



THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

Role of Adsorption Phenomena in Cubic Tricalcium Aluminate Dissolution

Citation for published version:

Myers, RJ, Geng, G, Li, J, Rodriguez, ED, Ha, J, Kidkhunthod, P, Sposito, G, Lammers, LN, Kirchheim, AP & Monteiro, PJM 2016, 'Role of Adsorption Phenomena in Cubic Tricalcium Aluminate Dissolution', *Langmuir*, vol. 33, no. 1, pp. 45-55. <https://doi.org/10.1021/acs.langmuir.6b03474>

Digital Object Identifier (DOI):

[10.1021/acs.langmuir.6b03474](https://doi.org/10.1021/acs.langmuir.6b03474)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

Langmuir

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.



The role of adsorption phenomena in cubic tricalcium aluminate dissolution

Rupert J. Myers^{1,2,*}, Guoqing Geng^{1,a}, Jiaqi Li^{1,b}, Erich D. Rodríguez^{3,4,c}, Juyoung Ha^{5,d}, Pinit Kidkhunthod^{6,e}, Garrison Sposito^{7,f}, Laura N. Lammers^{7,g}, Ana Paula Kirchheim^{3,h}, Paulo J. M. Monteiro^{1,i}

¹ Department of Civil and Environmental Engineering, University of California, Berkeley, California, United States. ² Yale School of Forestry & Environmental Studies, Yale University, 195 Prospect St, New Haven 06511 Connecticut, United States. ³ NORIE/UFRGS - Building Innovation Research Unit, Department of Civil Engineering, Federal University of Rio Grande do Sul, Brazil. ⁴ Politecnico School of Civil Engineering, IMED, Passo Fundo, Brazil. ⁵ School of Environmental and Sustainability Sciences, Kean University, New Jersey, United States. ⁶ Synchrotron Light Research Institute, 111 University Avenue, Muang District, Nakhon Ratchasima 30000, Thailand. ⁷ Department of Environmental Science, Policy, and Management, University of California, Berkeley, California, United States

* Corresponding author. Email: rupert.myers@gmail.com. Tel.: +1 510 646 6106. ^a guoqinggeng1989@gmail.com, ^b civiljiaqili@gmail.com, ^c erichdavidrodriguez@gmail.com, ^d haj@kean.edu, ^e pinit@slri.or.th, ^f gsposito@berkeley.edu, ^g lnammers@berkeley.edu, ^h anapaula.k@ufrgs.br, ⁱ monteiro@berkeley.edu.

Keywords: Adsorption; calcium sulfate; dissolution; gypsum; hydration; Portland cement (PC); retarder; tricalcium aluminate (C₃A); zeta potential

Abstract

The workability of fresh Portland cement (PC) concrete critically depends on the reaction of the cubic tricalcium aluminate (C₃A) phase in Ca- and S-rich pH > 12 aqueous solution, yet its rate controlling mechanism is poorly understood. In this paper, the role of adsorption phenomena in C₃A dissolution in aqueous Ca-, S- and polynaphthalene sulfonate (PNS)-containing solutions is

analysed. The zeta potential and pH results are consistent with the isoelectric point of C_3A occurring at $pH \approx 12$, do not show an inversion of its electric double layer potential as a function of S nor Ca concentration, and that PNS adsorbs onto C_3A , reducing its zeta potential to negative values at $pH > 12$. The S and Ca *K*-edge X-ray absorption spectroscopy (XAS) data obtained do not indicate structural incorporation nor specific adsorption of SO_4^{2-} on the partially-dissolved C_3A solids analysed. Together with supporting X-ray ptychography and scanning electron microscopy results, a model for C_3A dissolution inhibition in hydrated PC systems is proposed whereby the formation of an Al-rich leached layer and complexation of Ca-S ion pairs onto this leached layer provide the key inhibiting effect(s). This model reconciles the results obtained here with the existing literature, including the inhibiting action of macromolecules such as PNS and polyphosphonic acids on C_3A dissolution. Therefore, this paper advances the understanding of the rate controlling mechanism in hydrated C_3A and thus PC systems, which is important to better control the workability of fresh PC concrete.

1. Introduction

Portland cement (PC) concrete is the second most used commodity after fresh water. Approximately ~40 Gt of this material was produced in 2014 (assuming PC concrete contains ~10 wt.% PC).¹ Most concrete is ‘ready-mixed’ at a concrete plant and then placed on site as a concentrated slurry,¹ which sets to form the ubiquitous material that constitutes most civil infrastructure in existence today and will be built in the foreseeable future. Careful control of the PC concrete setting process is imperative to achieving a fluid, workable material throughout placement, and to produce a strong and durable construction material. The rheology and setting time of fresh PC concrete are significantly controlled by adding solid $CaSO_4$ (typically gypsum,

CaSO₄·2H₂O) to retard the hydration of the highly reactive cubic tricalcium aluminate (C₃A, Ca₃Al₂O₆, where C = CaO and A = Al₂O₃) phase in PC, which can be prolonged for hours.

In PC, C₃A is generally present as intimately intermixed crystallites with other phases, which are mostly tri- and di-calcium silicate (Ca₃SiO₅ and Ca₂SiO₄, respectively), and tetracalcium aluminoferrite (Ca₄Al₂Fe₂O₁₀).² The structure of C₃A contains tetrahedral Al in Al₆O₁₈¹⁸⁻ rings and Ca atoms in distorted octahedral or irregular bonding environments.^{3,4,5} Dissolution of C₃A in portlandite (Ca(OH)₂)-saturated aqueous CaSO₄ solutions leads mainly to the precipitation of ettringite (Ca₆Al₂S₃O₁₈·32H₂O) and ‘alumino-ferrite-mono’ (AFm) phases in CaO-Al₂O₃-SO₃-H₂O systems with mechanistically comparable yet slightly lower S/Al molar ratios (≈ 0.1⁶) than that present in PC systems (≈ 0.5⁷). AFm phases are layered double hydroxides based on substituted Ca(OH)₂-type structures. These AFm phases also precipitate initially in the absence of CaSO₄, although they are later destabilised to the more thermodynamically stable katoite (Ca₃Al₂O₆·6H₂O) phase.⁸ In the absence of CaSO₄, C₃A dissolution occurs so rapidly that most PC concrete irreversibly loses fluidity and prematurely ‘flash’ sets, greatly reducing workability and strength development.² Other compounds (admixtures), e.g., CaCl₂,⁹ and organic admixtures and polynaphthalene sulfonate (PNS),¹⁰ are also added to modify the reactivity of PC and workability of fresh PC concrete, their dosage depending on the reactivity of C₃A.¹¹ PNS is a synthetic commercial water-reducing admixture, typically polydispersed with mean molecular mass of >>1000 Da,^{12,13} that adsorbs onto hydrated PC particles and retards C₃A dissolution.^{11,13}

Despite the relatively low fraction of C₃A in PC (~5-10 wt.%), the properties of fresh PC concrete in the ‘induction period’ (i.e., the period of relatively high workability and low reaction rate of PC) critically depend on this phase. The C₃A/solution interface chemistry in aqueous CaSO₄ solutions and in water is significantly different,^{14,15,16} with adsorption phenomena generally agreed to

provide the key C₃A dissolution inhibiting mechanism in the former system. The seminal work on this topic^{14,17} used electron spectroscopy and Ar ion milling to identify an Al-rich ‘leached layer’ at the C₃A/solution interface, and electrophoresis and analytical chemistry methods to propose that both Ca ions and SO₄²⁻ complexes adsorb onto this layer and inhibit C₃A dissolution. This description is consistent with previous work^{2,16} and sustained by later research.^{6,18,19} The cement research community has recently rallied in support of adsorbed SO₄²⁻ complexes providing the key C₃A dissolution rate controlling factor in aqueous CaSO₄ systems,^{20,21} although not necessarily mentioning the Al-rich leached layer^{14,17} to which these SO₄²⁻ complexes would adsorb onto.

The postulated complexation of Ca and SO₄²⁻ on partially-hydrated C₃A is, however, based only on indirect macro- and/or microscopic evidence rather than direct molecular-scale information. Therefore, the chemistry and structure of the Al-rich leached layer and proposed Ca ions and SO₄²⁻ complexes are not known in enough detail to confirm the adsorption-controlled C₃A dissolution hypothesis. The proposed inhibiting effect of singly adsorbed SO₄²⁻ complexes on C₃A dissolution is also inconsistent with the adsorption behaviour of SO₄²⁻ in metal (hydr)oxide systems, where it interacts as a weak to intermediate adsorbate, similarly to SeO₄²⁻.²² For example, the tendencies of SO₄²⁻ and SeO₄²⁻ to specifically adsorb onto (bayerite-type) Al(OH)₃, γ-Al₂O₃, δ-Al₂O₃ and goethite (α-FeOOH) decrease strongly with increasing pH,^{23,24,25,26} with essentially no adsorption occurring above the pH of point of zero charge (pH_{pzc}), i.e., above pH 7-10. Therefore, specific adsorption of SO₄²⁻ onto the partially-dissolved C₃A surface at cement-relevant pH (i.e., pH > 12) is unlikely because this surface is Al-rich and is chemically similar to Al (hydr)oxide.¹⁴ Recent research has also identified the weak adsorption of Ca²⁺ on gibbsite (Al(OH)₃).²⁷ This finding contradicts the description of the partially-dissolved C₃A surface provided by Skalny and Tadros,¹⁷ who considered it to behave analogously to γ-Al₂O₃ and specifically adsorb Ca²⁺.²⁸ A better

understanding of the surface chemistry of partially-dissolved C_3A in aqueous solutions relevant to fresh PC concrete (i.e., containing Ca and S, and particularly at high pH) is needed to clarify these apparent contradictions. The effects of other commonly used admixtures (e.g., PNS) on the chemistry of the C_3A /solution interface chemistry are also incompletely understood.

Here, the surface chemistry of partially-dissolved C_3A in various Ca- and S-containing aqueous solutions is analysed by making use of the Gouy-Chapman-Stern model of the electric double layer (EDL).^{29,30,31} The EDL is thus conceptualised to contain: i) a ‘s-plane’ related to the structural and proton charge at the solid surface; ii) a ‘Stern layer’, which contains ‘ α ’ and ‘ β ’ planes associated with inner-sphere and outer-sphere (i.e., separated by at least one water molecule) complexes, respectively; and iii) a ‘d-plane’ further from the solid surface associated with the diffuse layer (‘diffuse ion swarm’) that balances the surface charge. Adsorption of inner-sphere complexes is specific, whereas adsorption of outer-sphere and diffuse layer complexes is non-specific. The Debye length (κ^{-1}) is an intrinsic length scale of the EDL that is a measure of the distance from the charged particle surface that coions (same charge as the particle surface) are excluded from.³¹ It is commonly associated with the ‘plane of shear’, which is assigned to the outer periphery of the Stern layer, including part of the diffuse layer.³⁰

Zeta potential measurements of aqueous C_3A samples are obtained systematically as functions of the pH and solution chemistry here. This is important because so far only a limited set of conditions have been used to characterise the chemistry of the C_3A / solution interface.^{14,15,32,33} S and Ca *K*-edge X-ray absorption spectroscopy (XAS) data are collected at the Synchrotron Light Research Institute (SLRI) and Brazilian Synchrotron Light Laboratory (LNLS), respectively. These data are analysed to characterise unreacted and partially-dissolved C_3A particles in gypsum-saturated solutions at the molecular level. This analysis represents a first attempt at simultaneously

characterising S and Ca *K*-edge XAS data of C₃A dissolution in aqueous CaSO₄ solutions, which is important to understand and develop model molecular structures for S and Ca adsorbates on calcium aluminate hydrates. S and Ca *K*-edge XAS and zeta potential results are also obtained and discussed for key solid phases in the C₃A-CaSO₄-H₂O system, which have generally not yet been comprehensively analysed.^{15,33,34,35} Morphological information of partially-dissolved C₃A particles is obtained by scanning electron microscopy (SEM) and complementary X-ray ptychographic imaging at the Advanced Light Source (ALS).³⁶ This paper aims to unify these results to provide an advanced description of the surface chemistry of partially-dissolved C₃A and insight into the rate-controlling mechanism of C₃A dissolution in PC-relevant aqueous solutions.

2. Experimental

Solids: The C₃A used (Mineral Research Processing Cie, hereafter MRP) was synthesised by firing a stoichiometric mixture of CaCO₃ and Al₂O₃ (both from Merck) twice at 1350°C for two hours in platinum vessels, and ground to a fine powder in an intermediate step. Its particle size distribution (PSD) and specific surface area is shown in the supporting information (SI). The powder was lightly reground for ~30 s by hand under a N₂ (g) atmosphere to create surface area that has been unexposed to air, and then stored in vacuum-sealed bags before use. Scanning electron microscope (SEM) imaging (see section 3.2) shows that particle diameters in the reground material are similar to the previously measured values. X-ray diffraction (XRD) and Rietveld analyses (using PANalytical HighScore Plus) showed that the C₃A powder contained ≥99 wt.% cubic C₃A (Powder Diffraction File (PDF)# 01-070-0839) (estimated uncertainty = ±3 wt.%). Free lime (CaO) was not identified in the X-ray diffractogram of the C₃A powder used (Figure S1, SI).

Reference zeta potential and XAS data were collected for several common phases in the C₃A-water(-calcium sulfate) system. These phases are ettringite (MRP), gypsum (Sigma-Aldrich),

calcium aluminate (CaAl_2O_4 , MRP), katoite (MRP), portlandite (Fisher Scientific), calcium hydroxyaluminate hydrate (OH-AFm, predominantly $\text{Ca}_4\text{Al}_2\text{O}_7 \cdot 13\text{H}_2\text{O}$), and calcium monosulfoaluminate hydrate (S-AFm, predominantly $\text{Ca}_4\text{Al}_2\text{SO}_{10} \cdot 12\text{H}_2\text{O}$). The procedures used to synthesise OH-AFm and S-AFm are described in the SI. The thermogravimetric analysis (TGA) and XRD data collected for these precursor materials are shown in Appendix C (SI). These reference data were used to assist in analysing the zeta potential, SEM, X-ray ptychography and XAS results obtained for the C_3A -containing samples.

Zeta potential and pH: Samples for zeta potential and pH analyses were synthesised under ambient laboratory conditions by hand-mixing 0.020 g solids and 4.0 g precursor solutions in polypropylene centrifuge tubes at a liquid/solid mass ratio (l/s) ≈ 200 , i.e. a large stoichiometric excess of water was used. The pH values of the precursor solutions used were adjusted with 1 M NaOH (Fisher Scientific) or 1 M HCl (synthesised from 37.7 wt.% HCl, J.T.Baker) before adding the solids, with an estimated ionic strength (I) range for these pH-adjusted solutions of $I < 0.3 \text{ mol kg}^{-1}$. The aqueous solutions are water ($18.2 \times 10^6 \text{ } \Omega \text{ cm}$, produced using a Barnstead NANOpure II with a filter size = $0.2 \text{ } \mu\text{m}$), 0.013 M K_2SO_4 produced from $\text{K}_2\text{SO}_4 (s)$ (Sigma-Aldrich), 0.013 M CaSO_4 produced from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} (s)$ (Sigma-Aldrich), 0.017 M CaCl_2 produced from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O} (s)$ (Fisher Scientific), and 0.03 wt.% PNS (Mira 151, W. R. Grace & Co.-Conn.). This PNS solution contains S and Na concentrations of 2.3×10^{-3} and $3.8 \times 10^{-3} \text{ mol L}^{-1}$ (determined by ICP-OES, estimated measurement error = $\pm 10\%$), respectively. Its PNS content was set to achieve a (dry) polymer to C_3A mass ratio of 0.06. This ratio value was chosen to approximately represent adsorption saturation of PNS in C_3A -containing K_2SO_4 systems at 30 minutes of hydration¹³ (the solids fraction in bulk PNS was determined using ASTM C494), acknowledging that the amount of PNS required to attain saturation likely varies from one C_3A source to another.

An Accumet pH meter (Fisher Scientific), calibrated to standard pH 4, 7 and 10 (Fisher Scientific), and pH 13 (Ricca Chemical Company) buffer solutions at $24\pm 2^\circ\text{C}$, was used to determine the pH of samples synthesised in this work (estimated absolute error = ± 0.3). Measurements of the sample pH were obtained at the reaction times analysed here (80 s, 130 s, 220 s, 550 s). Electrophoretic mobility (u_E) data were obtained using a Zetasizer ZSP (Malvern Instruments, particle size range of 3.8 nm to 100 μm) and ZetaPALS (Brookhaven Instruments Corporation) instruments operated at $22.0\pm 0.2^\circ\text{C}$. Two separate machines were used to improve the reliability of the results obtained. Zeta potentials (ζ) were calculated from the Smoluchowski equation (eq.(1)):

$$u_E = \frac{\varepsilon_0 \varepsilon \zeta}{\eta} \quad (1)$$

where ε_0 is the electric permittivity of free space ($8.854 \times 10^{-12} \text{ F m}^{-1}$), and ε and η are the relative permittivity and viscosity of the background electrolyte (values for water at 22°C of $\varepsilon = 79.6$ and $\eta = 0.9540 \text{ Pa s}$ were used). The Smoluchowski equation is valid for systems with $\kappa a > \sim 100$,³⁷ where a is the particle radius (\AA) and κ^{-1} is the Debye length (\AA) ($\kappa^{-1} = 2.8/T^{0.5} \text{ \AA}$ in the absence of organic compounds,³⁸ i.e., $\kappa^{-1} > 5.1 \text{ \AA}$ here). This condition is attained here due to the relatively large particle sizes of the solids used. Partial sedimentation of particles was identified in some samples during the electrophoresis experiments but was not corrected for.

Each zeta potential datum reported here represents the mean value of 15 measurements taken during specified time intervals after C_3A and precursor solutions were mixed (i.e., $80\pm 20 \text{ s}$, $130\pm 30 \text{ s}$, $220\pm 60 \text{ s}$, $550\pm 50 \text{ s}$). These reaction times were selected to sample the fastest times that the experiments could be reproducibly performed (limiting precipitation of reaction products), and the effects of precipitation and slight variation in $1/s$ values used on the results. Measurements were

repeated multiple times (see section 3.1) to obtain an overall picture of the experimental uncertainty (estimated measurement error for each datum = ± 15 mV).

SEM and X-ray ptychography: The same synthesis procedure used for the zeta potential and pH experiments was used to synthesise samples for the SEM and X-ray ptychography experiments (pH values modified to >12 by adding 1 M NaOH and mixing C₃A with precursor solutions at a l/s ≈ 200), with the exception of the additional steps described below.

SEM samples were filtered after 80 s of mixing using 0.45 μm nylon filters and then washed with $\geq 99.9\%$ ethanol (Koptec). The solids were then spread on carbon tape covered SEM sample holders and carbon coated. The SEM experiment was performed immediately afterwards using a Zeiss EVO Variable Vacuum Instrument -10 SEM operated at ~ 0.001 Pa and in secondary electron mode at an extra high tension voltage = 15.0 kV, a 50.0 μA beam current, a probe current = 14 pA, and a working distance of ~ 12 mm. SEM images were additionally obtained on unreacted C₃A and C₃A reacted in 0.013 M CaSO₄ for 300 s. Samples prepared for soft X-ray ptychographic imaging at beamline 5.3.2.1 of the ALS were drop-cast onto 100 nm-thick Si₃N₄ windows (Norcada) without a filtration step. Excess liquid was quickly removed using Kimwipes (Kimtech). The samples were then immediately transferred to the instrument chamber and subsequently exposed to a 750 eV X-ray beam at ~ 0.001 Pa. The pixel size of the reconstructed images obtained is ~ 5 nm \times 5 nm. Further details of the X-ray ptychography experimental setup used are presented in ³⁶.

S K-edge XAS: S K-edge XAS was performed at beamline 5.2 (SUT-NANOTEC-SLRI) at the SLRI, Thailand, which operates at 1.2 GeV and 50-150 mA, and produces 10^8 - 10^{10} photons s⁻¹ at a bending magnet source. The beam has a lifetime of ~ 12 hours and an emittance of 41 nm rad. Experiments were conducted in fluorescence mode using a 4-element Si drift detector (Vortex), an

InSb(111) crystal monochromator, and a beam size of 20 mm × 1 mm. The XAS data collected were referenced by assigning 2472.0 eV to the lowest energy inflexion point of the *K*-edge absorption spectrum of S powder (oxidation state = 0, Sigma-Aldrich #414980). S *K*-edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were collected from 2402 to 3120 eV with step sizes of 5 eV up to 2452 eV, 0.2 eV from 2452 to 2502 eV, and 1-5 eV from 2502 to 3120 eV.

Reference solid phases (S-AFm, ettringite and gypsum) were mixed with ~1 μm³-sized 98 wt.% BN (Sigma-Aldrich) at a respective mass ratio of 1:19, placed on a kapton tape backing, covered with polypropylene film, and then analysed. Data for the 0.013 M CaSO₄ precursor solution was obtained in a cell with polypropylene film windows. Hydrated samples were synthesised by consecutively immersing C₃A, S-AFm, ettringite or katoite in 0.013 M CaSO₄ at a l/s ≈ 360 up to 300 s, and then in two ≥99.9% ethanol (Koptec) solutions for 30 s, first at a l/s ≈ 210, and subsequently at a l/s ≈ 140. These samples were then immediately transferred to a desiccator and vacuum dried at 700 Pa over SiO₂ gel, pressed into smooth, thin (~1 mm) and flat disks once dry, and then stuck to a kapton tape backing and transferred to the He_(g)-filled instrument chamber.

Ca *K*-edge XAS: Unreacted and partially-reacted C₃A, and gypsum were prepared for Ca *K*-edge XAS analysis by first spreading 0.020 g of C₃A or gypsum onto carbon tape covered sample stages. The partially-reacted C₃A sample was produced by immersing a C₃A-covered sample stage into 20 ml saturated gypsum solution for 1 s, which was then immediately rinsed with ≥99.9% ethanol (EMSURE®, Merck) for 60 s to remove excess aqueous solution. Samples were analysed at the extended Ca *K*-edge (3960-4800 eV). Experiments were performed at beamline SXS, LNLS, located at the 4° port of the bending magnet station D004A, using a double crystal Si(111) monochromator, a photon flux of 2.4 × 10¹⁰ photons s⁻¹ at 3 keV machine energy, and a current of

100 mA. Spectra were collected in total electron yield (TEY) mode at 2×10^{-4} Pa. Three to ten spectra were collected and averaged for each sample. Energy calibration was performed using the $L_3 2p_{3/2}$ Mo peak by assigning the energy of the first edge inflection point to 2520 eV. The S and Ca K -edge XAS data are analysed using the Athena and Artemis modules of the Demeter v.0.9.24 software,³⁹ which utilises FEFF6 and IFEFFIT v.1.2.12.

3. Results and discussion

3.1 Zeta potential, pH and ICP-OES

The following coupled zeta potential and solution chemistry analysis is used to investigate the influence of cations (e.g., Ca^{2+} and CaOH^+), anions (e.g., SO_4^{2-} , Cl^-), and ion pairing (e.g., CaSO_4^0) on the surface potential of C_3A and chemistry at the C_3A /solution interface. Zeta potential values measured at different reaction times are similar at constant pH, for each reaction system. The data obtained for C_3A immersed in water are consistent with an isoelectric point (IEP) at $\text{pH} \approx 12$ and the existing data for this phase,¹⁴ with the zeta potential decreasing from ~ 40 mV below $\text{pH} \approx 10$ to -30 mV at $\text{pH} = 12.8$ (Figure 1A). The large range of zeta potentials measured for C_3A at $\text{pH} > 12$ here may result from heterogeneous C_3A dissolution and thus a variety of chemistries at the C_3A surface, and the presence of surface-bound reaction products (see section 3.2).

Significantly increased zeta potentials for C_3A in 0.017 M CaCl_2 relative to water are only measured at $\text{pH} > 12$ (Figure 1B), and are mostly non-negative in this pH range. The similar yet less negative zeta potentials measured for C_3A in 0.017 M CaCl_2 relative to water suggests that the EDL is compressed in the former system relative to the latter due to its increased ionic strength. The data do not show an inversion of the zeta potential at $\text{pH} > 12$ with respect to these systems, which does not support the assignment of specifically adsorbed Ca on partially-dissolved C_3A .

Figure 1. Zeta potentials of C₃A in (A) water, (B) 0.017 M CaCl₂, (C) 0.013 M K₂SO₄, (D) 0.013 M CaSO₄ and (E) 0.03 wt.% PNS, as functions of pH and time after mixing (80±20 s to 550±50 s). The dashed horizontal lines are intended as eye guides only. The estimated uncertainties of the pH and zeta potential values are indicated by the size of the symbols used and spread of the data points, respectively. Data from ¹⁴ are for C₃A reacted in water (l/s = 250) for two minutes with pH adjusted by aqueous HCl or NaOH solutions. The instruments used to produce each datum are indicated in the legend. Plots of the pH > 10 regions in (A)-(E) are shown in the SI.

The zeta potentials measured for C₃A in 0.013 M K₂SO₄ are close to zero over the range of pH values analysed (Figure 1C), and are within the range of zeta potentials measured for C₃A in water at pH ≥ 11.5. The IEP of C₃A is identified to occur at pH ≈ 12 in this system. The overall range of zeta potential values for C₃A immersed in 0.013 M K₂SO₄ is greatly reduced relative to the 0.017 M CaCl₂ system, indicating that SO₄²⁻ ions are much more effective at compressing the diffuse layer than Cl⁻ ions due to their increased effect on ionic strength. It is expected that SO₄²⁻ is the dominant aqueous S species here because K₂SO₄ is a strong electrolyte and pK_{a2}(H₂SO₄) ≈ 2. Charge reversal is not identified in the 0.013 M K₂SO₄ system relative to water, which can suggest that SO₄²⁻ is non-specifically adsorbed at pH < 12, although it is not possible to unambiguously determine the molecular structure of adsorbed SO₄²⁻ complexes from these zeta potential data alone. However, specific adsorption of SO₄²⁻ onto C₃A is not supported by existing work: adsorbed inner-sphere SO₄²⁻ would be consistent with C₃A dissolution inhibition by blocking surface sites from reacting with aqueous species, although only small differences in the rates of heat released and solid phases produced by C₃A dissolution in water, Na₂SO₄ and K₂SO₄ is measured (additional details regarding ⁴⁰ are provided as SI).^{13,40}

Similar results are obtained for C₃A in 0.013 M K₂SO₄ and 0.013 M CaSO₄ (Figures 1C-1D). The IEP of C₃A is identified to occur at pH ≈ 12 in the latter system. The significantly reduced range of zeta potentials measured for C₃A in 0.013 M CaSO₄ relative to 0.017 M CaCl₂ is again consistent with SO₄²⁻ more effectively compressing the diffuse layer of C₃A than Cl⁻, and shows

that this effect, assigned to ionic strength differences, is essentially independent of the balancing cation (Ca^{2+} or K^+). The absence of a reversal in zeta potential values at constant pH in this 0.013 M CaSO_4 system relative to water is consistent with assigning Ca complexes (e.g., Ca^{2+} and CaOH^+) and SO_4^{2-} to non-specifically adsorbed species in the aqueous C_3A systems analysed here.

On the basis of current and prior observations of zeta potentials in aqueous C_3A systems,^{14,15,32,33} it is not possible to conclude that Ca or S alone inhibit C_3A dissolution through an adsorption mechanism. However, the significance of Ca in inhibiting C_3A dissolution is supported by reported reduced C_3A dissolution rates in the presence of aqueous solutions with higher Ca concentrations, e.g., aqueous CaSO_4 ^{6,17} and CaCl_2 solutions,⁴¹ and also by reported uninhibited C_3A dissolution rates in aqueous Na_2SO_4 solutions (lower Ca concentration).⁴⁰ Given the consensus that CaSO_4 significantly affects C_3A dissolution rates, a cooperative effect can be proposed to arise whereby Ca and S together act to inhibit C_3A dissolution, with this effect being strongest in the presence of both elements. This effect could manifest through adsorption of Ca-S ion pair complexes (e.g., CaSO_4^0 , which occurs in $12 < \text{pH} < 13$ aqueous CaSO_4 solutions at significant non-zero concentrations that would not be lowered by adsorption because of continuous replenishment through rapid ion-pair formation in solution) onto the Al-rich leached layer to maintain a high concentration of Ca at the C_3A /solution interface, decreasing the local undersaturation of the aqueous solution with respect to C_3A . This effect would not require the presence of specifically adsorbed complexes. The Ca-S ion pair complexes may be viewed as an intermediate step to the nucleation and growth of surface-bound solid hydration products (e.g., AFm and ettringite)⁴² due to their close proximity to the C_3A surface, which could additionally inhibit C_3A dissolution through enhanced surface polymerisation and blocking of reactive surface sites (see section 3.5).³⁰ Surface-bound precipitates and adsorbed Ca-S ion pair complexes are explored further below. This

analysis does not preclude differences in adsorption behaviour with respect to different surface site types, e.g., step, kink, and adatom.⁴³

This pH and zeta potential analysis is also applied to aqueous PNS systems to better understand the adsorption behaviour of PNS on C₃A, as it is a commonly used admixture. Analogous to the 0.013 M K₂SO₄ and 0.013 M CaSO₄ systems, zeta potentials of C₃A are reduced to approximately zero in 0.03 wt.% PNS at pH < 11.5 (Figure 1E). However, the zeta potentials of C₃A in 0.03 wt.% PNS at pH > 11.5 are all negative; therefore, PNS has inverted the zeta potential of C₃A in this system relative to the positive values obtained in water in this pH range. This result indicates that PNS adsorbs onto partially-dissolved C₃A. This interpretation is consistent with the reported C₃A dissolution-inhibiting action of PNS,^{13,32} because adsorption of macromolecules such as PNS would facilitate blocking of reactive surface sites. The zeta potential results would then suggest that adsorption of PNS onto solid reaction products is also likely, particularly onto phases such as ettringite and ³⁴ AFm ⁴⁴ that specifically complex SO₄²⁻ (the latter of which precipitates here, see section 3.2), because the chemistry of SO₄²⁻ and –SO₃⁻ functional groups in PNS are similar.⁴⁵ Existing research shows that PNS alters the chemistry and morphology of ettringite,^{33,46} consistent with this interpretation. The influence of surface-bound precipitates are explored further below.

3.2 SEM and X-ray ptychography

X-ray ptychographic and SEM images of partially-dissolved C₃A particles were obtained to qualitatively assess the influence of surface-bound precipitates on the zeta potential and pH data, and to compare with the S and Ca *K*-edge XAS results (sections 3.3-3.4). Solid reaction products with predominantly hexagonal plate-type morphology, most likely AFm phases,^{9,40} are observed to precipitate directly on C₃A particles (red arrows) reacted for 80 s in NaOH-modified (pH = 12.5-13) water (Figure 2B), and 0.017 M CaCl₂ (Figure 2C), 0.013 M K₂SO₄ (Figure 2D), 0.03 wt.%

PNS (Figure 2E), and 0.013 M CaSO₄ (Figure 2F) by SEM (main plot areas) and X-ray ptychography (insets). Hexagonal platelets are also identified on C₃A particles reacted in 0.13 M CaSO₄ for 300 s (Figure 2G). Needle shaped precipitates are not observed, showing that ettringite has not formed to a major extent in any of the S-containing samples. This result is consistent with the literature for C₃A hydrated in aqueous CaSO₄^{6,8,40,47} and Na₂SO₄⁴⁰ solutions at these reaction times (typical bulk molar S/Al ratios = 0.1-0.5), where precipitation of AFm phases dominates.

Figure 2. SEM (main plot areas) and X-ray ptychographic (insets) images of (A) unreacted C₃A, C₃A reacted in (B) water, (C) 0.017 M CaCl₂, (D) 0.013 M K₂SO₄, (E) 0.03 wt.% PNS, and (F) 0.013 M CaSO₄ for 80 s with pH values of the precursor solutions adjusted to 12.5-13 using 1 M NaOH, and (G) C₃A reacted in 0.013 M CaSO₄ for 300 s. In B-G, precipitates with hexagonal platelet-type morphologies are marked by red arrows and exposed C₃A surface area is marked by unfilled yellow squares.

Moderate to high proportions of the partially-dissolved C₃A surface are exposed in the reacted samples (Figures 2B-2G, unfilled yellow squares). Exposed surface area is qualitatively assigned to visually smooth areas with no hexagonal plate-shaped features that are characteristic of solid reaction products. This interpretation is consistent with the visually smooth surfaces of the unreacted C₃A particles imaged by SEM (Figure 2A). Exposed C₃A surface area is irregularly spaced in each reacted sample. Moderate amounts of both solid reaction products and exposed C₃A surface area are observed in the images of C₃A partially reacted in water, 0.017 M CaCl₂, 0.013 M K₂SO₄, and 0.013 M CaSO₄. Less precipitates are identified on C₃A particles partially reacted in 0.03 wt.% PNS, thus PNS has inhibited the dissolution of C₃A in this system. In summary, the SEM and X-ray ptychography results show that precipitates cover low (Figure 2D) to moderate (Figures 2B, 2C, 2E and 2F) proportions of the partially-dissolved C₃A surface. Therefore, the SEM and X-ray ptychography results signify that surface-bound precipitates provide secondary, rather than dominant effects, on the zeta potential values and trends shown in Figure 1.

3.3 S *K*-edge XAS

S *K*-edge XAS data were obtained to directly analyse the chemistry of S adsorbed on C₃A partially reacted in 0.013 M CaSO₄. The S *K*-edge XANES spectra (Figure 3A) are all characteristic of S in the 6+ oxidation state (i.e., SO₄²⁻) with peak *a* located at 2483.5-2483.8 eV,⁴⁸ which represents the transition of the 1s core electron to the 3*p*-like *t*₂ state.⁴⁸ With the exception of gypsum, all the spectra show a broad peak *b* at 2499 eV that is assigned to multiple scattering (MS) resonances.⁴⁸ The S *K*-edge XANES spectrum for gypsum contains three distinct post-edge peaks, consistent with existing results.^{48,49} These peaks are also reported for anhydrite.⁵⁰ The features of the ettringite and S-AFm spectra are consistent with the published S *K*-edge XANES data for these phases.^{48,49,50}

Figure 3. Normalised S *K*-edge XAS results for reference phases and C₃A systems, with times (in seconds, abbreviated as s) denoting the durations that the specified materials were immersed in 0.013 M CaSO₄ prior to analysis (pH during immersion ≈ 11-12): (A) S *K*-edge XANES spectra; (B) *k*³-weighted χ data; and (C) magnitudes of the RSFs (radial structure functions) of the Fourier transformed χ data. Characteristic features are marked by labelled vertical grey shaded regions and lines (discussed in the text).

The S *K*-edge XANES spectra for C₃A and katoite immersed in 0.013 M CaSO₄ (Figure 3A) represent SO₄²⁻ in S-containing reaction products and/or residual (formerly aqueous or adsorbed) SO₄²⁻ remaining after washing with ethanol and drying. The significant differences between these XANES spectra and those obtained for gypsum show that gypsum is absent in the katoite and C₃A-containing samples. This analysis is supported by the *k*³-weighted χ data (Figure 3B) collected for these samples, as the spectrum for gypsum contains a shoulder at 4.5 Å⁻¹ (peak *) but the spectra for the C₃A- and katoite-containing samples do not. A shoulder at this *k*-value is also present in the *k*³-weighted χ data for ettringite (peak *, Figure 3B), both dry and after immersion in 0.013 M CaSO₄ for 300 s, ruling out the presence of this phase in the C₃A- and katoite-containing samples.

This result is consistent with the absence of ettringite (needle-like precipitates) in the SEM images at this reaction time (Figure 2G, section 3.2). The k^3 -weighted χ data for the katoite and C₃A samples, 0.013 M CaSO₄, and for the systems containing S-AFm, are qualitatively similar.

The magnitudes of the radial structure functions (RSFs) obtained by Fourier transforming the χ data (Figure 3C), which represent approximate interatomic correlations between S and nearby atoms in real space (modified slightly negatively from the true interatomic correlations by the phase function⁵¹), all show a dominant peak at ~ 1.1 Å (peak *c*) that is assigned to single scattering (SS) of S-O atoms in SO₄²⁻ tetrahedra. The minor peaks at smaller distances are artefacts caused by truncating the Fourier transform and do not correspond to scattering atoms. The position of this peak corresponds to true atomic S-O distances of ~ 1.3 - 1.5 Å, e.g., in ettringite,⁵² S-AFm,⁵³ and gypsum.⁵⁴ The RSF curves for ettringite and S-AFm immersed in 0.013 M CaSO₄ show a secondary peak at 2.2 Å (peak *d*) that is enhanced relative to the spectra obtained for these materials when measured without immersion in 0.013 M CaSO₄. This peak likely corresponds to MS of S-O-O atoms, which is predicted from FEFF path length calculations in Artemis software³⁹ using the bulk crystal structures of these materials.^{52,53} The RSF curve for gypsum shows a peak at 3.2 Å that can be assigned to SS of non-neighbouring S-O atom pairs positioned relatively closely to SO₄²⁻ tetrahedra. The S-O MS peak at 2.2 Å that is expected for gypsum (from FEFF calculations,³⁹ using its bulk crystal structure) is not apparent in the RSF data, potentially hidden behind the high-Å contributions from single scattering S-O atoms in SO₄²⁻ tetrahedra at this *R* distance.

The spectra for the C₃A samples show a broad secondary peak comprised of two resonances at ~ 2.4 Å (peak *e*) and ~ 2.7 Å (peak *f*). The slightly modified shape and position of this peak in the RSF curve for C₃A immersed in 0.013 M CaSO₄ for 300 s to lower *R* distances at ~ 2.3 Å (i.e., towards peak *d*, Figure 3C), is assigned to the increased number of S-AFm precipitates at this

reaction time relative to 1-10 s. This assignment is consistent with the hexagonal plate-like precipitates observed by SEM after immersion in 0.013 M CaSO₄ for 300 s (Figure 2G), and as ettringite, which is the only other material that contains this peak here, was previously discounted based on the k^3 -weighed χ data (Figure 3B). This analysis does not preclude the possibility that the hexagonal plate-like precipitates are partly AFm intercalated with other anions, e.g., OH⁻.

The broad secondary peak (peaks *e* and *f*) in the S *K*-edge XAS spectra for the C₃A samples is also present in the RSF for katoite immersed in 0.013 M CaSO₄ for 10 s, but not in the spectra for any other sample. Zeta potential and pH data obtained here for katoite are similar in water, -18.7 mV at pH = 12.5, and in 0.013 M K₂SO₄, -17.2 mV at pH = 12.4, consistent with a datum reported elsewhere.³⁵ Therefore, these data do not show a significant correlation between the EDL potential of katoite and the aqueous SO₄²⁻ concentration nor ionic strength. A recent electron microprobe analysis found no evidence for significant S incorporation in Si hydrogarnet (katoite is the Si-free end member of the hydrogarnet solid solution). The results of that work also indicate that the dissolution extent of katoite would be very low under the experimental conditions employed here (i.e., immersed in 0.013 M CaSO₄ for 10 s at room temperature).⁵⁵ Therefore, these results most likely indicate that the SO₄²⁻ in the RSF of the katoite system is not structurally incorporated into the solid phase nor specifically adsorbed, but is rather adsorbed outer-sphere, diffuse layer or residual aquo SO₄²⁻ from the bulk solution that has deposited on the particle surface during sample preparation (washed with ethanol and subsequently dried). Consequently, the broad secondary resonance containing peaks *e* and *f* in the C₃A samples can be assigned to these same deposited SO₄²⁻ complexes. A more detailed analysis comparing well-established model molecular structures of SO₄²⁻ adsorbates on calcium aluminate hydrate phases with these S EXAFS spectra, and a better

understanding of the molecular structure of the partially-dissolved C₃A surface, is necessary to confirm the identity of these S-bearing complexes: this work presents a first step towards this goal.

3.4 Ca *K*-edge XAS

Surface-sensitive Ca *K*-edge XAS data (typical TEY sampling depth is <several nm) were obtained to assess the chemistry of Ca at the C₃A/solution interface on initial dissolution in aqueous CaSO₄ solution (saturated with respect to gypsum, ~0.017 M CaSO₄). The Ca *K*-edge XANES spectra for gypsum, C₃A and C₃A reacted in this solution for 1 s are similar (Figure 4A). Each spectrum contains a major peak *b* at ~4055.5 eV corresponding to the 1s → 4p transition,⁵⁶ minor peaks *c* (4056 eV), *d* (4064.5 eV), *e* (4075 eV) and *f* caused by MS, and a peak *c*, which corresponds to the 1s → 5s transition.⁵⁶ Peak *f* occurs at a lower energy in the XANES spectrum for gypsum (4083 eV) relative to the C₃A samples (~4090 eV). The additional shoulders (peak *a*) at 4033.3 eV in the spectra for the C₃A samples are ~1 eV lower relative to its position in the spectrum for gypsum (at 4034.3 eV), which is consistent with the lower average coordination number of Ca atoms in C₃A (7.3) relative to 8 in gypsum⁵ because the Ca *K*-edge energy generally increases as a function of the coordination number.⁵⁷ The minor resonances in the gypsum Ca *K*-edge XANES spectrum are less intense relative to those previously reported,⁵⁸ although they occur at the same energies. The lack of a double peak at peak *b* in the spectra for the sample containing C₃A reacted in saturated gypsum solution for 1 s, characteristic of ettringite,⁵⁸ indicates that this phase is not present in this system, which is consistent with the S *K*-edge XAS results and analysis presented in section 3.3.

Figure 4. Normalised Ca *K*-edge XAS results. (A) Ca *K*-edge XANES spectra; (B) *k*³-weighted χ data; and (C) magnitudes of the RSFs of the Fourier transformed χ data. C₃A immersed in a gypsum-saturated solution (~0.017 M CaSO₄) prior to analysis (pH during immersion ≈ 11-11.5) for 1 second (abbreviated as s) is marked by 'C₃A 1 s' (black solid lines), and data for gypsum and C₃A are represented by dashed green and solid purple lines, respectively. In (C), the *g* peaks are marked by the grey shaded region.

The k^3 -weighted χ data for C₃A and C₃A reacted in saturated gypsum solution for 1 s are similar (Figure 4B), differing substantially from the data collected for gypsum. All of the data have relatively poor signal to noise ratios at $k > \sim 10 \text{ \AA}^{-1}$ and anomalous spikes in intensity at 4.1 \AA . The RSF for gypsum (Figure 4C) is generally consistent with both FEFF calculations³⁹ using its known crystal structure⁵⁴ and previously reported Ca EXAFS data for this phase,⁵⁸ which contains the major Ca-O SS peak *g* (1.7 \AA) and additional peaks *h* (2.7 \AA) and *i* (3.9 \AA) that correspond to SS of Ca-S⁵⁸ (Ca coordinated with O atoms in SO₄²⁻ groups⁵⁴) and Ca-Ca atoms, respectively. Peak * is anomalous as it is not present in the previously reported RSF⁵⁸ and does not correspond to any strong resonances determined through the FEFF calculations.

The RSF for gypsum differs greatly from the RSFs for the C₃A samples (Figure 4C). The positions of the features in the RSFs for the C₃A samples (Figure 4C) are consistent with FEFF calculations of Ca scattering paths in bulk C₃A:⁴ the major Ca-O SS peak *g* occurs at an *R*-distance of $\sim 1.9 \text{ \AA}$; peak *j* (2.9-3.1 \AA) corresponds to SS of Ca-Ca and Ca-Al atoms; peak *k* ($\sim 3.5 \text{ \AA}$) represents SS of Ca-Al, Ca-O and Ca-Ca atoms and MS of Ca-O-Al and Ca-O-Al-O atoms; and peak *l* (4 \AA) corresponds to SS of Ca-O atoms. However, the location of peak *j* is shifted by 0.2 \AA to a higher *R* value in the spectrum for C₃A immersed in 0.013 M CaSO₄ for 1 s relative to unreacted C₃A (3.1 \AA and 2.9 \AA , respectively, Figure 4C). This result shows that the initial reaction of C₃A in saturated gypsum solution has significantly modified the atomic configurations of Ca atoms that are next-nearest neighbours to Ca and Al atoms in C₃A. Specific adsorption of Ca on the Al-rich leached layer of partially-dissolved C₃A, i.e., through Ca-O-Al bonding, would result in distances between next-nearest neighbouring Ca and Al atoms of $\sim 3 \text{ \AA}$ and so can be consistent with this result, although this assignment cannot be made due to the preliminary nature of the analysis presented

here. Additional work, e.g., molecular simulations ³⁴ and/or an extension of this Ca EXAFS analysis through use of model adsorbate molecular structures and a better understanding of the chemistry of partially-dissolved C₃A is necessary to better determine the cause of this difference.

3.5 Model of C₃A dissolution inhibition in aqueous solutions

The results presented in sections 3.1-3.4 do not identify SO₄²⁻ or Ca cations as EDL potential-determining complexes and so do not indicate that they specifically adsorb to the Al-rich leached layer at the partially-dissolved C₃A surface. This adsorption behaviour is consistent with neither SO₄²⁻ nor Ca cations alone providing the key rate-controlling mechanism for C₃A dissolution in PC-relevant aqueous solutions, i.e., with pH > 12 and relatively high S and Ca concentrations ($\geq \sim 10$ mmol L⁻¹). A more complex mechanism and potentially involving more than one chemical constituent would then be needed, considering C₃A dissolution is uninhibited in Na₂SO_{4 (aq)},⁴⁰ overall inhibited⁴¹ although more precipitates are initially formed in CaCl_{2 (aq)} (i.e., within the first few minutes of hydration⁹), and is inhibited in CaSO_{4 (aq)}.⁶

Those previously reported results^{6,40} show that C₃A dissolution becomes increasingly inhibited as a direct function of the aqueous Ca concentration in S-containing aqueous solutions. There is also a prevailing general consensus that S plays a key C₃A dissolution rate-controlling role in PC-relevant aqueous solutions.^{20,21} This understanding can be reconciled with the results shown here if the presence of soluble S increases the local concentration of Ca at the C₃A/solution interface, thereby acting to decrease the dissolution rate of Ca in the Al-rich leached layer that forms through dissolution of C₃A (and consequently to inhibit dissolution of the underlying C₃A solid, Figure 5).^{17,59} Non-specific adsorption of Ca-S ion pair complexes (section 3.1) onto this leached layer can be consistent with this explanation and with the results presented here.

Solutions relatively rich in Ca and S are produced through the initial hydration of C₃A and PC in the presence of CaSO₄. Ca concentrations of 20-40 and 10-25 mmol L⁻¹, S concentrations of 10-20 and 50-200 mmol L⁻¹, and pH values of ~12.5 and ~13, are measured for CaSO₄-containing aqueous C₃A and PC systems before complete dissolution of the solid CaSO₄ source, respectively.^{6,7,60} If adsorption of Ca-S complexes controls the dissolution rate of C₃A in aqueous CaSO₄ solutions, then these adsorbates will accumulate at the partially-dissolved C₃A surface during this initial reaction period. Net desorption or consumption of adsorbed Ca-S complexes would occur if the bulk solution becomes and remains sufficiently depleted in Ca and/or S. The local undersaturation with respect to C₃A surface sites and the C₃A dissolution rate would then consequently increase, remaining elevated otherwise a net accumulation of Ca-S complexes at the C₃A/solution interface reoccurs (to again inhibit C₃A dissolution). This scenario is consistent with the reported rapid reaction of C₃A in PC-relevant systems once the solid CaSO₄ source completely dissolves, i.e., when the bulk aqueous Ca and S concentrations decrease rapidly in fresh hydrated PC,⁷ and when the bulk aqueous S concentration approaches 0 in hydrated C₃A and gypsum.⁶

Figure 5. Schematic representation of the model C₃A/solution interface in aqueous CaSO₄ solution with initially formed AFm (e.g., at 80 s in 0.013 M CaSO₄, Figure 2F) and subsequently precipitated ettringite (e.g., during dissolution of C₃A in aqueous solution saturated with respect to CaSO₄ and Ca(OH)₂⁶), at pH > 12, showing outer-sphere adsorption of Ca and Ca-S ion pair complexes (CaSO₄⁰) onto partially-dissolved C₃A. AFm is depicted as OH-AFm without precluding precipitation of AFm with other intercalated anions e.g., SO₄²⁻. The positions, number and size of the model units shown are approximate: readers are referred to the crystallographic literature for accurate structures of the solid phases depicted.^{4,5,52} C₃A dissolution is occurring from right to left and is shown to rearrange near-surface structural units in the Al-rich leached layer. The C₃A surface is depicted to bear a negative charge, which is expected at pH > 12, from preferential dissolution of Ca structural units,¹⁷ and from outer-sphere Ca adsorption in this pH range. The EDL and Stern layer are both enlarged relative to their expected size in fresh PC systems ($I \approx 0.4 \text{ mol kg}^{-1}$,⁶⁰ thus $\kappa^{-1} \approx 4 \text{ \AA}$ in the absence of organic compounds).

Adsorption of PNS onto C₃A, which is indicated by the zeta potential analysis shown in section 2.1 (Figure 2E), can be anticipated to further inhibit C₃A dissolution by blocking reactive surface

sites. This interpretation is corroborated by isothermal calorimetry results.¹³ The dissolution inhibiting effect of PNS would be stronger if it is added initially to the aqueous solution prior to introducing C₃A, rather than afterwards, because surface precipitates could partly hinder the transport of PNS to the C₃A surface, e.g., through adsorption. Additional evidence supporting the assignment of PNS adsorption to strongly inhibit C₃A dissolution is found in the similar inhibiting action of nitrile-tris(methylene)phosphonic acid (N[CH₂PO(OH)₂]₃), which deprotonates at neutral to high pH, forms bidentate complexes with Ca, and grows to form the stable precipitate [N[CH₂PO(OH)₂]₂[CH₂PO(OOCa)](H₂O)]_n·3.5H₂O.¹⁹ This pairing to form CH₂PO(OOCa) functional groups may analogously occur between PNS and Ca, and potentially also between Ca-S complexes and the partially-dissolved C₃A surface.. This latter effect would enhance the nucleation and growth of surface-bound precipitates (e.g., ettringite, Figure 5) and inhibit C₃A dissolution if blocking of reactive surface sites outweighs the relative increase in undersaturation that would occur through removal of Ca and S from solution (e.g., when aqueous Ca and S concentrations are effectively constant before complete gypsum dissolution in the C₃A-gypsum-H₂O system ⁶). Hydration of C₃A and PC is also inhibited by phosphates (e.g., Na₃PO₄^{10,61}), which form strong ion pair complexes with both Ca (e.g., CaHPO₄⁰) and Al (e.g., AlH₂PO₄²⁺), and can further support the significant role of Ca-S complex adsorption in the model.

Based on the model proposed here (Figure 5), compounds which adsorb onto the Al-rich leached layer of partially-dissolved C₃A and contain Ca (e.g., CaSO₄⁰), and block reactive surface sites (e.g., PNS), are expected to inhibit C₃A dissolution. These types of compounds can also be expected to inhibit the dissolution of other phases with similar chemistry to C₃A, e.g., tetracalcium aluminoferrite, which is experimentally observed.¹⁹ Therefore, the proposed C₃A dissolution model provides a more unified description of the rate-controlling factor in aqueous C₃A and CaSO₄

systems, and by extension PC systems, than previously reported. This understanding can, e.g., be used to facilitate the development of improved chemical admixtures for fresh PC concrete, to improve the workability of this material. However, further experimental and modelling work is needed to clarify the molecular structure of adsorbates in aqueous C_3A systems, and the surface chemistry of partially-dissolved C_3A . This paper represents a preliminary step towards that goal.

4. Conclusions

This paper presented experimental results on the chemistry and morphology of the C_3A /solution interface in aqueous Ca-, S- and PNS-containing aqueous solutions and a model of C_3A dissolution that is consistent with the data presented and is relevant to fresh PC concrete. The zeta potential and pH results showed that the diffuse layer of C_3A is compressed as a function of increasing ionic strength, with SO_4^{2-} much more effectively compressing the diffuse layer than Cl^- irrespective of the balancing cation (K^+ or Ca^{2+}). These data also showed that the IEP of C_3A occurs at $pH \approx 12$ and the absence of an EDL charge reversal caused by S or Ca. This latter result was interpreted to indicate that these elements do not alone provide the key C_3A dissolution rate controlling factor in fresh PC concrete. The SEM, X-ray ptychography and S and Ca *K*-edge XAS data obtained were consistent with this interpretation. Together with existing data which show that C_3A dissolution in aqueous solution is greatly inhibited in the presence of Ca and S but not additional S alone, a model was proposed whereby the formation of an Al-rich leached layer and adsorption of Ca-S ion pair complexes onto this leached layer provide the key C_3A dissolution rate limiting effect(s) in fresh PC concrete. This model also describes how macromolecules such as polyphosphonic acids and PNS are able to inhibit C_3A dissolution, by blocking reactive surface sites through adsorption.

Morphological information of the C_3A /solution interface obtained by SEM and X-ray ptychography indicated that predominantly AFm phases, including S-AFm and consistent with the

S and Ca *K*-edge XAS data, precipitated on the partially-dissolved C₃A particles analysed here. Low to moderate coverage of these phases on C₃A particles was found. Together with the zeta potential and pH data obtained, the results demonstrated that these surface precipitates partially contribute to but do not dominate the zeta potential results. Therefore, the proposed C₃A dissolution model reconciles the results obtained here and reported in the literature, advancing the understanding of C₃A dissolution in aqueous CaSO₄ solutions.

5. Supporting information

The procedures used to synthesise S- and OH-AFm are described in Appendix A. XRD, TGA, PSD and specific surface area data of solid phases are shown in Appendix B. Plots of the pH > 10 regions in Figures 1A-1E are shown in Appendix C. Appendix D contains a reanalysis of data presented in ⁴⁰. This material is available free of charge via the Internet at <http://pubs.acs.org>.

6. Acknowledgements

The postdoctoral research of Rupert J. Myers at the University of California, Berkeley, was funded by Siam Cement Public Company (SCG) Ltd. Research done at the Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. This research was funded by the Republic of Singapore's National Research Foundation through a grant to the Berkeley Education Alliance for Research in Singapore (BEARS) for the Singapore-Berkeley Building Efficiency and Sustainability in the Tropics (SinBerBEST) Program. BEARS has been established by the University of California, Berkeley as a center for intellectual excellence in research and education in Singapore. The study was also sponsored by the LNLS (Brazilian Synchrotron Light Laboratory) under project SXS1785/18902. The Laboratory of Ceramics (LACER, UFRGS) is thanked for the N₂ adsorption and particle size distribution results, Carlos A. O. Rios for insightful

discussions on admixtures, Ubonwan Khopongpaiboon, Panod Viseschchitra, Thanakrit Chantra and Anutchanan Kongkoon for help with S *K*-edge XAS (SLRI), David A. Shapiro for help with X-ray ptychography (ALS), Timothy Teague for support with XRD and XRF, Sunxiang Zheng for help with the electrophoresis experiments, Lucas Girotto, Marlon Longhi, and Flavio C. Vicentin for the Ca *K*-edge XAS results (LNLS). Financial support from CNPq BJT Grant 406684/2013-8 and CNPq PQ Grant 309949/2014-9 is acknowledged.

7. Conflict of interest

The authors declare no competing financial interests: the arguments presented in this paper reflect the impartial views of the authors.

8. References

1. van Oss, H. G. Mineral commodity summaries: cement. minerals.usgs.gov (accessed 17 December 2015).
2. Taylor, H. F. W. *Cement chemistry*; 2nd ed.; Thomas Telford Publishing: London, 1997.
3. Nishi, F.; Takéuchi, Y. The Al₆O₁₈ rings of tetrahedra in the structure of Ca_{8.5}NaAl₆O₁₈. *Acta Cryst.* **1975**, *B31*, 1169-1173.
4. Mondal, P.; Jeffery, J. W. The crystal structure of tricalcium aluminate, Ca₃Al₂O₆. *Acta Cryst.* **1975**, *B31*, 689-697.
5. Geng, G.; Myers, R. J.; Kilcoyne, A. L. D.; Ha, J.; Monteiro, P. J. M. Ca *L*_{2,3}-edge near edge X-ray absorption fine structure of tricalcium aluminate, gypsum and calcium (sulfo)aluminate hydrates. *Am. Mineral.* **2016**, *accepted*.
6. Minard, H.; Garrault, S.; Regnaud, L.; Nonat, A. Mechanisms and parameters controlling the tricalcium aluminate reactivity in the presence of gypsum. *Cem. Concr. Res.* **2007**, *37* (10), 1418-1426.
7. Lothenbach, B.; Winnefeld, F. Thermodynamic modelling of the hydration of Portland cement. *Cem. Concr. Res.* **2006**, *36* (2), 209-226.

8. Black, L.; Breen, C.; Yarwood, J.; Deng, C. S.; Phipps, J.; Maitland, G. Hydration of tricalcium aluminate (C₃A) in the presence and absence of gypsum-studied by Raman spectroscopy and X-ray diffraction. *J. Mater. Chem.* **2006**, *16* (13), 1263-1272.
9. Traetteberg, A. U. D.; Grattan-Bellew, P. E. Hydration of 3CaO·Al₂O₃ and 3CaO·Al₂O₃ + gypsum with and without CaCl₂. *J. Am. Ceram. Soc.* **1975**, *58* (5-6), 221-227.
10. Edmeades, R. M.; Hewlett, P. C. Cement admixtures. In *Lea's Chemistry of Cement and Concrete*; Butterworth-Heinemann: Oxford, 1998, pp 841-905.
11. Marchon, D.; Flatt, R. J. Impact of chemical admixtures on cement hydration. In *Science and Technology of Concrete Admixtures*, Aïtcin, P.-C.; Flatt, R. J., Eds.; Elsevier: Cambridge, 2016.
12. Bonen, D.; Sarkar, S. L. The superplasticizer adsorption capacity of cement pastes, pore solution composition, and parameters affecting flow loss. *Cem. Concr. Res.* **1995**, *25* (7), 1423-1434.
13. Alonso, M. M.; Puertas, F. Adsorption of PCE and PNS superplasticisers on cubic and orthorhombic C₃A. Effect of sulfate. *Constr. Build. Mater.* **2015**, *78*, 324-332.
14. Tadros, M. E.; Jackson, W. Y.; Skalny, J. A. N. Study of the dissolution and electrokinetic behavior of tricalcium aluminate. In *Hydrosols and Rheology*, Kerker, M., Ed.; Academic Press: London, 1976, pp 211-223.
15. Zingg, A.; Winnefeld, F.; Holzer, L.; Pakusch, J.; Becker, S.; Gauckler, L. Adsorption of polyelectrolytes and its influence on the rheology, zeta potential, and microstructure of various cement and hydrate phases. *J. Colloid Interf. Sci.* **2008**, *323* (2), 301-312.
16. Feldman, R. F.; Ramachandran, V. S. The influence of CaSO₄·2H₂O upon the hydration character of 3CaO·Al₂O₃. *Mag. Concr. Res.* **1966**, *66* (57), 185-196.
17. Skalny, J. A. N.; Tadros, M. E. Retardation of tricalcium aluminate hydration by sulfates. *J. Am. Ceram. Soc.* **1977**, *60* (3-4), 174-175.
18. Jansen, D.; Goetz-Neunhoeffler, F.; Lothenbach, B.; Neubauer, J. The early hydration of ordinary Portland cement (OPC): an approach comparing measured heat flow with calculated heat flow from QXRD. *Cem. Concr. Res.* **2012**, *42* (1), 134-138.
19. Bishop, M.; Bott, S. G.; Barron, A. R. A new mechanism for cement hydration inhibition: solid-state chemistry of calcium nitrilotris(methylene)triphosphonate. *Chem. Mater.* **2003**, *15* (16), 3074-3088.

20. Scrivener, K. L.; Juilland, P.; Monteiro, P. J. M. Advances in understanding hydration of Portland cement. *Cem. Concr. Res.* **2015**, *78A*, 38-56.
21. Bullard, J. W.; Jennings, H. M.; Livingston, R. A.; Nonat, A.; Scherer, G. W.; Schweitzer, J. S.; Scrivener, K. L.; Thomas, J. J. Mechanisms of cement hydration. *Cem. Concr. Res.* **2011**, *41* (12), 1208-1223.
22. Sposito, G. *The chemistry of soils*; 2nd ed.; Oxford University Press: New York, 2008.
23. Wijnja, H.; Schulthess, C. P. Vibrational spectroscopy study of selenate and sulfate adsorption mechanisms on Fe and Al (hydr)oxide surfaces. *J. Colloid Interf. Sci.* **2000**, *229* (1), 286-297.
24. Sigg, L.; Stumm, W. The interaction of anions and weak acids with the hydrous goethite (α -FeOOH) surface. *Colloid Surface.* **1981**, *2* (2), 101-117.
25. Charlet, L.; Dise, N.; Stumm, W. Acidification of soil sulfate adsorption on a variable charge soil and on reference minerals. *Agr. Ecosyst. Environ.* **1993**, *47* (2), 87-102.
26. Peak, D. Adsorption mechanisms of selenium oxyanions at the aluminum oxide/water interface. *J. Colloid Interf. Sci.* **2006**, *303* (2), 337-345.
27. Siretanu, I.; Ebeling, D.; Andersson, M. P.; Stipp, S. L. S.; Philipse, A.; Stuart, M. C.; van den Ende, D.; Mugele, F. Direct observation of ionic structure at solid-liquid interfaces: a deep look into the Stern Layer. *Sci. Rep.* **2014**, *4*, 4956.
28. Huang, C.-P.; Stumm, W. Specific adsorption of cations on hydrous γ -Al₂O₃. *J. Colloid Interf. Sci.* **1973**, *43* (2), 409-420.
29. Sposito, G. The operational definition of the zero point of charge in soils. *Scol Sci. Soc. Am. J.* **1981**, *45* (2), 292-297.
30. Stumm, W. Reactivity at the mineral-water interface: dissolution and inhibition. *Colloid. Surface. A* **1997**, *120* (1-3), 143-166.
31. Sposito, G. Gouy-Chapman theory. In *Encyclopedia of Earth Sciences Series, Encyclopedia of Geochemistry*, White, W. M., Ed.; Springer: New York, 2016.
32. Yoshioka, K.; Tazawa, E.-I.; Kawai, K.; Enohata, T. Adsorption characteristics of superplasticizers on cement component minerals. *Cem. Concr. Res.* **2002**, *32* (10), 1507-1513.
33. Plank, J.; Hirsch, C. Impact of zeta potential of early cement hydration phases on superplasticizer adsorption. *Cem. Concr. Res.* **2007**, *37* (4), 537-542.

34. Medala, M.; Labbez, C.; Pochard, I.; Nonat, A. Ettringite surface chemistry: interplay of electrostatic and ion specificity. *J. Colloid Interf. Sci.* **2011**, *354* (2), 765-770.
35. Elakneswaran, Y.; Nawa, T.; Kurumisawa, K. Electrokinetic potential of hydrated cement in relation to adsorption of chlorides. *Cem. Concr. Res.* **2009**, *39* (4), 340-344.
36. Shapiro, D. A.; Yu, Y.-S.; Tyliczszak, T.; Cabana, J.; Celestre, R.; Chao, W.; Kaznatcheev, K.; Kilcoyne, A. L. D.; Maia, F.; Marchesini, S.; Meng, Y. S.; Warwick, T.; Yang, L. L.; Padmore, H. A. Chemical composition mapping with nanometre resolution by soft X-ray microscopy. *Nature Photon.* **2014**, *8* (10), 765-769.
37. Hunter, R. J. *Zeta potential in colloid science: principles and applications*; 3rd ed.; Academic Press: London, 1988.
38. Stumm, W. Aquatic colloids as chemical reactants: surface structure and reactivity. *Colloid Surface. A* **1993**, *73*, 1-18.
39. Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.* **2005**, *12*, 537-541.
40. Collepardi, M.; Baldini, G.; Pauri, M.; Corradi, M. Tricalcium aluminate hydration in the presence of lime, gypsum or sodium sulfate. *Cem. Concr. Res.* **1978**, *8* (5), 571-580.
41. Tenoutasse, N. In *The hydration mechanism of C₃A and C₃S in the presence of calcium chloride and calcium sulfate*, Proceedings of the Fifth International Symposium on the Chemistry of Cement (II), Tokyo, 1968.
42. Bourg, I. C.; Sposito, G. Molecular dynamics simulations of the electrical double layer on smectite surfaces contacting concentrated mixed electrolyte (NaCl–CaCl₂) solutions. *J. Coll. Interf. Sci.* **2011**, *360* (2), 701-715.
43. Lasaga, A. C.; Lüttge, A. Mineralogical approaches to fundamental crystal dissolution kinetics. *Am. Mineral.* **2004**, *89* (4), 527-540.
44. Chrysochoou, M.; Dermatas, D. Evaluation of ettringite and hydrocalumite formation for heavy metal immobilization: literature review and experimental study. *J. Hazard. Mater.* **2006**, *136* (1), 20-33.
45. Myers, D. *Surfactant science and technology*; John Wiley & Sons: Hoboken, 2006.
46. Hekal, E. E.; Kishar, E. A. Effect of sodium salt of naphthalene-formaldehyde polycondensate on ettringite formation. *Cem. Concr. Res.* **1999**, *29* (10), 1535-1540.

47. Pourchet, S.; Regnaud, L.; Perez, J. P.; Nonat, A. Early C₃A hydration in the presence of different kinds of calcium sulfate. *Cem. Concr. Res.* **2009**, *39* (11), 989-996.
48. Fleet, M. E.; Liu, X.; Harmer, S. L.; King, P. L. Sulfur K-edge XANES spectroscopy: chemical state and content of sulfur in silicate glasses. *Can. Mineral.* **2005**, *43*, 1605-1618.
49. Wieland, E.; Dähn, R.; Vespa, M.; Lothenbach, B. Micro-spectroscopic investigation of Al and S speciation in hardened cement paste. *Cem. Concr. Res.* **2010**, *40* (6), 885-891.
50. Vespa, M.; Wieland, E.; Dähn, R.; Grolimund, D.; Scheidegger, A. M. Determination of the elemental distribution and chemical speciation in highly heterogeneous cementitious materials using synchrotron-based micro-spectroscopic techniques. *Cem. Concr. Res.* **2007**, *37* (11), 1473-1482.
51. Mishra, A.; Parsai, N.; Shrivastava, B. D. Simplified analysis of EXAFS data and determination of bond lengths. *Indian J. Pure Appl. Phys.* **2011**, *49* (1), 25-29.
52. Moore, A. E.; Taylor, H. F. W. Crystal structure of ettringite. *Acta Cryst.* **1970**, *B26*, 386-393.
53. Allmann, R. Refinement of the hybrid layer structure [Ca₂Al(OH)₆]⁺[1/2SO₄·3H₂O]⁻. *Neues Jahrb. Mineral. Monatsh.* **1977**, *3*, 136-144.
54. Pedersen, B. F.; Semmingsen, D. Neutron diffraction refinement of the structure of gypsum. *Acta Cryst.* **1982**, *B38*, 1074-1077.
55. Okoronkwo, M. U.; Glasser, F. P. Compatibility of hydrogarnet, Ca₃Al₂(SiO₄)_x(OH)_{4(3-x)}, with sulfate and carbonate-bearing cement phases: 5–85 °C. *Cem. Concr. Res.* **2016**, *83*, 86-96.
56. Eichert, D.; Salomé, M.; Banu, M.; Susini, J.; Rey, C. Preliminary characterization of calcium chemical environment in apatitic and non-apatitic calcium phosphates of biological interest by X-ray absorption spectroscopy. *Spectrochim. Acta B* **2005**, *60* (6), 850-858.
57. Sowrey, F. E.; Skipper, L. J.; Pickup, D. M.; Drake, K. O.; Lin, Z.; Smith, M. E.; Newport, R. J. Systematic empirical analysis of calcium-oxygen coordination environment by calcium K-edge XANES. *Phys. Chem. Chem. Phys.* **2004**, *6* (1), 188-192.
58. Pattanaik, S.; Huffman, G. P.; Sahu, S.; Lee, R. J. X-ray absorption fine structure spectroscopy and X-ray diffraction study of cementitious materials derived from coal combustion by-products. *Cem. Concr. Res.* **2004**, *34* (7), 1243-1249.
59. Glasser, F. P.; Marinho, M. B. Early stages of the hydration of calcium aluminate and its sodium-containing solid solutions. *Br. Ceram. Soc. J.* **1984**, *35*, 222-236.

60. Rothstein, D.; Thomas, J. J.; Christensen, B. J.; Jennings, H. M. Solubility behavior of Ca-, S-, Al-, and Si-bearing solid phases in Portland cement pore solutions as a function of hydration time. *Cem. Concr. Res.* **2002**, 32 (10), 1663-1671.
61. Lieber, V. W. Effect of inorganic admixtures on the setting and hardening of Portland cement. *Zem.-Kalk-Gips* **1973**, 26 (2), 75-79.