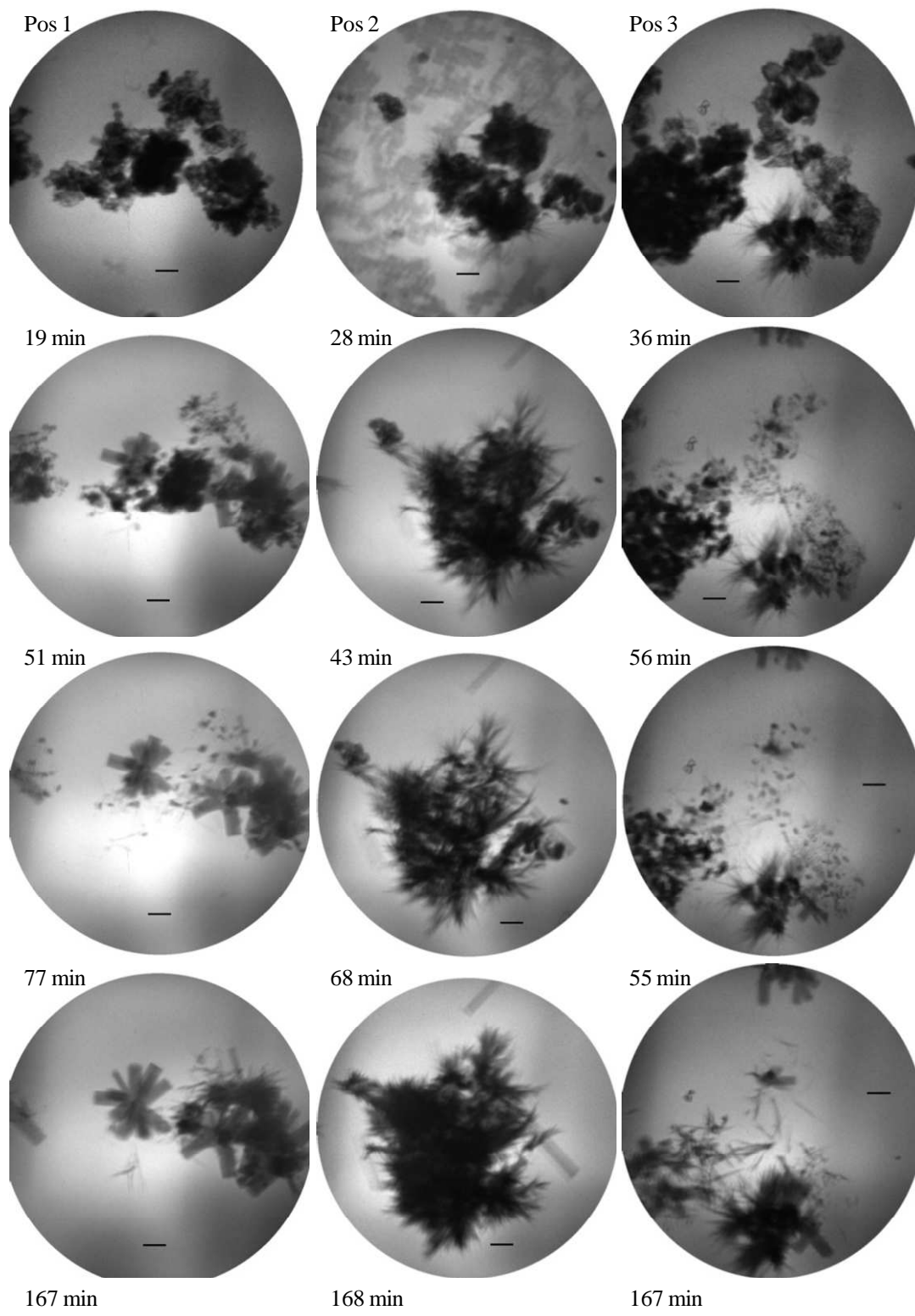1164 stellate growth pattern represents growth from a single central nucleus.
1165
1166 The question then arises about why such a growth form should occur. It is not easy to tell by
1167 looking at two-dimensional images such as these, but it seems possible that there may be defined
1168 angular relationships between the "arms" of each cluster, which brings to mind the possibility
1169 that twinning might be involved in the early growth phases. The possibility of twinning and
1170 defined angles between ettringite crystals is discussed more in the SEM investigation. As to why
1171 a stellate growth pattern should be favored at early ages in this system, this is probably related to
1172 details of the nucleation process. We hypothesize that a layer of amorphous hydrates initially
1173 forms around $C_4A_3\$$ due to its very rapid initial hydration. Due to surface energy considerations,
1174 the amorphous hydrate shells probably maintain a relatively spherical shape around small grains
1175 of $C_4A_3\$$. After a period of nucleation, well-defined ettringite crystals begin to form on the
1176 surface of the amorphous hydrate and then grow out radially forming stellate structures.
1177 Previous research has also shown the development of stellate ettringite (often referred to as
1178 spherulites, although this term implies that the radiating crystals are surrounded by a matrix). In
1179 2009, Komatsu et al. [145], showed the in-situ formation of ettringite from the reaction of CH
1180 with aluminum sulfate. They also observed stellate structures and found that the presence of
1181 small calcite crystals increased the amount and rate of stellate ettringite formation. Likewise,
1182 they confirmed in a SEM that calcite was at the core of the stellate cluster. Mehta [146] in 1976
1183 also showed ettringite growing in a stellate manner from the surface of C_3A immersed in a $C\$H_2$
1184 solution. Likewise, Lerch et al. in 1929 [147] presented a spherulite of ettringite that had grown
1185 in a mortar briquette, and Candlot [148] produced spherulites of 2 to 3 mm in diameter from
1186 mixed calcium aluminate and calcium sulfate solutions in 1890.
1187
1188 The images obtained from S2 with excess CH (Figure 14) are significantly different. At early
1189 ages (before about 40 minutes) we see almost no sign of the well-developed acicular crystals as
1190 seen in Figure 13. Well–developed ettringite crystals, which include some stellate clusters
1191 similar to but generally smaller than those seen in Figure 13, only become visible in the later
1192 images. We do see more of relatively dense clusters of very fine hair-like growths radiating from
1193 denser core particles which may well still contain anhydrous $C_4A_3\$$. These growths are very

reminiscent of the "sheaf-of-wheat" growth patterns seen around C_3S particles and PC grains in previous X-ray microscopy studies [149]. At the very early ages, we see what may well be the outlines of the original unreacted phases ($C_4A_3\$$ and also possibly solid CH) covered with a thin coating of what appears to be mainly an amorphous "gel" from which the hair-like crystals have already begun to grow at certain points such as the bottom center of Position 3. In the later images it is less easy to see any remnants of the original particles and a mixture of well-developed ettringite crystals similar to those of Figure 13 plus dense particles covered with a thick growth of fine hair-like products remain.

These observations suggest that the presence of excess CH initially retards the rate of ettringite formation, perhaps by stabilizing a gelatinous hydrate coating of poorly-crystalline phases on the hydrating grain's surface and, also, changes the morphology of some of the hydration products formed. This is consistent with the work of Mehta, who suggested that lime somewhat retards the formation of ettringite from $C_4A_3\$$ at early ages and causes smaller ettringite crystals to form [150]. Moreover, while studying hydration kinetics, Hanic et al. [151] found that hydration rates in some $C_4A_3\$$ systems with $C\$H_2$ and CH became diffusion limited, which implied that a hydration layer surrounded the reacting $C_4A_3\$$ grains.

To help determine how Figure 13 and Figure 14's high liquid/solids ratio was affecting the hydration products, a 5x lower liquid/solids of 10 was tested for S1, which lacked excess solid CH. A liquid/solids ratio of 10 approaches the limit of the wet cell experimental setup utilized. As was the case with the higher liquid/solids ratio, ettringite grew very rapidly and little growth occurred subsequently. Likewise, stellate and acicular ettringite crystal habits were observed.

Pos 1 · Pos 2 · Pos 3

19 min · 28 min · 36 min

51 min · 43 min · 56 min

77 min · 68 min · 55 min

167 min · 168 min · 167 min

1217
1218 Figure 14: In-situ soft X-ray images of hydrating $C_4A_3\$$ particles plus 10% solid CH in a
1219 saturated CH- $C\$H_2$ solution, liquid/solid = 50 ml/g. Hydration time is indicated. Scale bar is 1
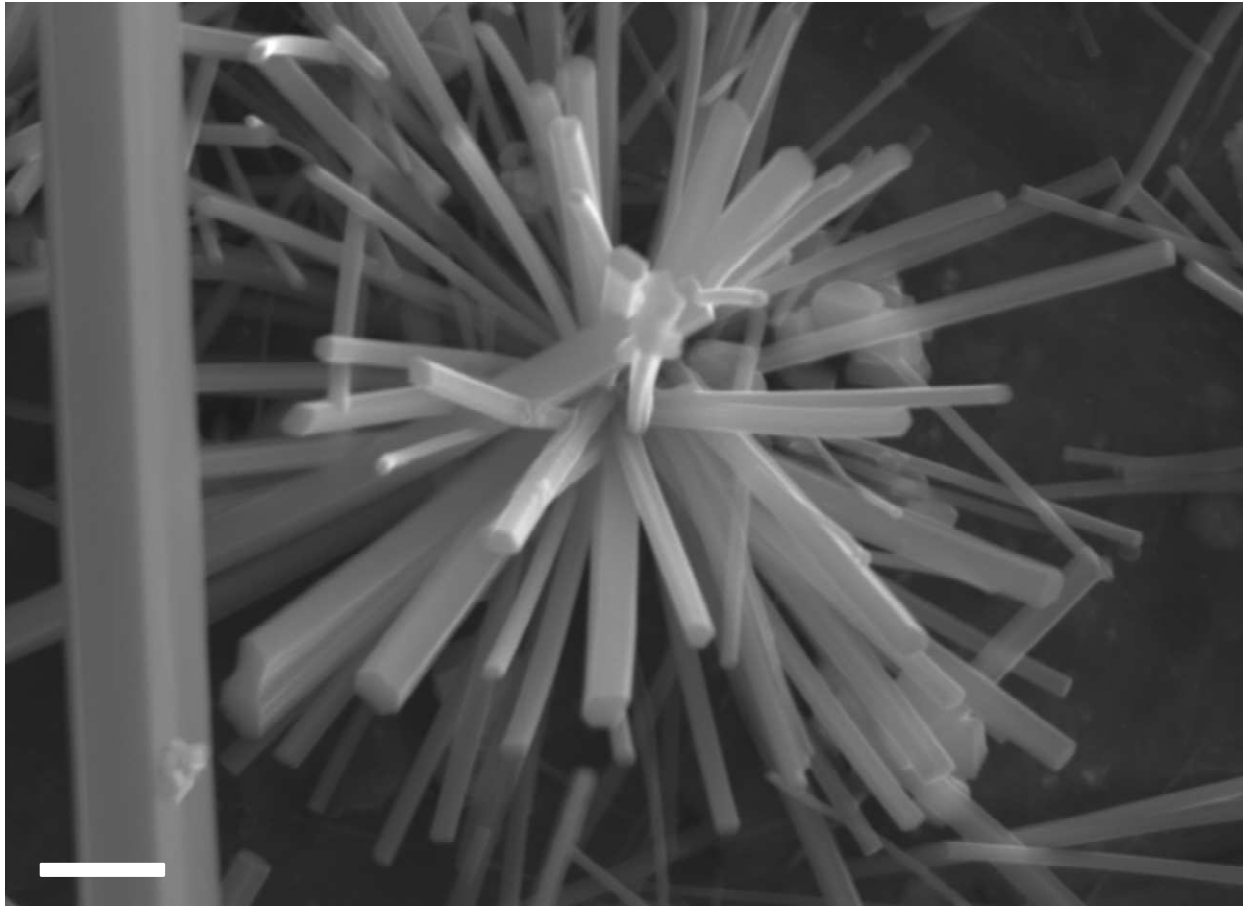1220 µm.

4.1.2 Scanning Electron Microscopy

1222 To confirm the observations made with the soft X-ray microscope and provide additional
1223 compositional information, ex-situ dried dilute suspensions were investigated using a SEM.
1224 Stellate ettringite crystals were observed in samples made from suspensions with and without
1225 excess CH, see Figure 15 & Figure 16. In addition to the stellate ettringite cluster in Figure 15,
1226 worm-like hydrates can be seen in the background; these worm-like structures are most likely
1227 poisoned ettringite crystals from organic compounds in the carbon tape placed on the mounting
1228 stubs before the dilute suspensions were placed on the mounting stubs. Only Figure 15 contains
1229 images from samples that were hydrated on stubs covered in carbon tape, and it is presented here
1230 to show the type of artifacts that can be introduced by hydrating samples on carbon tape. The
1231 rest of the SEM images contain samples that were hydrated directly on the mounting stubs
1232 without carbon tape to avoid any contamination.
1233
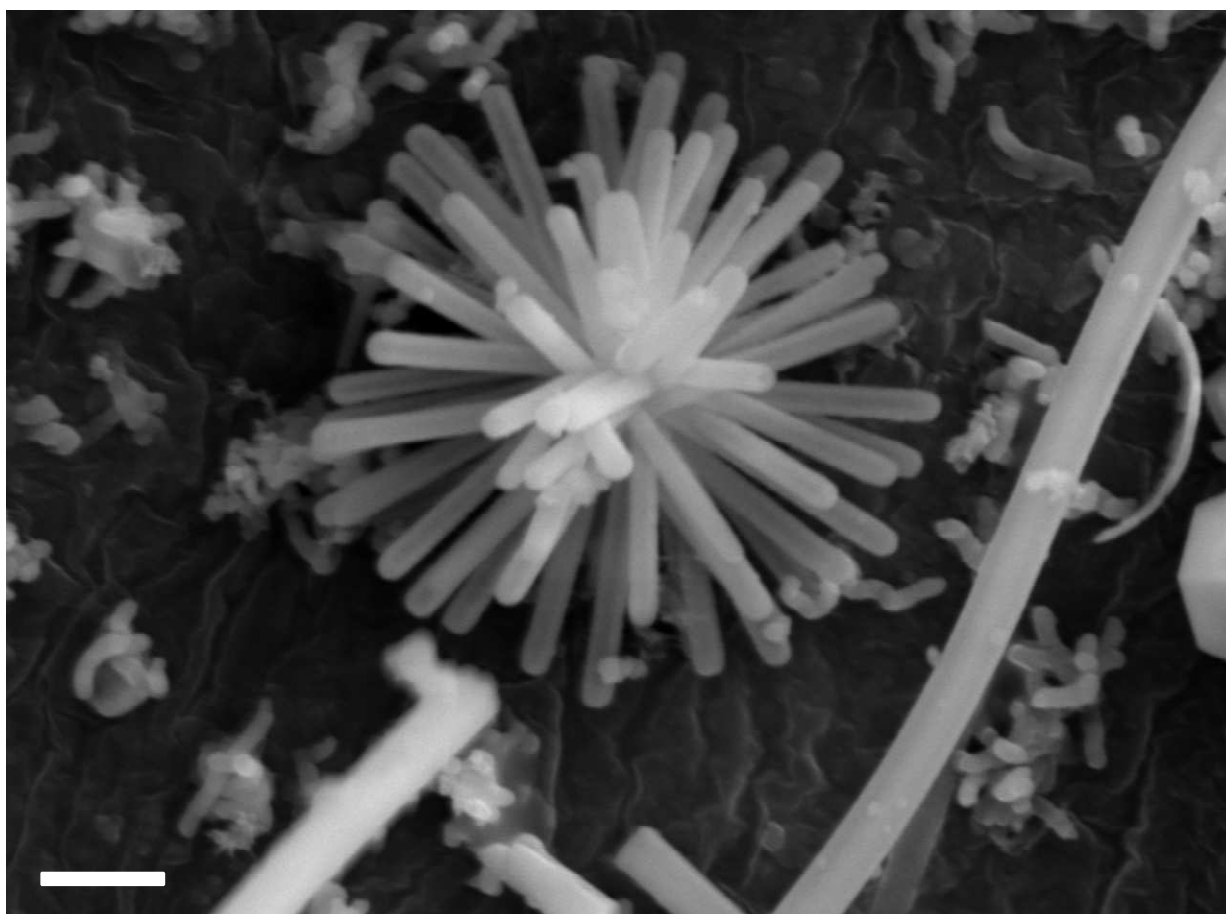
1234
1235 Figure 15: Ex-situ secondary electron (SE) SEM images of hydrating $C_4A_3\$$ particles in a
1236 saturated CH- $C\$H_2$ solution, liquid/solid = 50 ml/g. Hydration time was 2 hours. Accelerating
1237 voltage of 15.00 kV, a probe current of 248 pA, working distance of 12.0 mm, and scale bar is 2
1238 μm.

1239
1240 In Figure 16, another ettringite crystal can be seen penetrating from the lower left to the upper
1241 right of the stellate ettringite cluster, illustrating the beginning of ettringite crystals that began in

1242 separate regions and intergrew. Figure 17 presents an EDS spectrum from a stellate ettringite
1243 cluster. Several clusters were analyzed with EDS and were found to have similar compositions
1244 regardless of whether or not the suspension contained excess CH. The specimens were not flat,
1245 so the EDS results cannot provide accurate quantitative data, but they can be used to eliminate
1246 the possibility that the observed phases were other calcium aluminum hydrates with similar
1247 morphologies. The calculated Ca/S atomic ratio from Figure 17 was 2.2, which is close enough
1248 to the theoretical value of 2 for ettringite, considering the non-ideal EDS conditions.
1249

1250
1251 Figure 16: Ex-situ SE SEM images of hydrating $C_4A_3\$$ particles plus 10% solid CH in a
1252 saturated CH- $C\$H_2$ solution, liquid/solid = 50 ml/g. Hydration time was 2 hours. Accelerating
1253 voltage of 15.00 kV, a probe current of 248 pA, working distance of 14.0 mm, and scale bar is 2
1254 μm.

39

1255
1256   Figure 17: EDS Spectrum of stellate ettringite cluster collected with an accelerating voltage of
1257   15.00kV and a probe current of 2.0 nA.
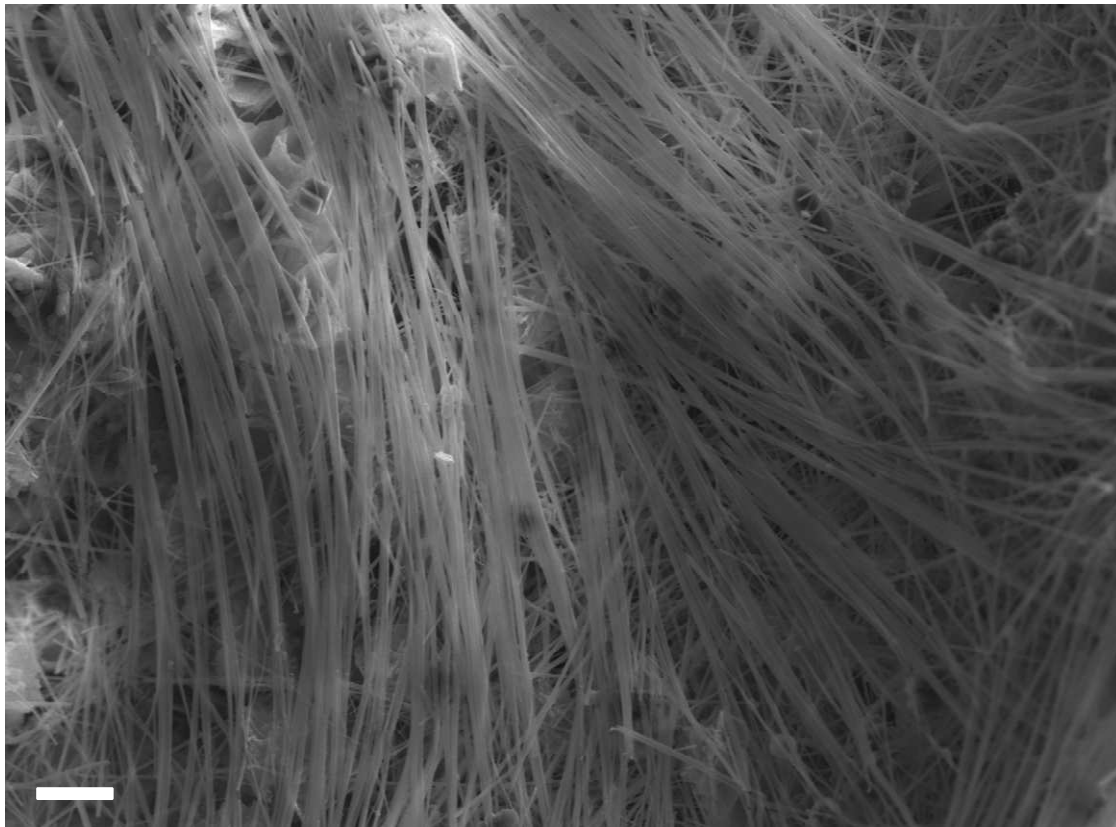
Voltage (kV)

1258
1259   Figure 18: Ex-situ SE SEM images of hydrating $C_4A_3\$$ particles plus 10% solid CH in a
1260   saturated CH- $C\$H_2$ solution, liquid/solid = 50 ml/g. Hydration time was 2 hours. Accelerating

1261 voltage of 15.00 kV, a probe current of 248 pA, working distance of 13.5 mm, and scale bar is
1262 10 μm.

1263 In suspensions made with excess CH, filiform (very long thin, hair-like) ettringite needles were
1264 common, see Figure 18. This crystal habit was absent in the suspensions made without excess
1265 CH. Rosettes of AFm were also much more common in the suspensions made with excess CH
1266 as were fields of reticulated (slender crystals intergrown in a lattice-like array) ettringite, see
1267 Figure 19. Both the suspensions with and without excess CH produced the typical acicular
1268 ettringite crystals.
1269

1270
1271 Figure 19: Ex-situ SE SEM images of hydrating $C_4A_3$$ particles plus 10% solid CH in a
1272 saturated CH- CH_2 solution, liquid/solid = 50 ml/g. Hydration time was 2 hours. Accelerating
1273 voltage of 15.00 kV, a probe current of 248 pA, working distance of 13.0 mm, and scale bar is
1274 10 μm.

1275 During the SEM and soft X-ray microscopy investigations many ettringite crystals were
1276 observed diverging and forming angles. These diverging crystals appeared to have originated
1277 from the same nucleus. Stellate ettringite clusters as well as small groups of crystals displayed
1278 this morphology. To determine if there was a common angle between all the diverging crystal
1279 groups which would imply that twinning could be the cause of the diverging crystals,
1280 stereoscopic measurements were made in the SEM to determine the true 3D angle between the
1281 crystals from the 2D images. Figure 20 shows a stereo pair of SE SEM images. The image on

1282 the left is tilted 5° off the electron beam axis in relation to the image on the right, and the same
1283 positions on the crystals are marked in each image. Small surface deposits or imperfections on
1284 the crystals were used for locations so that the exact same positions could be located between the
1285 2 images. The origin is selected as a very recognizable spot in both images and is subtracted
1286 from all the other coordinates measured; this corrects the measurements in case the image has
1287 drifted horizontally or vertically.   The positions of the image origin (O), crystal vertex (V), left
1288 (L), and right (R) crystals were determined, and the angle between the crystals was determined
1289 using the law of cosines. A wide distribution of angles (approximately 8° - 37°) was found
1290 implying that twinning was not the principal mechanism for creating the diverging angles. If
1291 twinning had been the principal mechanism then exactly the same angle(s) would have been
1292 encountered repeatedly due to crystal twinning laws.
1293
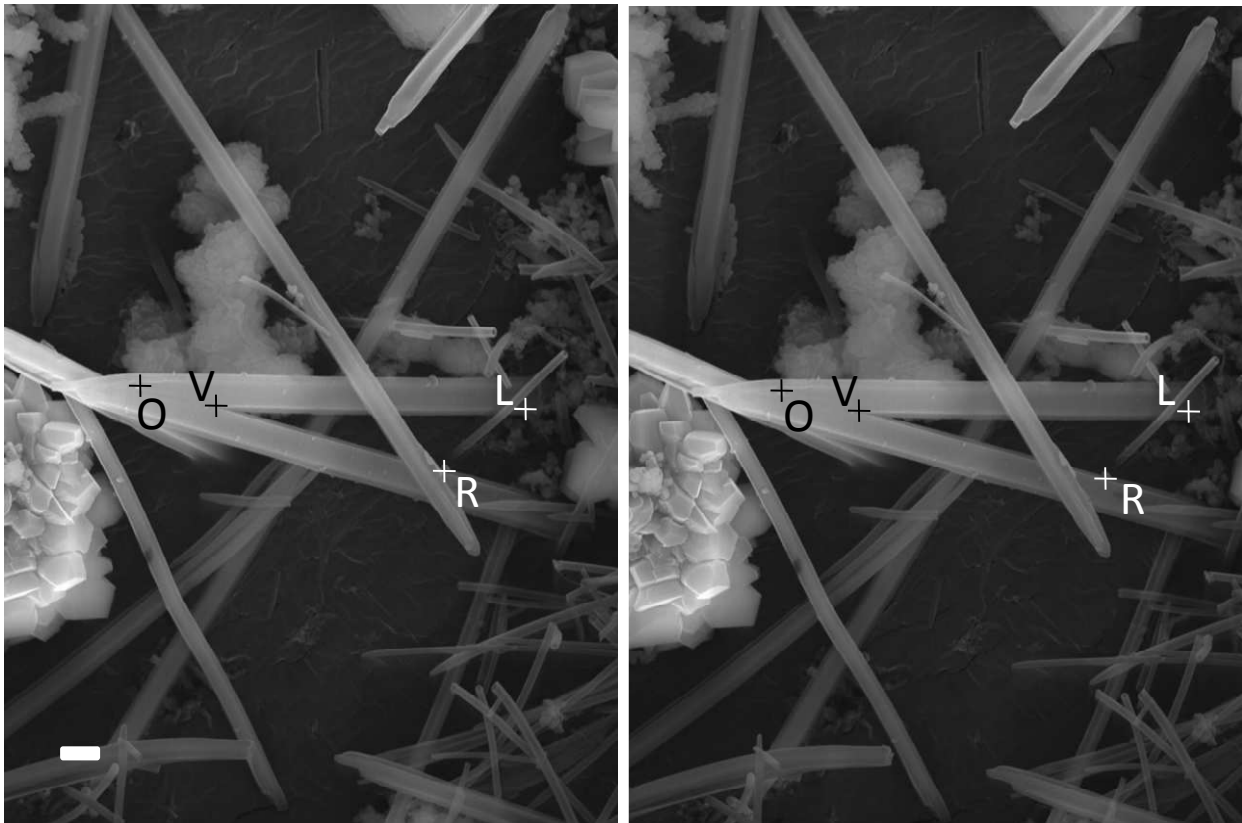
1294
1295 Figure 20: Stereo pair of SE SEM images. Image on the left is tilted 5° off the electron beam
1296 axis. Accelerating voltage of 25.00 kV, probe current of 101 pA, working distance of 20.0 mm,
1297 and scale bar is 2 μm.

1298
1299 A possible explanation for the distribution of angles encountered for the diverging ettringite
1300 crystals can be formulated based upon differences in the nucleation site's curvature. If the
1301 nucleation site was a perfectly flat plane then one would expect that the crystals growing off its
1302 surface would be parallel for the most part; however, as the nucleating plane becomes curved and
1303 crystals continue to grow normal to its surface then angles begin to form between the crystals.
1304 As the curvature of nucleation site becomes sharper or in other words as the radius of the
1305 nucleating site becomes smaller, the angle between the diverging crystals would become greater.

42

1306   Figure 21 provides an example of a stellate ettringite cluster with very different angles between
1307   the ettringite crystals compared to those of Figure 15 & Figure 16. We hypothesize that stellate
1308   ettringite clusters exist in pastes that contain $C_4A_3\$$ as a result of ettringite nucleating from the
1309   surface of the gelatinous hydrates that form on the surface of $C_4A_3\$$ grains. Additionally, the
1310   interpenetration of adjacent stellate ettringite structures could contribute to the strength of the
1311   matrix. Future research is needed to definitively establish the existence/role of stellate structures
1312   in pastes.
1313
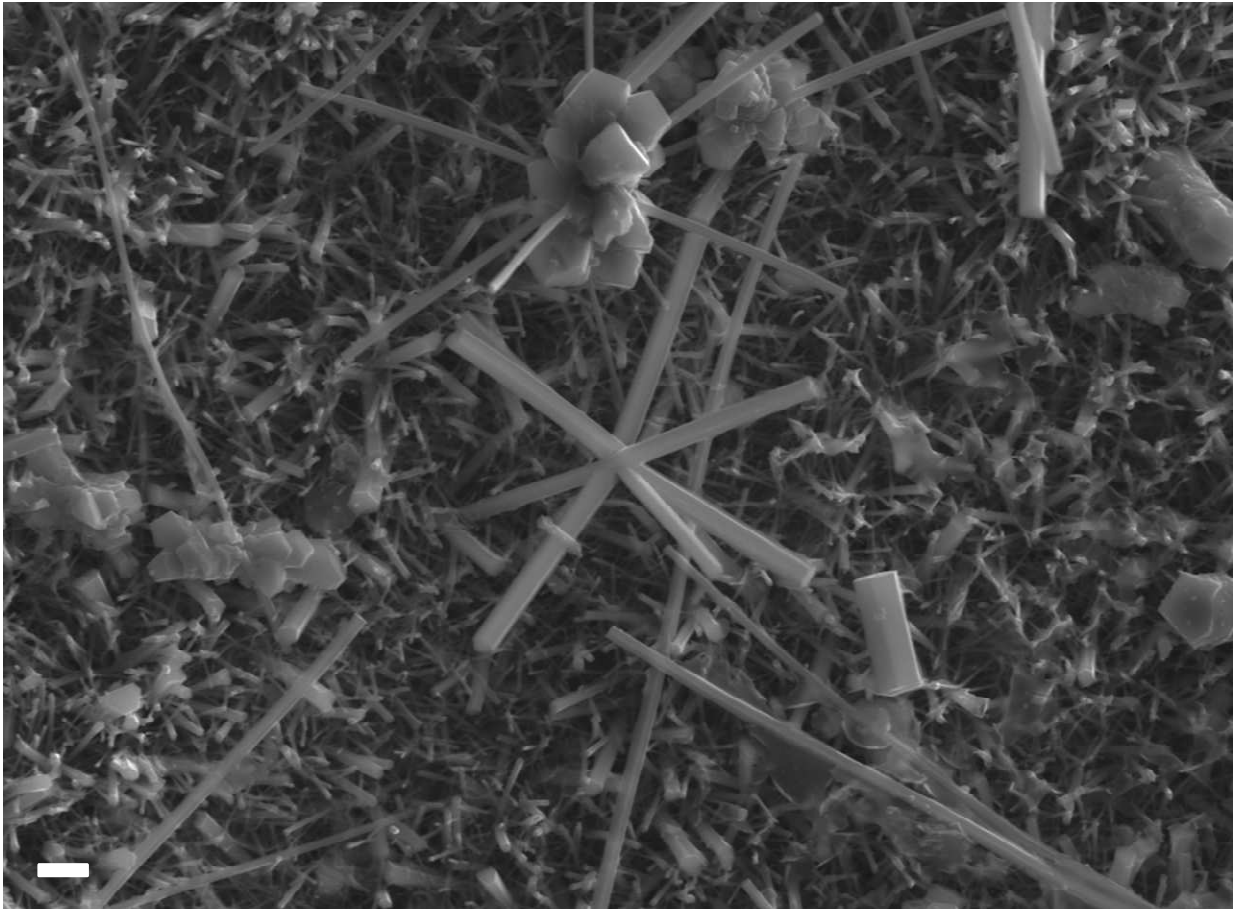
1314
1315   Figure 21: Ex-situ SE SEM image of hydrating $C_4A_3\$$ particles plus 10% solid CH in a
1316   saturated CH- $C\$H_2$ solution, liquid/solid = 50 ml/g. Hydration time was 2 hours. Accelerating
1317   voltage of 15.00 kV, a probe current of 248 pA, working distance of 13.5 mm, and scale bar is 2
1318   μm.

1319
1320   Although twinning does not appear to be the dominant mechanism for the formation of stellate
1321   ettringite clusters, Figure 22 gives some visual evidence that twinning may also occur. The
1322   crystal appears to have grown wider as it grew away from its nucleation site, and eventually split
1323   into diverging crystals, perhaps due to a crystallographic offset which led to the crystal twinning
1324   [152]. A more detailed study utilizing electron backscattered diffraction (EBSD) or single
1325   crystals would be needed to definitively identify twinning in this system.
1326

1327
1328 Figure 22: Ex-situ SE SEM image of hydrating $C_4A_3\$$ particles in a saturated CH- $C\$H_2$
1329 solution, liquid/solid = 50 ml/g. Hydration time was 2 hours. Accelerating voltage of 15.00 kV,
1330 a probe current of 20 pA, working distance of 14.0 mm, and scale bar is 1 μm.
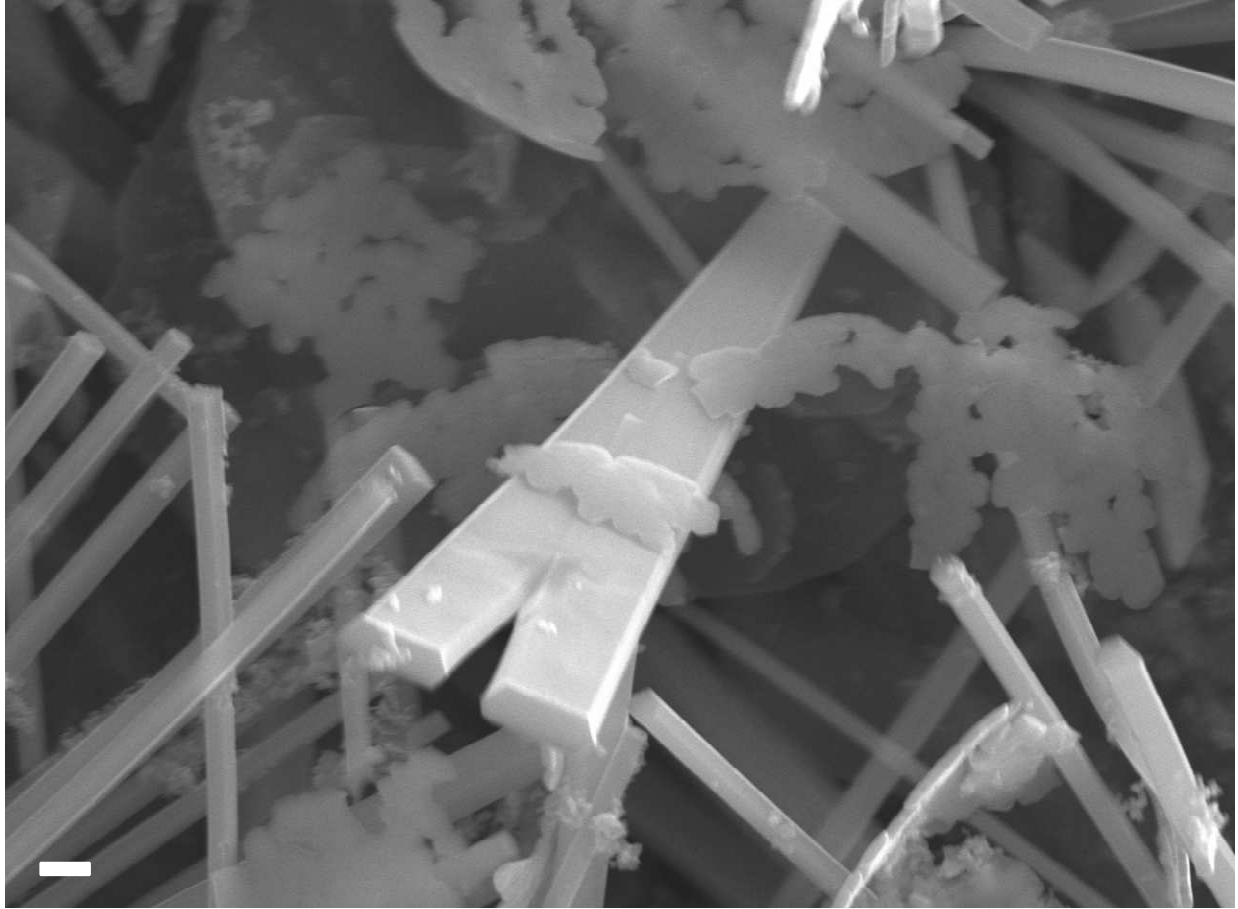
1331 **4.1.3 X-ray Diffraction**

1332 To confirm the observations with regard to ettringite formation in S1 (the sample without excess
1333 CH), an in-situ XRD experiment was performed on the supernatant phases of samples
1334 synthesized under the same experimental condition as were used in the soft X-ray microscopy
1335 studies. Figure 23 confirms that $C_4A_3\$$ decreases and ettringite increases with time, although the
1336 rate of ettringite formation appears to be slightly different than in the soft X-ray microscopy
1337 study. The difference in rates is probably in part a result of the different w/c and a potentially
1338 different particle size distribution in the supernatant phases since different centrifuges were
1339 utilized.
1340

Figure 23: In-situ synchrotron X-ray diffraction recording the evolution of ettringite over time from the hydration of $C_4A_3\$$ in a saturated CH-calcium sulfate solution, liquid/solid = 10 ml/g (E = ettringite, C = $C_4A_3\$$).

4.2 Paste Experiments

When water was added to mixes with CH, clumps of reaction products formed immediately that could be broken up by further mixing to give workable pastes, so this phenomenon could be described as a "false set." However, as the CH amount increased, the time to initial set reduced rapidly. During mixing, the samples with higher amounts of CH could be felt to be releasing a significant amount of heat very rapidly. This phenomenon could be described as a "flash set."

4.2.1 X-ray Diffraction

XRD was performed to better understand which phases were forming over time when $C_4A_3\$$ was hydrated in the presence of $C\$H_2$ and varying amounts of CH (Figure 24). The 0.5, 1, and 2.5 h times were selected to correspond with the soft X-ray microscopy experiments, and the 1 and 7 d times were chosen to show how the phases in the pastes evolve during the first week of curing. CH was not observed in any of the samples. Increasing CH accelerated the rate of $C\$H_2$ depletion. This is easily seen comparing P0, P1, and P2. All pastes containing CH form ettringite very rapidly. At 0.5 h, 2-5% CH seems to maximize the amount of ettringite formed. At 0.5 h as the CH continues to increase from 5 to 10%, the dominant phase formed switches

45

1360   from ettringite to a solid solution (S.S.) AFm phase containing OH^- and SO_4^{2-} [153]. Moreover,
1361   P10 shows a significant increase in ettringite from 0.5 to 2.5h. This is consistent with the soft X-
1362   ray microscopy investigation which showed that in S2, the suspension with 10% excess CH, the
1363   formation of ettringite was somewhat delayed compared to S1, the suspension that only had CH
1364   from the saturated solution. From the composition of the dissolving $C_4A_3\$$, the ions in the
1365   solution, and the XRD results, it is probable that the diffusion barrier observed in Figure 14 is a
1366   calcium hydroxyl-sulfoaluminate hydrate.
1367
1368   In the samples with CH after 1 d, there does not to appear to be major changes in the amount of
1369   ettringite or solid solution AFm; however, there is a significant increase in the amount of
1370   monosulfate formed. This is because the CH needed to form the S.S. AFm and the $C\$H_2$ need to
1371   form ettringite was entirely consumed by 1 d of hydration. It is interesting to note that even P0
1372   contains humps where the S.S. AFm peaks appear. Potential explanations for this hump include:
1373   carbonation forming a S.S. AFm with CO_3^{2-} and SO_4^{2-} (this could only occur during preparing
1374   the sample for XRD, since the paste was mixed in a nitrogen glove box) or a poorly ordered
1375   monosulfate phase with a range of reduced interlayer spacings. Our experimental set up was
1376   unable to satisfactorily answer this question. Winnefeld and Barlag also had this hump in their
1377   XRD patterns at 1 and 7 d in their CSA sample with ~20% $C\$H_2$ and 0% CH, but it appears to be
1378   gone by 28 d [63]. The hydration phases produced in our experiments are also fairly consistent
1379   with Klein and Mehta [154]; however, our $A/\$= 1.8$ is slightly higher than the systems that they
1380   studied and for our range of $C/\$ = 2.8$-3.4 instead of ettringite, $C_xA_yH_z$, and monosulfate we
1381   observed S.S. AFm, monosulfate, and ettringite.

Figure 24: X-ray diffraction patterns for hydrated pastes P0 - P10 from 0.5 h to 7 d (E = ettringite, M = monosulfate, M* = S.S. AFm, C = $C_4A_3\$$, G = $C\$H_2$).
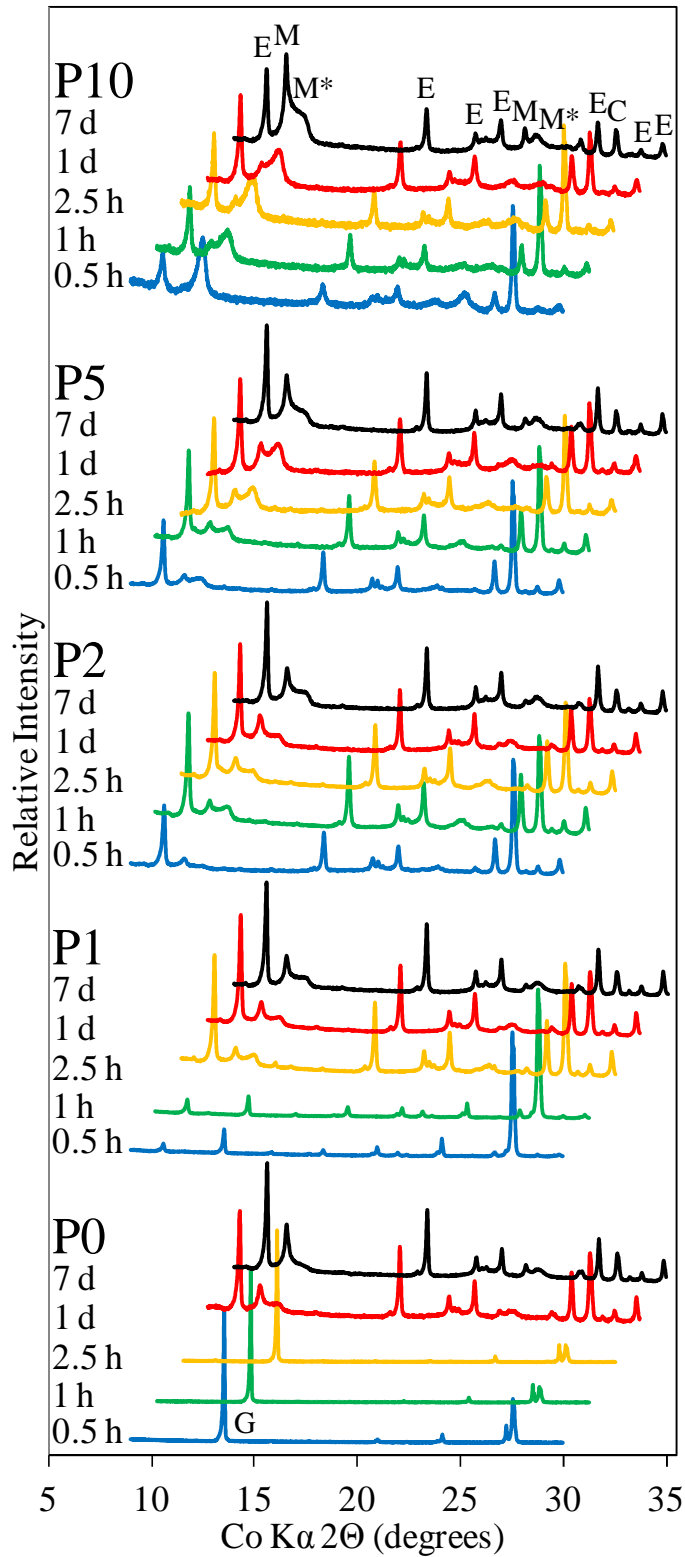
4.2.2 Isothermal Conduction Calorimetry

1387 Isothermal conduction calorimetry confirmed the empirical observations about heat evolution
1388 made during the casting of prior samples. Figure 25 shows how the initial rate and duration of
1389 heat evolution increases with increasing CH. This is consistent with the XRD results which
1390 showed that increasing CH increased the quantity of S.S. AFm produced and that all samples
1391 with CH produced ettringite at very early ages. The initial heat evolution peak can therefore be
1392 attributed to heat of wetting and S.S. AFm and ettringite formation.

1393
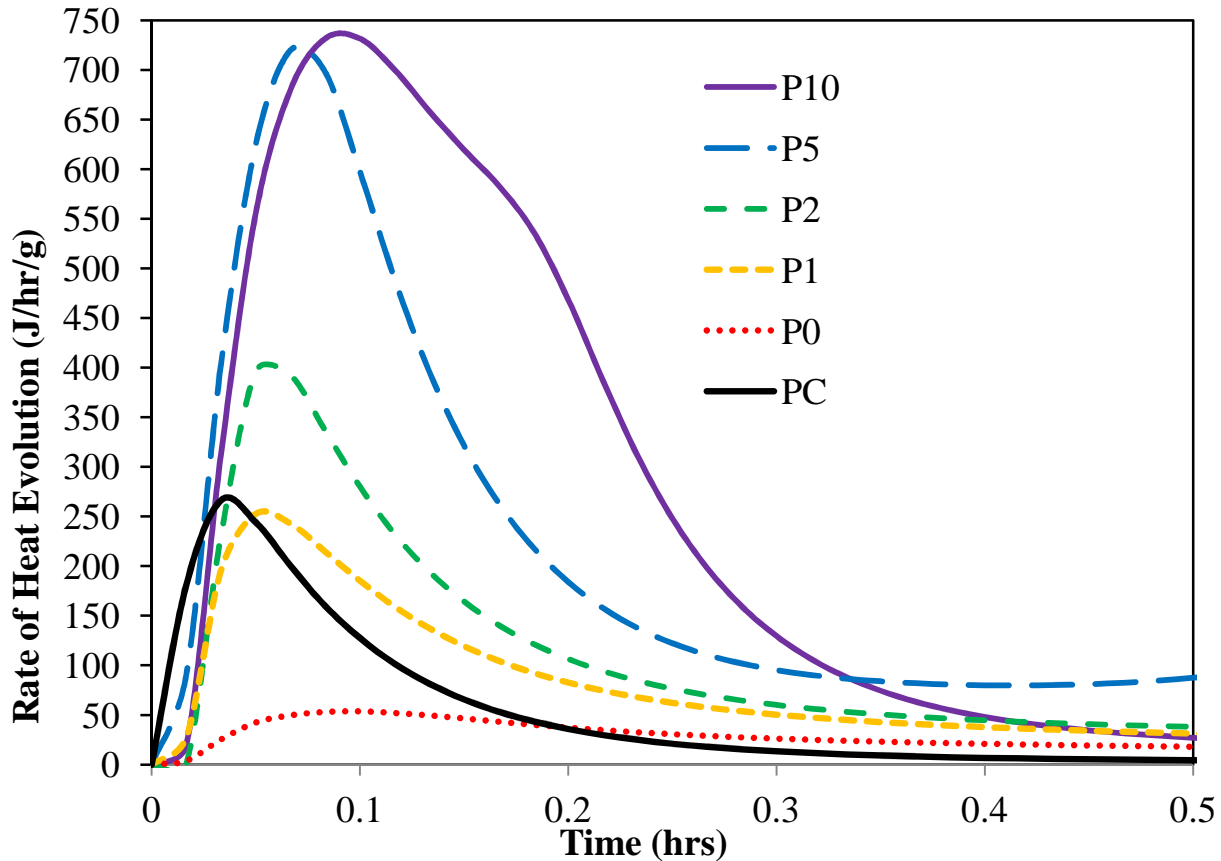
1394
1395 Figure 25: Influence of increasing CH on the initial rate of heat flow due to $C_4A_3\$$ hydration
1396 with 15% $C\$H_2$.

1397

1398 Figure 26 shows how increasing CH generally reduces the time to the 2nd peak in the rate of heat
1399 evolution; with one exception, P10's 2nd peak occurs after P5's. This is probably due to the
1400 rapid formation of large amounts of S.S. AFm in P10 creating a diffusion barrier slowing
1401 hydration (analogous to blocking ettringite or outer C-S-H). This is consistent with the soft X-
1402 ray microscopy analysis which showed what appeared to be a gelatinous hydrate on the surface
1403 of a $C_4A_3\$$ grain in the sample with 10% solid CH (Fig. 3). The XRD results would suggest that
1404 P10 and P5's second peak are mostly attributable to the formation of additional ettringite and
1405 various AFm types. Likewise, the XRD results would suggest that the leading shoulder of P0,
1406 P1, and P2's 2nd peak is mostly attributable to ettringite formation, and the following peak is a
1407 $C\$H_2$ depletion peak where the formation of monosulfate takes over. Winnefeld et al., also,

1408 showed a reduction in the dormant period between the samples with CH compared to those
1409 without [63]. Likewise, Palou and Majling [155] showed an increase in the initial rate of heat
1410 evolution with increasing CH.

1411
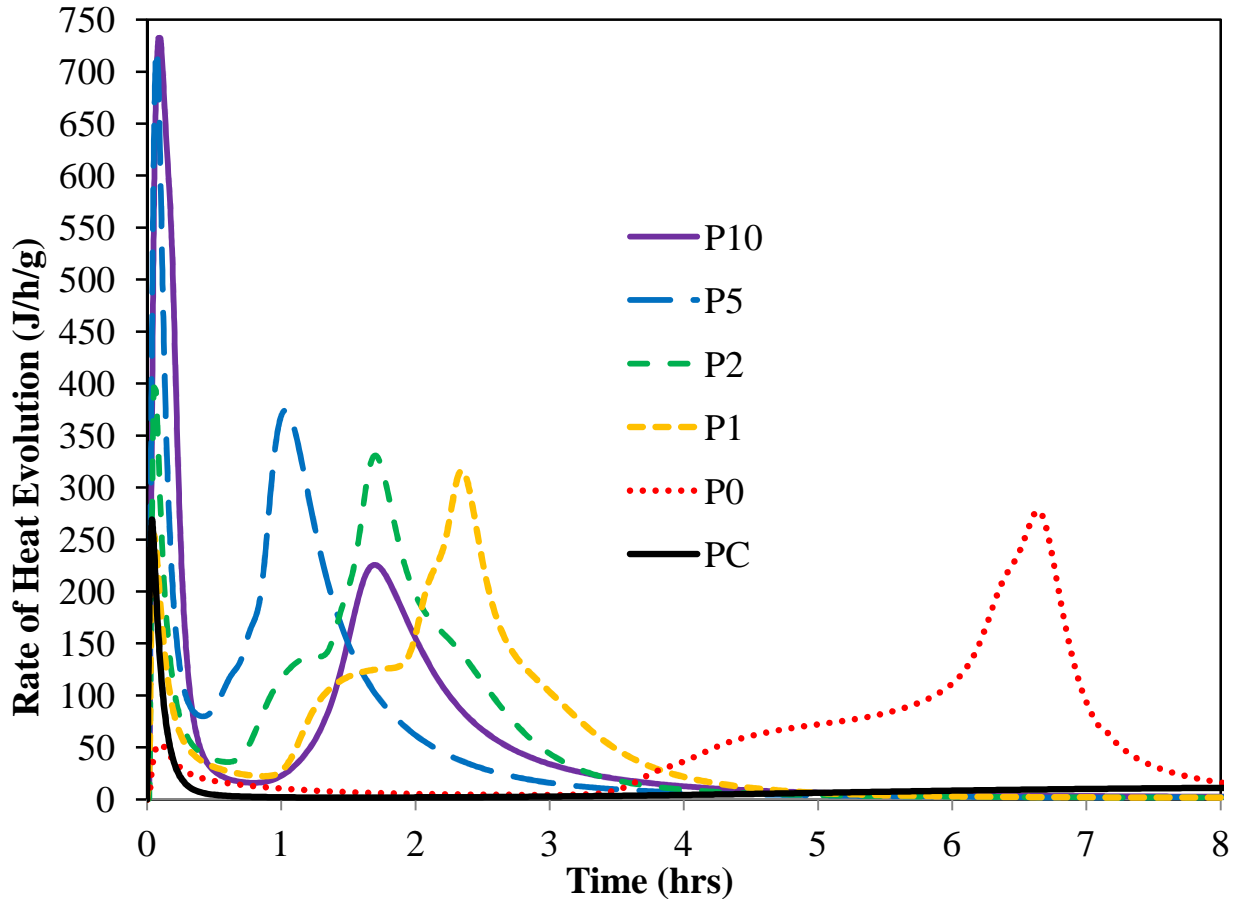
1412
1413 Figure 26: Influence of increasing CH on the rate of heat flow due to $C_4A_3\$$ hydration with 15%
1414 $C\$H_2$.

1415 In the soft X-ray microscopy experiments, gelatinous hydrates formed on what is most likely an
1416 anhydrous $C_4A_3\$$ core, followed by crystalline hydrates growing out radially. This is consistent
1417 with the reaction rims around $C_4A_3\$$ grains observed by Chen et al. [27] and Ogawa and Roy
1418 [156]. Moreover, the observations lend visual evidence to the confined volumetric expansion
1419 theory for CSA cements and is consistent with expansion mechanism of cement hydrating
1420 discussed by Scherer [98] where a cement grain is coated in a crust of hydration products and
1421 when the core continues to hydrate the crust must crack to accommodate the volume increase
1422 that results from hydration. Many such microscopic hydration product crusts cracking and
1423 expanding outward due to the volume increase of the hydration products and the crystallization
1424 pressures could result in the expansion observed in the cement paste.

1425 **4.2.3 Dimensional Stability**

1426 All pastes showed the tendency to expand in water with length increases of approximately 0.5%
1427 at 10 days (Figure 27). After 10 days when the pastes were allowed to dry in ambient

conditions, the pastes with less CH showed more contraction than the pastes with more CH; however, this trend did not hold for the sample with no CH. After 10 days of air drying all the pastes had stopped shrinking and at that time the pastes were again immersed in water. All pastes resumed expanding. Additionally, the rate of expansion was much higher than during the initial 10 days of curing in water. The faster rate of expansion is most likely attributed to a change in the AH_3. During the early age hydration, AH_3 precipitates out as a gel with additional water incorporated and could be represented as $AH_3 \cdot H_x$. This gel helps to block pores and limit water and ion mobility in the hydrating CSA paste microstructure. Upon drying, the $AH_3 \cdot H_x$ loses some of its secondary bonded water and contracts. As the AH_3 contracts and goes through its leather hard point, it decreases in volume opening up porosity in the CSA matrix and more effectively glues its surroundings together. Upon reintroduction of water to the pastes, the unhydrated $C_4A_3\$$ cores resume hydration with easier access to the water. The hydration of the unhydrated cores causes localized volume increases which are restrained by the surrounding matrix. Stresses generated by the localized volume increases (strains) are relieved by microcracking around the hydrating $C_4A_3\$$ cores. As microcracks coalesce they from macrocracks which can be observed visually and are evidenced by macroscopic length changes. The transmission X-ray microscopy experiment provides a probably explanation for why expansion tended to increase with increasing CH content. Figure 14 shows that $C_4A_3\$$ hydration in an excess of CH develops a globular microstructure at early ages instead of forming ettringite. This globular microstructure is presumed to be the result of a coating product forming on the surface of the $C_4A_3\$$ grains. The XRD results indicate that this coating product is most likely a solid solution ($SO4^{2-}/OH^-$) AFm phase. The coating is preventing the initial formation of ettringite causing ettringite to form at later ages. Ettringite forming after the cement matrix has hardened has been shown to cause expansion. It is proposed that the reason that prior researchers have correlated CSA expansion with CH content is because of this mechanism of coating the $C_4A_3\$$ surface with a solid solution ($SO4^{2-}/OH^-$) AFm phase resulting in a delay of the ettringite formation. A coating forming on the $C_4A_3\$$ surfaces early during hydration would also be consistent with the confined volumetric expansion theory. Furthermore, a diffusion barrier forming on $C_4A_3\$$'s surface would inhibit its reaction providing for additional anhydrous cement to react at later ages to cause expansion. Through particle size distribution studies, prior researchers have shown that anhydrous $C_4A_3\$$ persisting into later ages is correlated with expansion [27, 28].

Figure 27: Dimensional stability changes with CH content and curing condition.

CHAPTER 5: $C_4A_3\$$ HYDRATION IN THE PRESENCE OF CALCITE AND VATERITE WITH VARYING GYPSUM
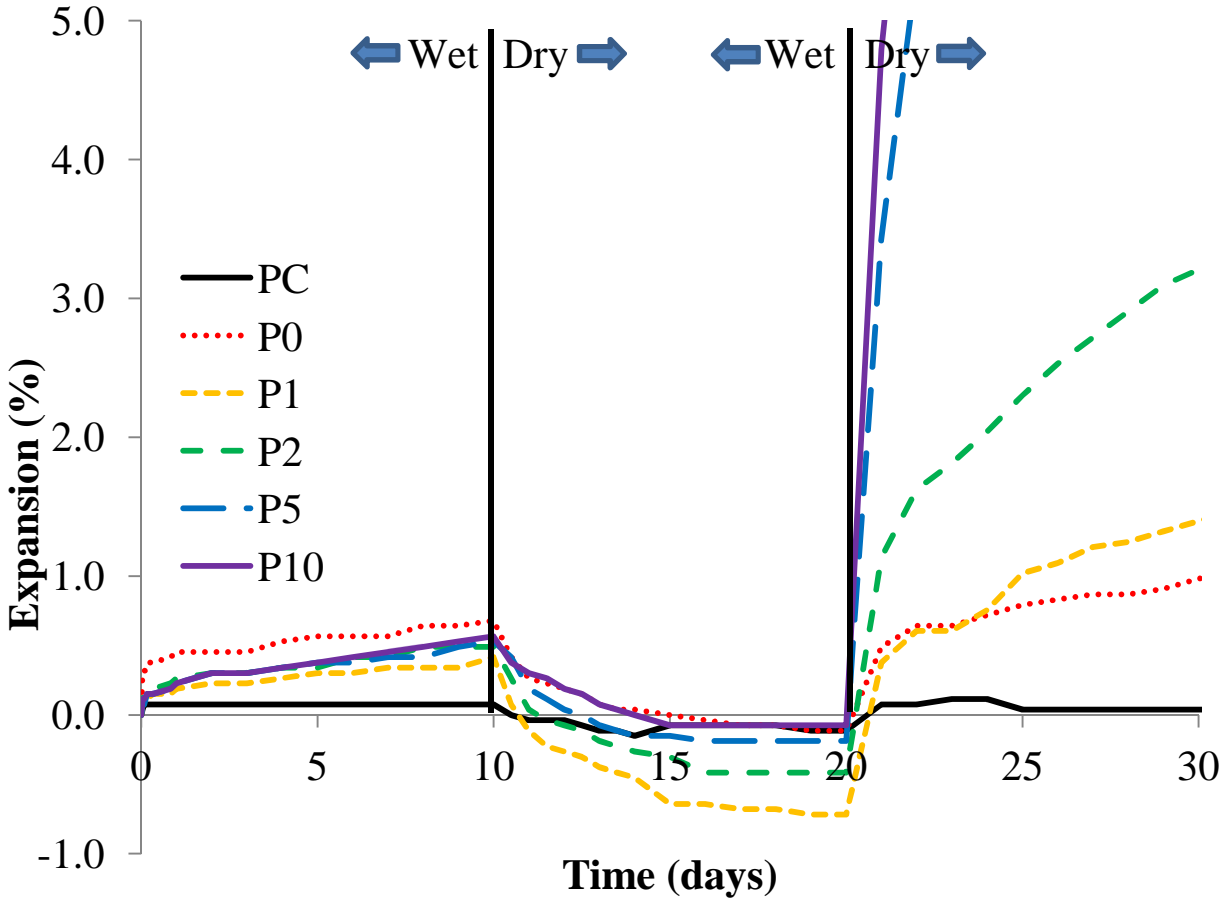
5.1 Early-Age Hydration

The presence of $C\$H_2$, calcite and/or vaterite affected the set time of CSA pastes. Table 4 demonstrates that the inclusion of 15% $C\$H_2$ 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 μm, respectively. In the mixes without $C\$H_2$, calcite and vaterite delayed the final set; whereas, in the mixes with $C\$H_2$, calcite and vaterite accelerated the final set. This would suggest that calcite and vaterite act as better nucleation sites for ettringite than monosulfate. Both with and without $C\$H_2$, the final set times for the mixes with calcite were slightly less than the mixes with vaterite, which is a reversal from the initial set trend.

1477   Table 4: Set times for C$_4$A$_3$\$ 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

1478
1479   Isothermal conduction calorimetry (Figure 28) showed that calcium carbonates caused the
1480   maximal rate of heat evolution to occur earlier than for the mixes without calcium carbonates.
1481   Vaterite had a stronger effect than calcite, and this acceleratory effect on heat evolution was
1482   more pronounced in the mixes without CH_2$.   This is consistent with calcium carbonates
1483   reducing the initial set times.
1484
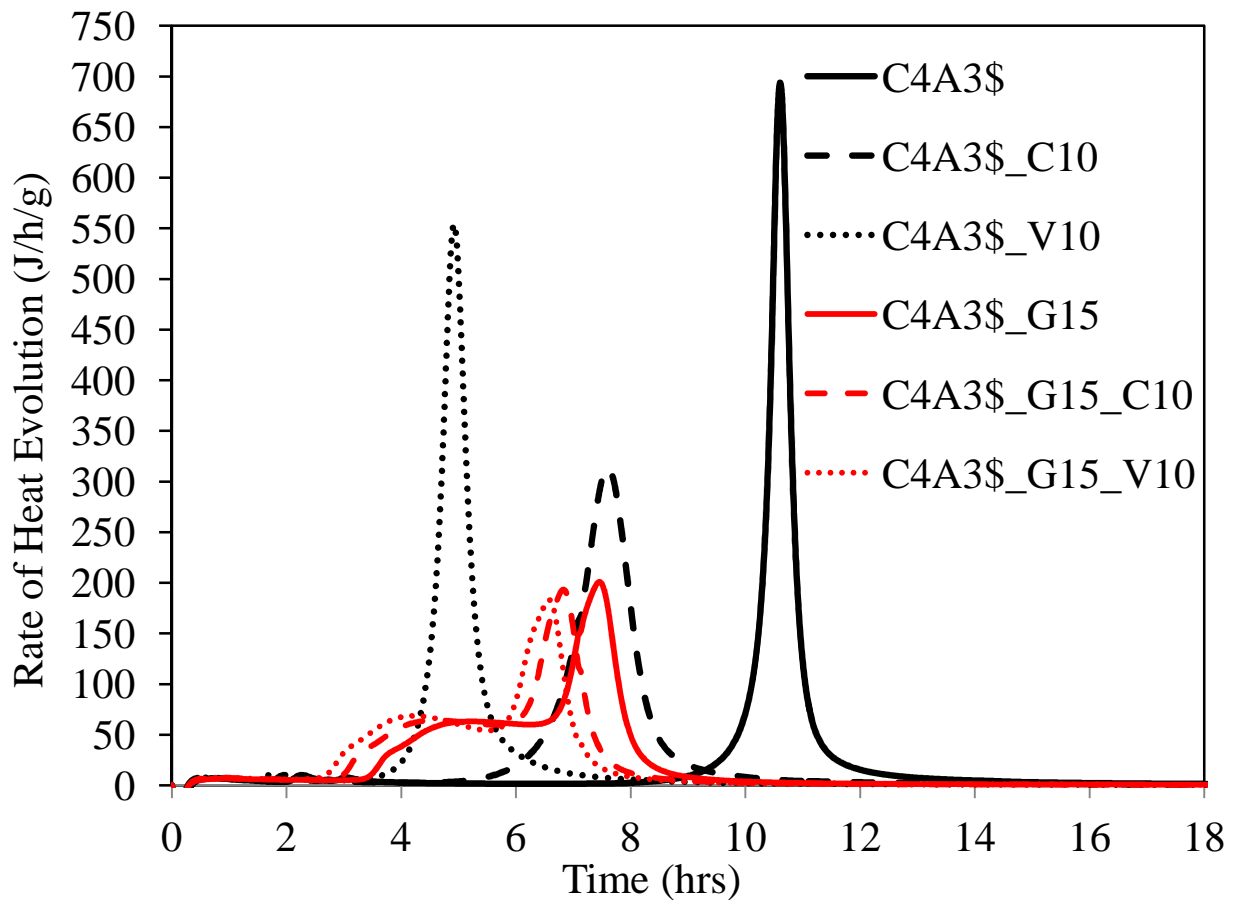
1485
1486   Figure 28: Rate of heat evolution for C$_4$A$_3$\$ with varying replacements.

5.2 Mechanical Properties

At 1 d, including 15% C$H_2 in the mix doubled the compressive strength of the mortars without calcium carbonates, see Table 5. A 10% replacement of $C_4A_3$$ with calcite or vaterite increases the 1 d strength of the mortars containing C$H_2. Vaterite had a more pronounce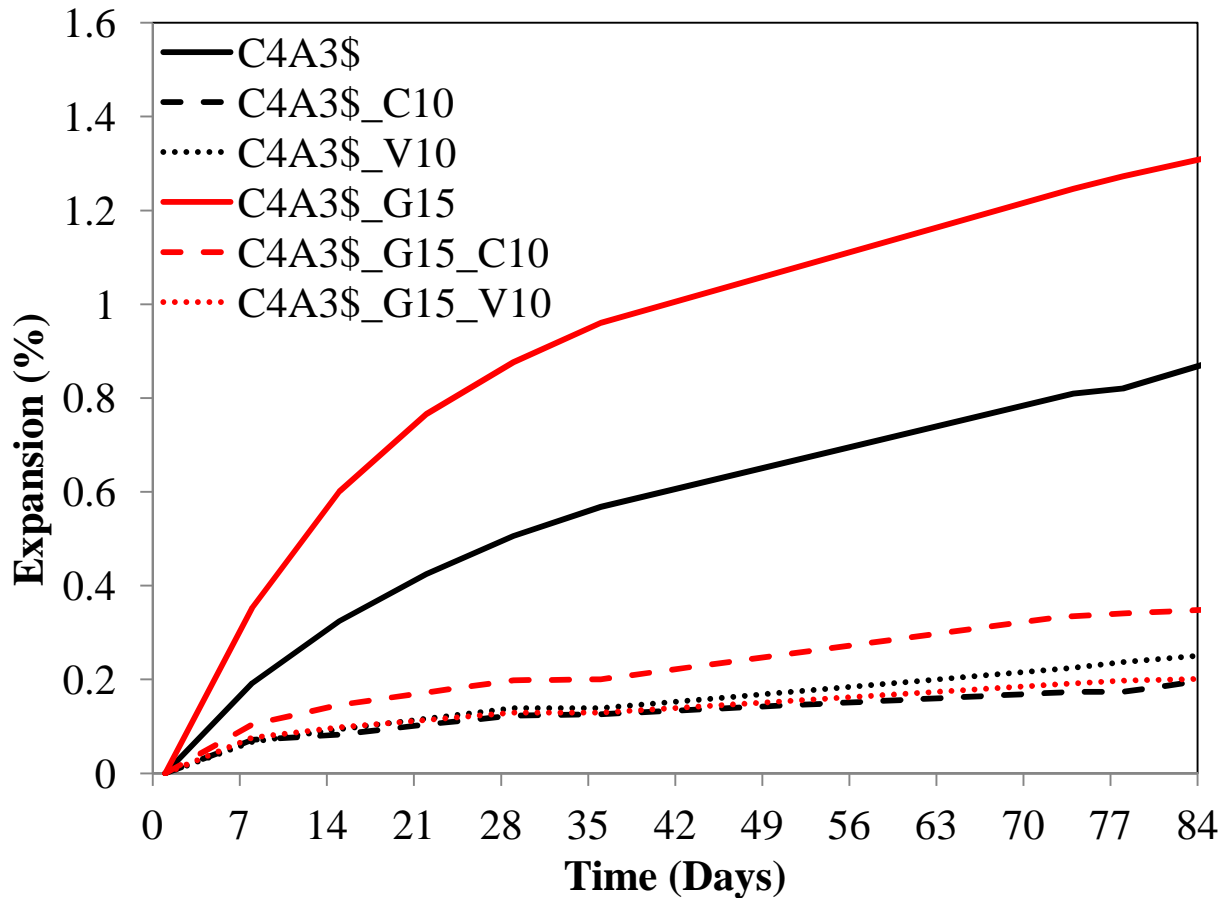d effect on 1 d compressive strength than calcite. The mortars without C$H_2 experienced decreases in 1 d strength with calcite and vaterite replacements; the decrease was less pronounced for C4A3$_G0_V10 than for C4A3$_G0_C10. At 1 d, the pure $C_4A_3$$ mix has achieved its maximum strength; however, C4A3$_V10 continued to gain strength through 28 d then looses 7% of its strength at 84 d. Additionally, C4A3$_C10 had a slower rate of strength gain than C4A3$_V10 and continued to gain strength through 84 d. C4A3$_V10 achieved its maximum strength of 45 GPa at 28 d, and C4A3$_C10 achieved its maximum strength of 46 GPa at 84 d. The timing of these maximal strengths will be further explained by XRD and DTA later. For the mixes with C$H_2, the discussion turns from increases in strength to reductions in compressive strength losses. All mixes with C$H_2 lost strength after 1 d. Between 1 and 84 d, C4A3$_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.

Table 5: Compressive strength development of mortar cubes with time.

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)

$C_4A_3$$ replacements with 10% calcium carbonates reduced the amount of expansion through 84 d in both the mixes with and without C$H_2 (Figure 29). For C4A3$_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 [8, 27, 90]. However, it is interesting to note that the pure CSA mortar without any C$H_2 or calcium carbonates expanded 0.9% by 84 d of hydration. XRD results (Table 6) will later show that this mortar would contain little ettringite, which is the phase normally assigned blame for deleterious expansion. The expansion of a CSA mortar without additional ettringite production or without any of the fine/"colloidal" ettringite found during hydration in the presence of hydroxides [150], strongly supports the confined volumetric expansion theory for CSA cements [98]; 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. Scherer [98] 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 dimension changes.

1524

1525
1526 Figure 29: Dimensional stability of $C_4A_3\$$ with varying replacements.

5.3 Chemical Reactions

Figure 30 shows a highlighted region of the XRD plots showing the monosulfate reduction and ettringite and monocarboaluminate production for C4A3$_C10 and C4A3$_V10 with time. Likewise from the figure it is clear that the kinetic of the monocarboaluminate producing reaction was faster for vaterite than calcite. Table 6 provides a summary of the quantitative XRD results. All pastes contain anhydrous $C_4A_3\$$ at 1 d, which is necessary for the confined volumetric expansion theory. Additionally, the pastes containing $C\$H_2$ retain $C\$H_2$ through 7 d of hydration. Although stoichiometrically the $C\$H_2$ should have been consumed before 7 d, it most probably persists due to the system becoming diffusion limited. As expected in the pastes without $C\$H_2$, $C_4A_3\$$ initially reacts to form monosulfate (AFm) and in the pastes with $C\$H_2$, $C_4A_3\$$ reacts with $C\$H_2$ to form ettringite (AFt). The solubility of calcium carbonates is too low to take part significantly in the early-age hydration reactions. By 28 d, C4A3$_V10 had reacted 69% of its vaterite and 97% of its monosulfate to form 18% monocarboaluminate (AFm-CO_3) and 27% ettringite has formed according to Eqn 17.

$$3(3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O) + 2CaCO_3 + 18H_2O \rightarrow$$
$$2(3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O) + 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \qquad (17)$$

54

1545   Calcite is a more stable form of calcium carbonate than vaterite and thus it would be expected to
1546   react slower with the monosulfate to form monocarboaluminate, and this is evidenced by
1547   C4A3$_C10 forming monocarboaluminate at a slower rate than C4A3$_V10. Likewise,
1548   C4A3$_C10's slower rate of monocarboaluminate and ettringite formation corresponded to its
1549   slower rate of strength gain. It is interesting that although all the mixes with calcium carbonates
1550   produced significant quantities of ettringite, they expanded less than the mixes without calcium
1551   carbonate additions that produced much less ettringite over the same time periods. CH_2$ in the
1552   pastes lead to ettringite formation and reduced the amount of monosulfate formed, thus CH_2$
1553   reduced the ability of the pastes to react the calcium carbonates and form monocarboaluminate.
1554

1555
1556   Figure 30: XRD results highlighting monocarboaluminate and ettringite formation with time for
1557   mixes without CH_2$.

1558   Table 6: Quantitative XRD results in percent.

Paste	Day	C$_4$A$_3$$	Gyp.	Calc.	Vater.	AFt	AFm	AFm-CO$_3$	Gibbs.	Unchar.*
C4A3$	1	16.2	n/a	n/a	n/a	5.6	29.7	0.0	6.9	41.7
C4A3$	7	7.8	n/a	n/a	n/a	4.8	28.7	0.0	7.3	51.4
C4A3$	28	2.7	n/a	n/a	n/a	4.6	42.4	0.0	10.0	40.4
C4A3$	84	1.4	n/a	n/a	n/a	5.0	39.9	0.0	8.2	45.4
C4A3$_C10	1	11.7	n/a	7.6	n/a	6.3	30.0	0.0	6.6	37.9
C4A3$_C10	7	6.4	n/a	7.6	n/a	5.0	31.1	1.9	7.6	40.4
C4A3$_C10	28	2.6	n/a	6.8	n/a	10.2	28.6	5.6	8.6	37.7
C4A3$_C10	84	2.3	n/a	3.8	n/a	27.4	5.5	17.0	6.3	37.7
C4A3$_V10	1	10.1	n/a	0.4	5.9	4.7	27.0	0.0	6.5	45.4
C4A3$_V10	7	6.2	n/a	0.7	6.1	5.8	24.9	2.1	7.6	46.7
C4A3$_V10	28	5.1	n/a	0.7	1.8	26.6	0.8	18.1	7.2	39.8
C4A3$_V10	84	2.5	n/a	0.3	1.1	31.8	0.6	25.7	5.7	32.3
C4A3$_G15	1	20.7	2.6	n/a	n/a	35.4	2.8	0.0	4.4	34.1
C4A3$_G15	7	14.9	2.0	n/a	n/a	33.7	3.9	0.0	4.2	41.3
C4A3$_G15	28	4.1	0.0	n/a	n/a	33.5	9.4	0.0	7.7	45.3
C4A3$_G15	84	1.0	0.0	n/a	n/a	36.8	12.7	0.0	6.9	42.6
C4A3$_G15_C10	1	15.0	2.1	7.1	n/a	37.0	2.7	0.0	3.3	32.8
C4A3$_G15_C10	7	11.3	1.4	6.9	n/a	34.2	3.7	1.4	4.3	36.7
C4A3$_G15_C10	28	3.0	0.0	5.3	n/a	35.9	1.0	3.9	5.3	45.6
C4A3$_G15_C10	84	1.8	0.0	5.1	n/a	45.2	0.7	9.0	5.7	32.6
C4A3$_G15_V10	1	16.7	2.7	0.0	5.1	33.0	1.0	0.0	3.1	38.4
C4A3$_G15_V10	7	13.7	1.9	0.2	5.7	35.0	2.2	2.6	4.7	34.0
C4A3$_G15_V10	28	3.8	0.0	0.4	3.7	41.4	1.2	8.1	5.2	36.1
C4A3$_G15_V10	84	1.2	0.0	0.4	3.3	46.5	0.4	11.8	5.8	30.6
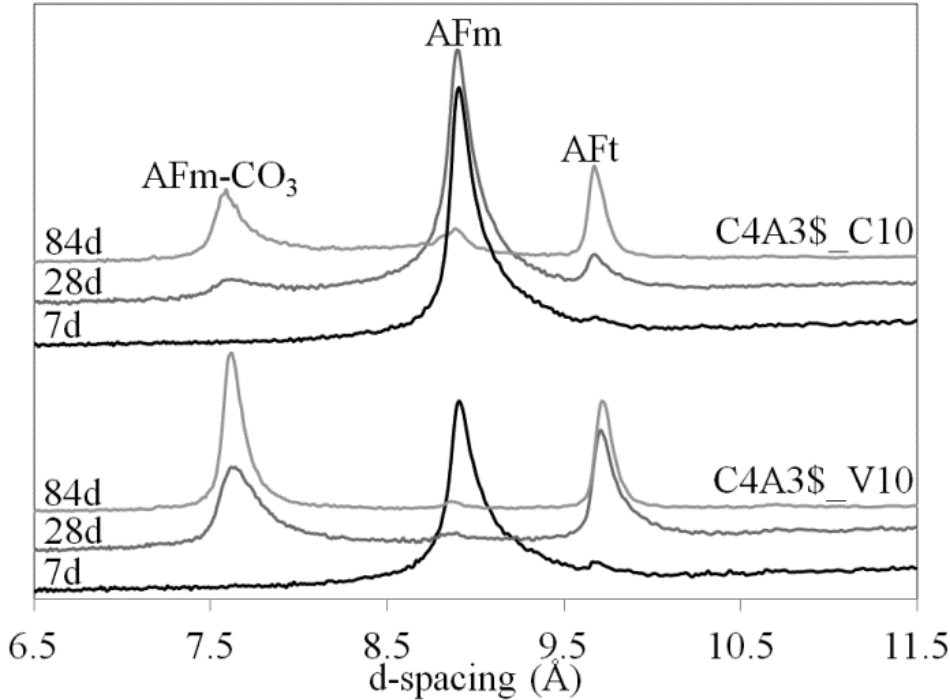
1559   *Includes amorphous material (mainly Al(OH)$_3$) and contributions from AFm phases with
1560   variable d-spacings due to variable interlayer molecules/ions.
1561
1562   Thermal analysis confirms the trends established by XRD. The DTA results in Figure 31 show
1563   that at 7 d of hydration the hydrated phases for C4A3$, C4A3$_C10 and C4A3$_V10 were
1564   monosulfate and aluminum hydroxide and calcium carbonate was still mainly unreacted. At 28
1565   d of hydration, C4A3$_V10 had reacted more of its calcium carbonate and monosulfate and
1566   produced more ettringite and monocarboaluminate than C4A3$_C10. Finally, the absence of
1567   hemicarboaluminate in all samples can probably be attributed to the low hydroxide
1568   concentration present in our system.
1569
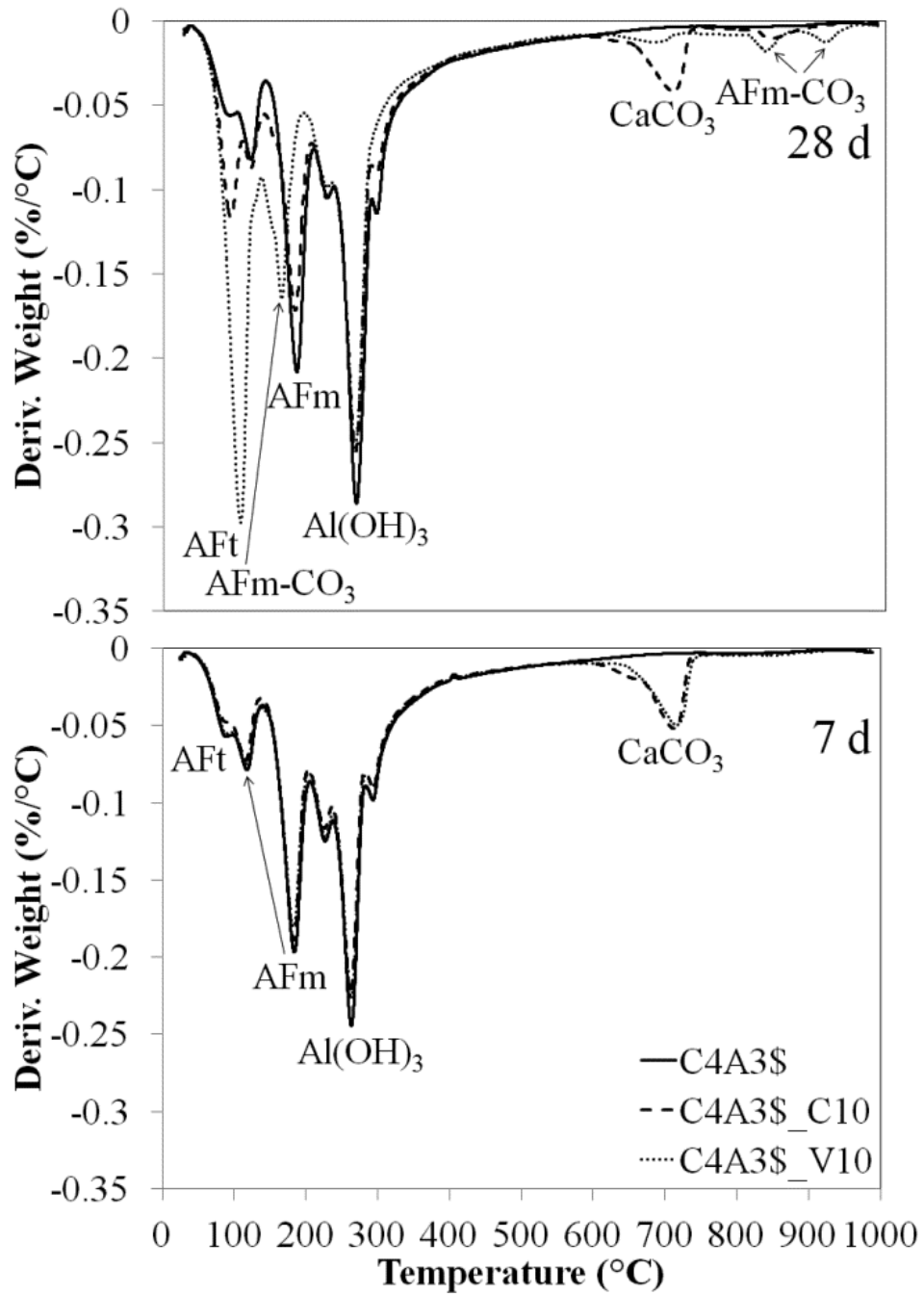
Figure 31: DTA results for specimens without CH_2$ at 7 and 28 d.

CHAPTER 6: CONCLUSION

Rietveld refinements showed the orthorhombic crystal structure [35] to best match the observed peak intensities and positions for pure $C_4A_3\$$; however, a future single crystal study is still needed to confirm/identify the actual space group and symmetries of the crystal structure. A high-pressure synchrotron XRD experiment was successfully carried out on $C_4A_3\$$ at the Advanced Light Source. The isothermal bulk modulus of $C_4A_3\$$ was found to be 69(6) GPa. Whether the orthorhombic unit-cell or cubic subcell was used to calculate the compressibility of $C_4A_3\$$ had little effect on the value obtained for the bulk modulus. The higher charge of the anion, SO_4^{2-}, and the cation, Ca^{2+}, of $C_4A_3\$$ may contribute to $C_4A_3\$$ having a higher bulk modulus than other sodalites with smaller charged ions such as Na^+, Cl^- and OH^-. Similarly, by comparing the bulk modulus of $C_4A_3\$$ with $Sr_8(Al_{12}O_{24})(CrO_4)_2$ (72 GPa calculated from [141]), the effect that the caged ions' sizes have on the lattice compressibility can be observed. As the size of the caged ions increases, the compressibility of the lattice decreases. $C_4A_3\$$ is more compressible than other cement clinker phases such as C_3A {102(6) GPa} [134] and less compressible than hydrated cement phases such as ettringite 27(7) GPa [135]. The elastic constants for many phases in this system are now known such as ettringite and monocarboaluminate, but determining the elastic properties of amorphous phases in the system such as AH_3 will be challenging and should be a focus of future research in this area. Determining the elastic constants of the remaining phases will enable future micromechanical modeling that will allow expansion models to be validate and will enable cement formulations to be validated and optimized on the microstructural scale. This will allow high performance cements and more durable/sustainable cements to be formulated.

CSA cement hydration produces a large amount of crystalline hydrates which contribute to the cement's early-age strength gain, and how polycrystalline binders develop strength is still not fully understood. This work demonstrated that the addition of solid CH to a very dilute (50:1) suspension of $C_4A_3\$$ in water pre-saturated with respect to both $C\$H_2$ and CH tends to reduce the initial rate of formation of well-crystallized ettringite needles. This reduction in rate seems to be associated with the stabilization of a layer of hydrates on the surface of the $C_4A_3\$$ particles. This hydrate layer has a rather gelatinous appearance but it is also covered with fine "hairy" outgrowths which are probably fine ettringite. From the composition of the dissolving $C_4A_3\$$, the ions in the solution, and the XRD results, it seems possible that this initial diffusion barrier might be a poorly crystalline calcium hydroxyl-sulfoaluminate hydrate.

Relatively large acicular crystals of ettringite (typically of the order of 0.5 μm in width and ranging from about 2μm to over 10μm in length) also appear to have grown from individual nuclei in the suspension fluid, especially in the system without added CH. An interesting observation is that many of these acicular crystals are joined together in the form of stellate clusters which appear to radiate from a central point which we assumed to be either a single original nucleus or else a particle, presumably of $C_4A_3\$$, that serves as a site for multiple surface nucleation points. The lack of evidence for any regular form of twinning between the arms of the stellate clusters suggests that the multiple surface nucleation points hypothesis is the more likely explanation.

1616
1617 It is hypothesized that such stellate clusters may make an important contribution to the
1618 mechanical properties of hydrated $C_4A_3\$$ pastes. It is easy to imagine that an assembly of such
1619 stellate clusters would have significant rigidity due to the interlocking of the "arms" from
1620 adjacent clusters. This type of model is consistent with models that have been proposed to
1621 explain the mechanical strengths of other polycrystalline hydraulic binders, such as hardened
1622 $C\$H_2$ plasters [112]. It would be interesting to know whether the type of "domain" that is formed
1623 by all of the arms of a single stellate cluster might be identifiable in more dense hydrated paste
1624 systems. Techniques exist nowadays to do this fairly efficiently in certain cases, e.g. by means of
1625 "3D XRD," coupled with X-ray tomography [157]. The observations of gelatinous hydrates
1626 forming on what is most likely an anhydrous $C_4A_3\$$ core, followed by crystalline hydrates
1627 growing out radially is consistent with the confined volumetric expansion theory in CSA
1628 cements.
1629
1630 In the $C_4A_3\$$ pastes containing 15% $C\$H_2$ upon adding increasing amounts of solid CH, the
1631 pastes showed greatly increased rates of hydration at very early ages (evidenced by a dramatic
1632 increase in the rate of heat evolution), producing what XRD showed to be mainly an AFm solid
1633 solution hydrate phase and ettringite. After a brief decline in the rate of heat evolution in the
1634 pastes highest in CH (P5 & P10), $C_4A_3\$$ hydrated to form monosulfate as the major phase, since
1635 the $C\$H_2$ had been depleted during the prior formation of AFm solid solution. Likewise,
1636 increasing CH accelerated the consumption of $C\$H_2$ and generally decreased the induction
1637 period. At zero and lower levels of CH (P0 – P2) after an induction period, the heat evolution
1638 can be attributed to the continued hydration of $C_4A_3\$$ to form ettringite followed by the
1639 formation of monosulfate upon the depletion of $C\$H_2$.
1640
1641 The transmission X-ray microscopy experiment provides a probably explanation for why
1642 expansion tended to increase with increasing CH content. $C_4A_3\$$ hydration in an excess of CH
1643 develops a globular microstructure at early ages instead of forming ettringite. This globular
1644 microstructure is presumed to be the result of a coating product forming on the surface of the
1645 $C_4A_3\$$ grains. The XRD results indicate that this coating product is most likely a solid solution
1646 (SO_4^{2-}/OH^-) AFm phase. The coating is preventing the initial formation of ettringite causing
1647 ettringite to form at later ages. Ettringite forming after the cement matrix has hardened has been
1648 shown to cause expansion. It is proposed that the reason that prior researchers have correlated
1649 CSA expansion with CH content is because of this mechanism of coating the $C_4A_3\$$ surface
1650 with a solid solution (SO_4^{2-}/OH^-) AFm phase resulting in a delay of the ettringite formation. A
1651 coating forming on the $C_4A_3\$$ surfaces early during hydration would also be consistent with the
1652 confined volumetric expansion theory. Furthermore, a diffusion barrier forming on $C_4A_3\$$'s
1653 surface would inhibit its reaction providing for additional anhydrous cement to react at later
1654 ages to cause expansion, and $C_4A_3\$$ persisting into later ages is correlated with expansion [27,
1655 28].
1656
1657 Although CSA cements are promoted as a more environmentally friendly alternative to PC, their
1658 manufacture still consumes a large quantity of resources and energy. One way to reduce CSA
1659 cement's environmental impact is to blend it with calcium carbonate. This study demonstrated
1660 that although calcium carbonate solubility is not high enough to take place in the initial
1661 hydration reactions significantly, calcium carbonate does react with monosulfate to produce

1662 monocarboaluminate and ettringite. The reaction is approximately three times faster for vaterite
1663 than calcite because of vaterite's lower stability. Vaterite showed significant reaction by 28 d;
1664 whereas, calcite showed significant reaction by 84d. CH_2$ promotes the early age formation of
1665 ettringite at the expense of monosulfate; thus, limiting calcium carbonate's ability to react.
1666
1667 Vaterite and calcite also benefited the mortar's mechanical properties. In the mortars without
1668 CH_2$, both calcium carbonates reduced mortar expansion and increased the mortar's
1669 compressive strength. The timing of the increase in strength corresponded to when the calcium
1670 carbonate reacted. In the samples with CH_2$, both calcium carbonates reduced expansion and
1671 reduced the compressive strength lost with time due to expansion. Vaterite was more effective
1672 at mitigating the compressive strength loss than calcite. The mortar without CH_2$ or calcium
1673 carbonate also expanded significantly despite a low ettringite content (~5%). This strongly
1674 supports that the confined volumetric expansion theory where an anhydrous $C_4A_3$$ core
1675 continues to react with water after being surrounded by a confining matrix causing localized
1676 volume increases and results in a macro expansion. When formulating an industrial CSA
1677 cement, it is imperative to impose restrictions on the amount of $C_4A_3$$ in the clinker, the particle
1678 size distribution of the clinker, w/c and the amount of CH_2$ added to achieve the desired
1679 amount of expansion. The incorporation of calcium carbonates into CSA cements appears to be
1680 very promising from both an environmental and performance standpoint. Particularly, if a
1681 cement plant could capture its CO_2 emissions and utilize them to make vaterite, the
1682 sustainability of the cement could be greatly advanced.
1683

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