



## Solution chemistry of cubic and orthorhombic tricalcium aluminate hydration



Rupert J. Myers<sup>a,b,\*</sup>, Guoqing Geng<sup>a</sup>, Erich D. Rodriguez<sup>c,d</sup>, Priscila da Rosa<sup>c</sup>, Ana Paula Kirchheim<sup>c</sup>, Paulo J.M. Monteiro<sup>a</sup>

<sup>a</sup> Department of Civil and Environmental Engineering, University of California, Berkeley, CA, United States

<sup>b</sup> Yale School of Forestry & Environmental Studies, Yale University, New Haven, CT, United States

<sup>c</sup> Department of Civil Engineering, Universidade Federal do Rio Grande do Sul (UFRGS), Porto Alegre, RS, Brazil

<sup>d</sup> Department of Civil Engineering, IMED, Passo Fundo, RS, Brazil

### ARTICLE INFO

#### Keywords:

Kinetics  
Hydration  
Retardation  
Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>  
Sulfate  
Cement

### ABSTRACT

This paper presents a solution chemistry-focused analysis of orthorhombic and cubic tricalcium aluminate (orth-C<sub>3</sub>A and cub-C<sub>3</sub>A, respectively) hydration. It is shown that the different solubilities of cub- and orth-C<sub>3</sub>A influence the bulk aqueous Ca to Al concentration ratio and the C<sub>3</sub>A/solution interface chemistry. The results are consistent with the bulk solution chemistry controlling orth-C<sub>3</sub>A dissolution, and with cub-C<sub>3</sub>A dissolution controlled by the formation of an Al-rich leached layer and adsorption of Ca-sulfur ion pair complexes onto this layer. The polynaphthalene sulfonate-based admixture used here is identified to modify the solution chemistry and retard cub-C<sub>3</sub>A dissolution. Strategies to inhibit C<sub>3</sub>A dissolution in Portland cement are discussed.

### 1. Introduction

The setting time and workability of Portland cement (PC) concrete critically depend on the kinetics of tricalcium aluminate (C<sub>3</sub>A) hydration. The rapid dissolution of C<sub>3</sub>A in water and initial precipitation of solid hydration products, including ‘Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-mono’ (AFm) phases (e.g., OH-AFm, C<sub>4</sub>AH<sub>x</sub>, where the water content, *x*, is a function of the relative humidity and is typically 13 or 19 [1], or C<sub>2</sub>AH<sub>7.5</sub> [2]), and the subsequent formation of katoite (C<sub>3</sub>AH<sub>6</sub>) [2–4], can cause fresh PC concrete to prematurely and irreversibly lose fluidity and workability (‘flash set’), resulting in poor strength development [5]. For these reasons, a small amount (typically 2–5 wt%) of solid calcium sulfate is added to PC to retard C<sub>3</sub>A dissolution. Gypsum (C $\bar{S}$ H<sub>2</sub>) is most commonly added, although hemihydrate (C $\bar{S}$ H<sub>0.5</sub>) and anhydrite (C $\bar{S}$ ) are also used and/or may be produced by dehydration of gypsum during cement production.

The C<sub>3</sub>A phase occurs as a series of solid solutions in PC, typically involving substitutions of Ca for 2 *M* (M<sub>2x</sub>Ca<sub>3-x</sub>Al<sub>2</sub>O<sub>6</sub>), where *M* is an alkali metal, normally Na or K. The Na and K present in PC clinker (~1 wt% Na<sub>2</sub>O + K<sub>2</sub>O [5,6]) are mainly distributed into soluble solid sulfates and C<sub>3</sub>A, with partitioning of K biased towards incorporation in arcanite [6–9]. The structure of C<sub>3</sub>A is cubic (cub-C<sub>3</sub>A) at low Na content (0 ≤ *x* ≤ 0.10) and orthorhombic (orth-C<sub>3</sub>A) at moderate Na

content (0.16 ≤ *x* ≤ 0.20) [5,10–12], with a miscibility gap existing over intermediate compositions (0.10 ≤ *x* ≤ 0.16) [5,10–12]. The alkali content in PC is typically too low to produce monoclinic C<sub>3</sub>A (0.20 ≤ *x* ≤ 0.25) [5–7,13,14]. The crystal structures and composition limits of the Na- and K-substituted C<sub>3</sub>A solid solutions are similar [12]. Other substitutions can occur e.g., Mg for Ca, and Si or Fe for Al, but the crystal symmetry of this phase is reportedly only affected by the alkali content [11]. The extent that cub-C<sub>3</sub>A dissolution is inhibited by calcium sulfate is directly related to the amount added [15,16]. However, orth-C<sub>3</sub>A dissolution occurs more rapidly in aqueous sulfate solutions than in water, and orth-C<sub>3</sub>A also dissolves faster than cub-C<sub>3</sub>A in aqueous sulfate solutions [17–20], meaning that the crystal chemistry of C<sub>3</sub>A and the calcium sulfate content are both important factors in PC hydration, as well as in the production of high performance PC concrete.

The reactions involved in cub-C<sub>3</sub>A-water-calcium sulfate and PC systems at bulk  $\bar{S}$ /A molar ratios of ~0.05 [15] and ~0.25 [8], respectively, are mechanistically comparable. In these systems, ettringite (C<sub>6</sub>A $\bar{S}$ <sub>3</sub>H<sub>32</sub>) precipitates from relatively sulfur- and Ca-rich aqueous solutions (10 < [S] < 20 mmol L<sup>-1</sup> and 20 < [Ca] < 40 mmol L<sup>-1</sup>) [15,21] and is the major solid hydration product before complete gypsum dissolution [8]. Ettringite is typically also the major solid phase produced by orth-C<sub>3</sub>A hydration in the presence of calcium sulfate in

\* Corresponding author.

E-mail addresses: [rupert.myers@gmail.com](mailto:rupert.myers@gmail.com) (R.J. Myers), [guoqinggeng1989@gmail.com](mailto:guoqinggeng1989@gmail.com) (G. Geng), [erich.rodriguez@imed.edu.br](mailto:erich.rodriguez@imed.edu.br) (E.D. Rodriguez), [priscila.rosa@ufrgs.br](mailto:priscila.rosa@ufrgs.br) (P. da Rosa), [anapaula.k@ufrgs.br](mailto:anapaula.k@ufrgs.br) (A.P. Kirchheim), [monteiro@berkeley.edu](mailto:monteiro@berkeley.edu) (P.J.M. Monteiro).

<http://dx.doi.org/10.1016/j.cemconres.2017.06.008>

Received 8 February 2017; Received in revised form 20 June 2017; Accepted 29 June 2017

0008-8846/ © 2017 Elsevier Ltd. All rights reserved.

this range of bulk  $\bar{S}/A$  concentration ratios [18]. Hexagonal platelets (most likely AFm-type phases) are initially formed on hydrating orth-[17] and cub- $C_3A$  [15,21,22] particles, and a surface layer of solid reaction products with ill-defined morphology is identified when viewed on the micron length scale during this initial reaction period (up to a maximum of a few hours) [17,23]. The chemistry of this layer has been described in terms of AFm-type phases in the cub- $C_3A$ -gypsum-water system [24]. X-ray diffraction (XRD) and calorimetry data for this system [25] suggest that an initially formed amorphous aluminate phase (possibly this ill-defined layer of solid reaction products) destabilises over time, leading to ettringite precipitation.

Ettringite precipitation continues in cub- $C_3A$  systems with bulk molar  $\bar{S}/A$  ratios  $< \sim 0.25$  until the calcium sulfate source has completely reacted, which is reported to coincide with renewed rapid dissolution of cub- $C_3A$ , a release of heat, precipitation of  $\bar{S}$ -AFm ( $C_4A\bar{S}H_{12}$ , where the water content is again a function of the relative humidity [11]), and destabilisation of the initially formed ettringite [15,16]. Reduced aqueous Ca and sulfur concentrations are also measured in calcium sulfate containing aqueous cub- $C_3A$  systems after complete dissolution of the calcium sulfate source [15,21,26]. Less information is reported for orth- $C_3A$  hydration relative to cub- $C_3A$  hydration, although ettringite is the dominant solid phase produced from orth- $C_3A$  and gypsum hydration after 14 days at a bulk molar  $\bar{S}/A$  ratio of 0.75 [18].

Consensus is only now being reached on the rate controlling factors of cub- and orth- $C_3A$  dissolution in the presence of calcium sulfate, despite decades of research on this topic [4,9,15,16,18,21,26–33]. It is increasingly thought that a dissolution rate controlling ‘barrier’ covering cub- $C_3A$  particles (e.g., [9,19,34]) does not exist in the gypsum-containing aqueous cub- $C_3A$  system throughout the induction period [35]. This argument is supported by micro- and macro-scale analyses and a crystallographic understanding of the chemical system [15]. As a result, and consistent with research published decades earlier [29,30,33], numerous researchers have hypothesised that adsorption of sulfur and/or Ca complexes is the key cub- $C_3A$  dissolution rate controlling factor in aqueous calcium sulfate solutions [20,21,24,35,36]. However, these hypotheses are not all supported by the geochemical literature, which report little or no adsorption of  $SO_4^{2-}$  and  $SeO_4^{2-}$  onto Al and Fe (hydr)oxides above pH 7–10 [37–40] (these complexes exhibit similar adsorption behaviour). Recent zeta potential, Ca and sulfur *K*-edge X-ray absorption spectroscopy (XAS) results similarly confer a lack of evidence for specific adsorption of  $SO_4^{2-}$  complexes onto partially dissolved cub- $C_3A$  particles in aqueous solutions [41]. A more complex role of adsorption phenomena in inhibiting cub- $C_3A$  dissolution was thus proposed for better consistency with the relevant literature [41]. It attributes the adsorption of Ca-sulfur ion pair complexes onto partially dissolved cub- $C_3A$  particles, the surfaces of which are relatively Al-rich, to increase the local saturation extent near  $C_3A$  surface sites and consequently retard the cub- $C_3A$  dissolution rate.

Polynaphthalene sulfonate (PNS) is a synthetic commercial water-reducing admixture that is commonly added to PC concrete in addition to calcium sulfate to further modify its workability. It is typically polydispersed with a mean molecular mass of  $\gg 1000$  Da [20,42], and contains  $-SO_3^-$  ligands [43]. It is reported to adsorb onto hydrated PC particles and retard  $C_3A$  dissolution [20,41,44], although its effect on the solution chemistry of  $C_3A$  hydration systems is poorly understood. Much less information has also been published on the rate-controlling factor(s) of orth- $C_3A$  dissolution in aqueous solutions relative to cub- $C_3A$  hydration systems, although existing research suggests that the solution chemistry plays a key role [9,17,20,45].

Here, inductively coupled plasma optical emission spectroscopy (ICP-OES) and pH experiments are performed and supplemented by thermodynamic modelling to better understand the role of the solution chemistry on  $C_3A$  hydration in three systems: (1) in water; (2) in water and with gypsum; and (3) in aqueous solutions containing PNS and with gypsum. It has been demonstrated that the transition between inhibited

and rapid dissolution of cub- $C_3A$  in aqueous calcium sulfate containing solutions is strongly linked to the solution chemistry, although only a few publications have reported aqueous phase chemical composition data [15,21,26,33]. Solution chemistry datasets for orth- $C_3A$  systems are scarcer [45]. This work is also needed to provide a more coherent description of the dissolution inhibiting role that adsorption phenomena plays in retarding cub- $C_3A$  dissolution in calcium sulfate containing aqueous systems, particularly in light of recent results [41]. Complementary isothermal calorimetry (IC), XRD, and thermogravimetric analysis (TGA) data are obtained and used to complete the analysis. The results are discussed to provide an advanced description of cub- and orth- $C_3A$  dissolution in alkaline Ca- and sulfur-rich aqueous solutions, i.e., in a similar chemical environment to that which exists in fresh PC concrete.

## 2. Materials and methods

### 2.1. Materials for ICP-OES, pH and XRD

The cub- $C_3A$  (cub- $C_3A_1$ ,  $Na_{0.06}Ca_{3.11}Al_2O_{6.14}$ , Mineral Research Processing Cie, hereafter MRP) and orth- $C_3A$  (orth- $C_3A_2$ ,  $Na_{0.37}Ca_{2.92}Al_2O_{6.11}$ , MRP) powders used to produce the hydrated samples measured by ICP-OES, pH, and XRD were synthesised by firing  $CaCO_3$  (s),  $Al_2O_3$  (s), and  $Na_2CO_3$  (s) (all from Merck) twice at 1350 °C for 2 h in platinum vessels. The material was ground to a fine powder in an intermediate grinding step.

The chemical composition, purity and crystal structures of cub- $C_3A_1$ , orth- $C_3A_2$ , and the gypsum precursors used, gypsum\_1 (Fisher Scientific) and gypsum\_2 (Sigma-Aldrich) (the use of two gypsum precursors is discussed below), were quantified by X-ray fluorescence (XRF), TGA, XRD, and Rietveld analysis (estimated uncertainty =  $\pm 3$  wt%). The data show that cub- $C_3A_1$  contains 95 wt% cub- $C_3A$  (Powder Diffraction File (PDF)# 01-070-0839), 4 wt% katoite ( $C_3AH_6$ , PDF# 00-024-0217), and 1 wt% portlandite (CH, PDF# 01-072-0156). Orth- $C_3A_2$  was identified to contain  $\sim 89$  wt% orth- $C_3A$  (PDF# 01-070-0859),  $\sim 10$  wt% cub- $C_3A$ , and  $\leq 1$  wt% CH. Gypsum\_1 is pure, and gypsum\_2 contain 93 wt% gypsum (PDF# 01-070-0982) and 7 wt% hemihydrate (PDF# 01-081-1848). Free lime (CaO) was not identified in any of the X-ray diffractograms of the cub- and orth- $C_3A$  powders used. Thermogravimetric analysis (TGA) confirmed the presence of CH and additionally showed that small amounts of  $Al(OH)_3$  ( $\frac{1}{2}AH_3$ ) had formed in both cub- $C_3A_1$  and orth- $C_3A_2$  prior to sample preparation ( $< 2.5\%$  mass lost to 550 °C). Therefore, these results indicate that the cub- $C_3A_1$  and orth- $C_3A_2$  powders used were slightly hydrated during storage and/or sample preparation.

The Brunauer-Emmett-Teller (BET) surface areas of cub- $C_3A_1$  ( $523 \text{ m}^2 \text{ kg}^{-1}$ ,  $d_{50} = 16.8 \mu\text{m}$ ), orth- $C_3A_2$  ( $762 \text{ m}^2 \text{ kg}^{-1}$ ,  $d_{50} = 9.2 \mu\text{m}$ ), gypsum\_1 ( $474 \text{ m}^2 \text{ kg}^{-1}$ ,  $d_{50} = 415 \mu\text{m}$ ), and gypsum\_2 ( $313 \text{ m}^2 \text{ kg}^{-1}$ ,  $d_{50} = 54.3 \mu\text{m}$ ) were measured on a Quantachrome Nova 1000 after heating to 300 °C under vacuum for 4 h for cub- and orth- $C_3A$ , and at 70 °C under vacuum for 10 min for gypsum. Particle size distributions were measured on a Cilas Granulometer 1180 in isopropyl alcohol after ultrasonication at 38 kHz for 60 s. Additional experimental details and results are reported in Appendix A (Electronic Supporting Information, ESI).

### 2.2. Materials for IC

Hydrated samples analysed by IC were synthesised using orth- $C_3A_2$ , gypsum\_2 and a different batch of cub- $C_3A$  (cub- $C_3A_2$ ) to the powder used in the ICP-OES, pH and XRD experiments (cub- $C_3A_1$ ), but synthesised using the same method. This cub- $C_3A_2$  powder was characterised using the same instruments as the solid precursors described in Section 2.1. It was determined to contain  $\geq 99$  wt% cub- $C_3A$  by XRD and Rietveld analysis, to have a  $d_{50}$  of 20.8  $\mu\text{m}$  (Appendix A, ESI), and a BET surface area of  $473 \text{ m}^2 \text{ kg}^{-1}$ , i.e., cub- $C_3A_2$  is slightly coarser and

Download English Version:

<https://daneshyari.com/en/article/5437019>

Download Persian Version:

<https://daneshyari.com/article/5437019>

[Daneshyari.com](https://daneshyari.com)