

A Critical Comparison of 3D Experiments and Simulations of Tricalcium Silicate Hydration

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Abstract

Advances in nano-computed X-ray tomography (nCT), nano X-ray fluorescence spectrometry (nXRF), and high-performance computing have enabled the first direct comparison between observations of three-dimensional nanoscale microstructure evolution during cement hydration and computer simulations of the same microstructure using HydratiCA. nCT observations of a collection of triclinic tricalcium silicate (Ca_3SiO_5) particles reacting in a calcium hydroxide solution are reported and compared to simulations that duplicate, as nearly as possible, the thermal and chemical conditions of those experiments. Particular points of comparison are the time dependence of the solid phase volume fractions, spatial distributions, and morphologies. Comparisons made at 7 h of reaction indicate that the simulated and observed volumes of Ca_3SiO_5 consumed by hydration agree to within the measurement uncertainty. The location of simulated hydration product is qualitatively consistent with the observations, but the **outer envelope of hydration product observed by nCT encloses more than twice** the volume of hydration product in the simulations at the same time. Simultaneous nXRF measurements of the same observation volume imply calcium and silicon concentrations within the observed hydration product **envelope that**

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are consistent with $\text{Ca}(\text{OH})_2$ embedded in a sparse network of calcium silicate hydrate (C–S–H) that contains about 70 % occluded porosity in addition to the amount usually accounted as gel porosity. An anomalously large volume of $\text{Ca}(\text{OH})_2$ near the particles is observed both in the experiments and in the simulations, and can be explained as originating from the hydration of additional particles outside the field of view. Possible origins of the unusually large amount of observed occluded porosity are discussed.

Key words: tricalcium silicate, hydration, computer simulation, nano-tomography

1. Introduction

This paper describes a detailed, point-by-point comparison of computer simulations with experimental observations of the developing 3D microstructure of a small collection of tricalcium silicate (Ca_3SiO_5) particles as they react in an aqueous solution of calcium hydroxide. “Point-by-point” means here that the simulated and observed microstructures will be compared in terms not only of the total volumes of each phase, but also of how those phases are distributed in space at a resolution of 500 nm. The system under consideration was chosen as a reasonably simple and well-defined analog of portland cement binders in concrete. Tricalcium silicate (Ca_3SiO_5), stabilized in its monoclinic polymorph by impurities such as aluminum or magnesium, is the majority mineral component of portland cement and is known to be the major determinant of early reaction rates and strength gain in concrete binders, at least during the first day. The primary solid product of reaction between Ca_3SiO_5 and water, calcium silicate hydrate gel (C–S–H),¹ is the most complex material, both structurally and chemically, that forms in concrete binders. Therefore, the reaction of even a small cluster of Ca_3SiO_5 particles in water can provide useful insights about microstructure development and strength gain in concrete.

¹Conventional cement chemistry notation is used to designate the calcium silicate hydrate phase, where C = CaO , S = SiO_2 , H = H_2O , and the dashes generically indicate that the phase has variable structure and composition.

18 Such a 3D comparison has not been possible until recently. Models of cement mi-
19 crostructure development, with varying levels of rigor, have existed for about three
20 decades [1–8]. Simulated microstructures using these models have often been com-
21 pared to macroscopic indicators of hydration rates [3–5, 7, 8]. Sometimes they are
22 also compared with 2D micrographs of actual hydrated cement paste microstructure
23 either qualitatively [2, 4] or by statistically analyzing the spatial distribution of the
24 solid phases or capillary porosity using radial distribution functions or autocorrela-
25 tion functions [8–10]. However, 2D micrographs are typically acquired only after
26 interrupting hydration by solvent exchange or drying, and under the high vacuum
27 conditions of a scanning electron microscope (SEM) These conditions may alter the
28 microstructure considerably compared to that in a fully saturated system, especially
29 the C–S–H [11–13], although a recent report showed that solvent exchange with iso-
30 propyl alcohol followed by supercritical drying, which should exert no drying stresses
31 on the structure, yield C–S–H morphologies observed by SEM that are at least quali-
32 tatively like those obtained by normal solvent exchange and drying [14]. In contrast,
33 the advent of nanoscale X-ray computed tomography (nCT) has made it possible to
34 examine the 3D microstructure of porous cementitious media with a spatial resolu-
35 tion on the order of tens of nanometers, and coupling tomography with nanoscale
36 X-ray fluorescence spectrometry (nXRF) has enabled the mapping of the elemental
37 concentrations with about the same spatial resolution [15]. Several papers published
38 in the last few years [15–18] have shown the rich 3D data that can be acquired and an-
39 alyzed with these methods, which make it possible for the first time to make true 3D
40 microstructure comparisons with microstructure-based computer models of cement
41 hydration.

42 Among the microstructure models available for the purpose, this paper uses the
43 kinetic cellular automaton model called HydratiCA [10, 19]. The choice was made
44 because HydratiCA models the 3D microstructure evolution according to locally cal-
45 culated kinetics of reactions, including nucleation kinetics and nonlinear [rates of dis-](#)
46 [solution and growth](#), as a function of the local thermodynamic driving force for those
47 reactions. HydratiCA therefore invokes fewer assumptions about the overall mecha-
48 nisms of cement hydration than do other [models](#) [2, 4, 6, 8, 20], and the assumptions

49 it does make are the values of thermodynamic, structural, and kinetic properties of
50 substances that, at least in principle, can be measured in the laboratory.

51 Quantitative comparisons between experiment and simulation at the microstruc-
52 ture scale provide an exceptionally stringent test of this kind of model. The great
53 majority of hydration model interpretation and testing [2, 4, 6, 7, 21–26] has been
54 based on the quality of parameter fitting to observed *macroscopic* measurements of
55 hydration progress such as isothermal calorimetry, chemical shrinkage, or bound wa-
56 ter. This kind of testing involves the implicit yet untested assumption that the under-
57 lying model captures all the important physical and chemical mechanisms that are
58 involved in the process. However, the danger of that approach is that almost equally
59 good fits can be made to such macroscopic data with different models that are based
60 on different sets of kinetic mechanisms [26, 27]. In contrast, comparisons based on the
61 detailed microstructural evolution trajectory can quickly reveal if incorrect or incom-
62 plete mechanisms are being assumed based on the amount and spatial distribution of
63 the phases in the microstructure as a function of time. HydratiCA attempts to model
64 our current mechanistic understanding of hydration with as much detail as we have
65 available. The point of comparing HydratiCA-simulated microstructure development
66 with experimental observation in this paper is not to demonstrate that the model
67 works well, but to reveal gaps in our current understanding of the mechanisms of
68 hydration.

69 2. Materials and Methods

70 The experimental data reported in this paper have been published in a previous
71 paper with full details on the procedures used [18]. A brief summary of the procedure
72 is provided here.

73 2.1. *Tricalcium silicate powder*

74 A triclinic Ca_3SiO_5 powder^{1,2} was used for the hydration study. Table 1 shows
75 the elemental composition of the powder as measured by inductively coupled plasma
76 optical emission spectroscopy (ICP-OES), together with the specific surface area mea-
77 sured by multipoint BET nitrogen adsorption isotherms. Quantitative X-ray powder
78 diffraction (XRD) indicates that the powder is composed almost entirely of triclinic
79 (T3) Ca_3SiO_5 , with approximately 1.5 % by mass of CaO.

80 The particle size distribution (PSD) was estimated by automated scanning elec-
81 tron microscopy (ASEM) using 4000 individual dispersed particles. About 95 % of the
82 particles had an average diameter between 1 μm and 7.5 μm .

83 2.2. *Specimen preparation*

84 Specimens were prepared by attaching several of the powder particles, with a total
85 mass of about 1.57 ng, to the tip of a tungsten needle with a rapid-curing epoxy,³ as
86 illustrated in Fig. 1. An inverted plastic cone was tightly affixed to the needle to hold
87 the solution. Approximately 2 mg of additional Ca_3SiO_5 powder was glued with the
88 same epoxy to the side of the needle to make the average water:cement mass ratio
89 (w/c) be 5.0 after 10 μL was added to the cone.

90 The whole assembly was placed in an ultrahigh-purity N_2 environment to avoid
91 carbonation. An initial nCT scan of the dry particle-needle configuration was made
92 with the cup in the lowest position. Afterward, the prescribed volume of 15 mmol L^{-1}
93 calcium hydroxide solution was added to the cone to submerge the particles. The
94 whole assembly was maintained at $(25 \pm 1)^\circ\text{C}$ throughout the experiment. The dilute
95 calcium hydroxide solution was used instead of pure deionized water to intentionally
96 reduce the otherwise very rapid rate of Ca_3SiO_5 dissolution that occurs on first con-

¹SARL Mineral Research Processing, Meyzieu France

²Certain commercial equipment, instruments, or materials are identified in order to specify the experimen-
tal procedure adequately. Such identification is not intended to imply recommendation or endorsement
by the National Institute of Standards and Technology, nor is it intended to imply that the materials or
equipment identified are necessarily the best available for the purpose.

³ITW Devcon 5 Minute® Epoxy (Danvers, MA)

97 tact with water [28, 29]. The particles remained submerged for 7 h, after which the seal
98 was removed and hydration arrested by solvent exchange with 99 % isopropyl alcohol
99 (IPA) for 5 min. IPA was used because it has been shown previously to cause no ob-
100 servable differences in the C–S–H morphology or other aspects of the microstructure
101 of hydrated specimens [18].

102 2.3. *nCT*

103 All nCT measurements were made in the Hard X-ray Nanoprobe at Sector 26
104 in a shared space between the Advanced Photon Source (APS) and the Center for
105 NanoScale Materials (CNM) at Argonne National Laboratory. More information on
106 the instrument and the settings used for this study can be found in Hu *et al.* [18].
107 The sample was scanned once at each of a large number of incidence angles to pro-
108 duce a collection of two-dimensional radiographs, from which a single digitized three-
109 dimensional tomograph was reconstructed. The reconstruction technique used mo-
110 saic tomography to post-align partially overlapping radiographs, using Stanford TXM-
111 Wizard software [30]. Full details of the reconstruction method, including its specific
112 application to these data, are beyond the scope of this paper but are provided else-
113 where [31]. The final segmented tomograph is rendered as a three-dimensional array
114 of voxels at a resolution of 15.6 nm per voxel.

115 Quantitative volume data for each phase can be obtained from nCT by separat-
116 ing the tomograph into regions of different components based on grayscale values, as
117 described fully in Reference [31]. The nanometric length scale of the nCT data make
118 it highly susceptible to small translations or rotations that can occur due to thermal
119 expansion or stage positioning errors. These shifts can be accommodated by align-
120 ing the data from separate scans using the tungsten needle or gold nanoparticle as a
121 registration marker (see Fig. 1). The alignment procedure has been automated with a
122 computer algorithm that finds a rigid-body translation and rotation needed to match
123 the scans [31].

124 2.4. *nXRF*

125 Emitted characteristic X-ray fluorescence radiation was detected with a four-element
126 silicon drift energy dispersive detector [15, 32]. Fluorescence spectra were analyzed

127 using the software package MAPS [33]. Fitting and quantification of the fluorescence
 128 data were performed using thin film standards (National Bureau of Standards, Stan-
 129 dard Reference Materials 1832 and 1833). Further details on the analysis of nXRF data
 130 for this system are provided elsewhere [15, 18, 31].

131 3. Computer Simulations

132 3.1. Model description

133 The computer simulations reported here were performed using a kinetic cellular
 134 automaton model, called HydratiCA, developed at the National Institute of Standards
 135 and Technology (NIST), which tracks 3D microstructure evolution in aqueous sus-
 136 pensions by coupled transport and reactions. Full details of the model algorithms and
 137 verification are given elsewhere [10, 19], so only a brief synopsis will be provided
 138 here.

139 Stoichiometric solid phases (*e.g.*, $\text{Ca}(\text{OH})_2$, Ca_3SiO_5), water, and aqueous solute
 140 species (*e.g.*, Ca^{2+} , OH^-) are defined as separate chemical components. Each material
 141 component is discretized into *cells*, each cell corresponding to a prescribed number
 142 of moles of that component. The initial microstructure of cement particles and water
 143 is mapped onto a cubic lattice by assigning cell occupations numbers for each com-
 144 ponent at each site. Chemical and structural changes are simulated by iterating over
 145 small time steps during which independent reaction and transport processes occur.
 146 The probability, p_t , of a cell executing a random walk to a neighboring site is deter-
 147 mined by that cell's local diffusivity, D , the time increment, Δt , and the lattice site
 148 spacing, λ :

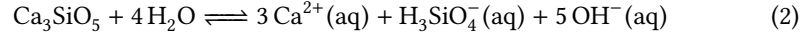
$$p_t = \frac{D\Delta t}{\lambda^2} \quad (1)$$

149 Based on published mobilities of ions at infinite dilution [34] and the fact that the
 150 solutions used in this system are dilute, with ionic strengths not exceeding 0.1 mol L^{-1} ,
 151 species released by Ca_3SiO_5 dissolution should be able to diffuse, on average, a dis-
 152 tance of $50 \mu\text{m}$ within 1 s and $100 \mu\text{m}$ within 3 s [19]. Consequently, for numerical
 153 efficiency in this and several other studies of HydratiCA on small systems [19, 35, 36],

diffusion rates through the aqueous solution are assumed to be so high compared to the rates of all other processes that the solution is perfectly mixed. This assumption is also supported by the likelihood that locally generated heat of dissolution at the Ca_3SiO_5 particle surfaces will promote convective mixing of the liquid near the particles.

Following the procedure developed by Karapiperis [37], the probability of a unit reaction happening in a time step Δt depends on its rate constant and on the cell occupation number of each reactant.

Table 2 lists the material components used in the simulations and their assumed thermophysical properties, including their molar volumes, molar mass, and, for mobile species, their mobility at infinite dilution. In addition, Table 3 gives the values used to characterize the rates of the various reactions that are assumed to occur among these components during Ca_3SiO_5 hydration. Based on prior measurements of solution composition during supposed “pure” dissolution (*i.e.*, under conditions designed to prevent the precipitation of C–S–H) [28, 38, 39], Ca_3SiO_5 is assumed to dissolve congruently in water according to the reaction



with an apparent solubility product K .

The nonlinear molar dissolution rate is described by

$$\frac{dN_{\text{Ca}_3\text{SiO}_5}}{dt} = -k_{\text{Ca}_3\text{SiO}_5} A_{\text{eff}} \left(1 - \exp \left[- \left(\frac{\ln K - \ln Q}{s} \right)^r \right] \right) \quad (3)$$

where $k_{\text{Ca}_3\text{SiO}_5}$ is the dissolution rate constant in pure water, approximated from the experimental data [28] as $112.5 \mu\text{mol m}^{-2} \text{s}^{-1}$ and A_{eff} is the reacting Ca_3SiO_5 surface area, which may be less than the actual Ca_3SiO_5 surface area due to coverage by hydration product. An earlier regression analysis using measurements obtained over a wide range of undersaturations [28] yielded $k_{\text{Ca}_3\text{SiO}_5} = 125 \mu\text{mol m}^{-2} \text{s}^{-1}$, $\ln K = -41.1$, $s = 21.05$, and $r = 3.73$ [36]. The activity product, Q , is defined for reaction (2) by

$$Q = \frac{\{\text{Ca}^{2+}\}^3 \{\text{H}_3\text{SiO}_4^-\} \{\text{OH}^-\}^5}{\{\text{H}_2\text{O}\}^4} \quad (4)$$

At the low ionic strengths of these experiments, the activity of water should equal the mole fraction of water according to Raoult's law. The form of the rate law used in Eq. (3) is empirical, but has the satisfying property that it collapses to the standard rate law for an elementary reaction (*i.e.*, if the order is equal to the molecularity) when $r, s \rightarrow 1$:

$$\frac{dC}{dt} = -ck \left(1 - \frac{Q}{K}\right) \quad (5)$$

where C is the molar concentration of a reactant in an elementary reaction, c is the molar stoichiometric coefficient for that reactant, k is the absolute forward rate constant, and K is the equilibrium constant. Therefore, the same general form as Eq. (3) can embrace a wide range of rate behavior.

For reasons given more fully in the Discussion, a small cluster of Ca_3SiO_5 particles is likely too small of a sample to exhibit the bulk mean dissolution rate behavior upon which the parameters $\ln K$, r , and s were obtained earlier. Because of this and the inherent variability in mineral dissolution rates, also taken up more fully in the Discussion, three of the regression parameters were modified in this study to $k = 112.5 \mu\text{mol m}^{-2} \text{s}^{-1}$, $\ln K = -39.0$ and $s = 20.05$. The effect of these modifications on the rate law function is shown in Fig. 2 along with the experimental data upon which the earlier regression was based. These modifications still give a reasonable fit to the prior measurements and have the advantage of yielding a better agreement with the observed total volume of Ca_3SiO_5 after 7 h of hydration, as will be shown in the Results.

The effective Ca_3SiO_5 surface area at a lattice site is defined in HydratiCA as

$$\frac{A_{\text{eff}}}{A} = 1 - \eta \min \left(1, \frac{\phi_{\text{CSH}}}{\phi_{\text{max}}}\right)^{2/3} \quad (6)$$

where A is the physical surface area of Ca_3SiO_5 , η is the "opacity" of the product layer that forms on the surface (a measure of how effectively a unit area of coverage can inhibit dissolution), ϕ_{CSH} is the volume fraction of the lattice site occupied by C-S-H, and ϕ_{max} is the site volume fraction at which the surface is considered to be completely covered with a layer having opacity η . Phases with a low contact angle on Ca_3SiO_5 ,

or those that grow essentially in 2D along the surface, will have relatively lower values of $\phi_{\max}$. The use of A_{eff} is necessitated by the fact that any lattice-based model cannot resolve the microstructure on a scale smaller than a single lattice site, which for these simulations is $1\text{ }\mu\text{m}$. Drawing from a recent modeling study that assumed the same mechanisms, the values chosen for these opacity parameters, as well as the other physical parameters for all components used in the simulations, are given in Table 2. The Discussion section briefly takes up the question of whether these values are justified in light of the unusual morphology of the hydration product that were observed in this experiment.

In the context of the colloidal model of C–S–H [40, 41], an individual globule of C–S–H produced by Ca_3SiO_5 hydration for 28 d has been reported to have the composition $\text{C}_{1.7}\text{SH}_{1.8}$ in the saturated state and saturated density of 2604 kg m^{-3} [42, 43], which would correspond to a molar volume $\bar{V}_{\text{C–S–H}}$ of about $7.2 \times 10^{-5}\text{ m}^3$. Hydrat-
iCA does not attempt to explicitly model these individual globules, but considers a fundamental growth unit of C–S–H to include several clusters of these globules together with saturated intercluster pores. The intercluster porosity is assumed to be 70 % by volume and saturated with aqueous solution [44]. The water in the porosity is assumed to be available for further reactions, except for 2.2 formula units of physically adsorbed water per formula unit of SiO_2 in C–S–H [36].

Of equal importance in this study, solution equilibria measurements indicate that during C_3S hydration at early times, a plot of the solution’s Si concentration against its Ca concentration generally lies on the upper of two curves (often called Curve B) first identified by Jennings [45] and later refined by Chen [46]. The composition of C–S–H is modeled here as an ideal solid solution [47] (*i.e.*, assuming zero enthalpy of mixing) with two stoichiometric end members. Generalized regression [48] of that two-component model to published data for Curve B was used to estimate the composition and solubilities of the model end members, which are $\text{C}_2\text{S}_3\text{H}_{12}$ and $\text{C}_5\text{S}_3\text{H}_{12}$. The molar volumes, $\bar{V}$, of these components, given in Table 2, were calculated by linear extrapolation from known values of other calcium silicate hydrate compositions [36, 43]. The formula unit volumes needed in Eqs. (7) and (8) are found by dividing the appropriate molar volume by Avogadro’s number.

Table 3 shows the collection of reactions that were used in the simulations, along with the assumed equilibrium constants, reaction rate constants, and nucleation parameters. Nucleation rates of C–S–H and $\text{Ca}(\text{OH})_2$ are assumed to follow classical nucleation theory, with C–S–H and $\text{Ca}(\text{OH})_2$ nucleating heterogeneously on the surface of the cement grain and on C–S–H, respectively. The rate of formation of C–S–H nuclei ($\text{m}^{-2} \text{s}^{-1}$) is given by [36, 49]

$$I_{\text{het}} = I_0^B O_V^B \exp \left[-\frac{q}{\ln^2 \beta} \right] \quad (7)$$

where I_{het} is the nucleation rate, O_V^B is the area of Ca_3SiO_5 per unit volume available for nucleation, and β is the saturation index of the end member that is nucleating, that is, its activity product divided by its solubility product. The other pre-exponential factor is $I_0^B = D/\Omega^{4/3}$, where D is the diffusivity in solution of an attaching formula unit and Ω is the formula unit volume of the solid. Finally, the factor q in the exponential argument of Eq. (7) is given by

$$q = \frac{16\pi\gamma_{\text{CL}}^3\Omega^2 f(\theta)}{3k_{\text{B}}^3 T^3} \quad (8)$$

where γ_{CL} is the C–S–H interfacial energy with the solution, k_{B} is Boltzmann’s constant, θ is the contact angle between the crystal and the substrate, and

$$f(\theta) = [2 + \cos(\theta)] \sin^4(\theta/2) \quad (9)$$

The interfacial energies of the end members CSH(I) and CSH(II) have not been directly measured, but were recently estimated [36], based on a solubility relationship proposed by Söhnel [50], to be 84.0 mJ m^{-2} and 77.6 mJ m^{-2} , respectively.

Equilibrium constants for speciation reactions and for $\text{Ca}(\text{OH})_2$ dissolution at 25°C were taken from the Nagra/PSI thermochemical database [51], which did not report uncertainties in these values. The rate constants for these solution reactions have been chosen to be sufficiently great to ensure that departures from speciation equilibrium are erased, to within 1 % in the concentration of any species, in 0.1 s or less. The dissolution rate constant for $\text{Ca}(\text{OH})_2$ at 25°C is estimated in Table 3 from the one extant report of solution composition changes in a particulate suspension [52].

259 Uncertainties in the solution data and solid surface area were not reported in that
260 study.

261 Reaction data for C–S–H are more challenging to obtain because of the wide va-
262 riety of results in numerous published studies of solubility [46, 53–58], and the lack of
263 data on C–S–H growth rates. Nonlinear regression of the C–S–H ideal solid solution
264 model with the two end members given in Table 2 provides nearly as good an agree-
265 ment with published solubility data as other solid solution models, and the solubility
266 constants given in Table 3 are those that yield the minimum sum of squared residuals
267 (SSR) for those compositions, as described fully in Reference [47]. The rate constants
268 and form of the rate law for C–S–H growth,

$$\frac{dN_{\text{CSH}}}{dt} = k_{\text{CSH}} A_{\text{CSH}} (\beta_{\text{Tot}} - 1)^3 \quad (10)$$

269 are those shown to provide the closest agreement to recent experimental measure-
270 ments of C–S–H growth on calcite crystals [44]. In Eq. (10), k_{CSH} is the rate constant
271 given in Table 3 and is assumed to be the same for both end members, A_{CSH} is the
272 surface area, and β_{Tot} is the *total saturation* of the solid solution, which is the driv-
273 ing force for the growth of the most favorable composition of the solid solution as a
274 function of the aqueous solution composition, as described fully elsewhere [47].

275 The sensitivity of simulation results to some of the input parameters in Table 3
276 has been discussed in other papers [36, 47]. A more complete sensitivity analysis is a
277 subject for future work.

278 3.2. Implementation

279 Each lattice site in HydratiCA is occupied by numbers of cells of differing types,
280 each of which represents a discrete number of formula units of a particular material
281 component or phase. Periodic boundary conditions are used on the four vertical sides
282 of the system. The additional 2 mg of Ca_3SiO_5 powder placed below the needle tip in
283 the experimental setup was simulated by using non-periodic boundaries at the top and
284 bottom of the system and adding one additional layer of Ca_3SiO_5 lattice sites below the
285 needle. The total volume of the system was chosen to match the average water/cement
286 mass ratio $w/c = 5.0$ used in the experiment. However, the volumes of Ca_3SiO_5 and

287 hydration products located below the needle tip were not included in the volume
288 totals for solids in either the experiments or the simulations. This was done primarily
289 to keep the computational domain at a feasible size for the simulations and because the
290 primary objective of the study is to focus on the microstructure of the isolated cluster
291 arrangement above the needle. The main impact of excluding the additional material
292 below the needle is that any significant migration of material between the two regions
293 can be inferred only indirectly when comparing the simulations and experiments. This
294 issue will be revisited in more detail in the Results and Discussion sections.

295 The algorithms used to compute changes in a site’s cell occupation numbers re-
296 quire information only from the site and its nearest and next-nearest neighbor sites.
297 This localization of the algorithms leads to a natural parallel decomposition of the
298 simulation, by which the lattice is partitioned into sublattices, each of which is as-
299 signed to a separate computational *process*. Each process uses one CPU processor. A
300 process *owns* each of the lattice sites of the sublattice it is assigned, and the owner
301 of a lattice site is responsible for all of the computations needed to update that lat-
302 tice site during each time step of the simulation. Therefore, lattice sites that are on
303 the surface of a sublattice must gather data from neighboring lattice sites that are
304 owned by other processes. This updating is accomplished by surrounding each sub-
305 lattice with a layer of “ghost” lattice sites that are images of the actual lattice sites
306 owned by adjacent processes. In the simulations reported here, the lattice was de-
307 composed into orthorhombic sublattices that were as close to the same size and as
308 close to cubic as possible for the lattice shape and number of processes, in an effort to
309 minimize the number of ghost lattice sites. Inter-process communication is handled
310 using MPI (Message Passing Interface), the dominant communications protocol used
311 in high-performance parallel computing [59]. The simulations were performed using
312 the Stampede supercomputer at the University of Texas, a resource of the Extreme
313 Science and Engineering Discovery Environment (XSEDE) [60].

4. Results

4.1. Evolution and Morphology of Solids

Figure 3 shows the tomograph acquired experimentally for the initial particle configuration on the tungsten needle before the aqueous solution was introduced, together with the tomograph acquired after 7 h of reaction in the calcium hydroxide solution. Comparison of the two tomographs shows that dissolution of Ca_3SiO_5 particles happens nonuniformly, as previously observed for similar particle cluster systems by Hu *et al.* [18]. Although most of the particles have eroded to some extent, a few particles, and isolated regions of other particles, have dissolved more extensively. An example is the area in contact with the needle and the middle region, where the original hole between particles has opened significantly. Other regions show considerably less dissolution, such as the top right particle. Even more striking is the nonuniform distribution of hydration product surrounding the Ca_3SiO_5 particles after 7 h of hydration. A relatively thin layer of product, approximately 1 μm thick, is visible to the left, while more voluminous regions are evident in the lower left, right, and especially the upper right portions of the figure. These larger regions are between 5 μm and 10 μm thick. Though not indicated in the figure, these regions seem to have a large fraction of $\text{Ca}(\text{OH})_2$ [18]. The thickest regions of hydration product are often in the vicinity of regions with relatively less dissolution of the nearest Ca_3SiO_5 particles.

For comparison purposes, each lattice site in the model should ideally be mapped to a single voxel of the initial tomograph. However, the tomographs in Fig. 3 are resolved at 15.6 nm per voxel, so a direct mapping of voxels to lattice sites would generate a computational mesh with approximately 10^9 sites. Such a large number of lattice sites cannot be feasibly accommodated, so the experimental system of voxels was coarse-grained to a resolution of 500 nm per voxel. The volume-averaged grayscale value of the voxels in each subset was determined. Based on this average grayscale value, the corresponding coarse-grained voxel was thresholded by tagging each voxel with an identification number value of 0 (empty), 100 (partially filled with Ca_3SiO_5 , the remaining volume being solution) or 255 (filled with Ca_3SiO_5). The resulting coarse-grained tomograph, with a resolution of 500 nm per voxel, is shown to the left in Fig. 4;

344 it retains the relative phase volume fractions and topology of the original tomograph.
 345 Each voxel of this coarser tomograph was mapped to a lattice site in a $51 \times 51 \times 37$
 346 computational mesh to simulate hydration at 25 °C under saturated conditions using
 347 HydratiCA. The simulated microstructures after 7 h is shown to the right in Fig. 4. The
 348 entire product region is shown in the middle image as a transparent gray envelope
 349 to better reveal the remaining Ca_3SiO_5 cluster. The $\text{Ca}(\text{OH})_2$ precipitates are shown
 350 in light green in the right image, with C–S–H remaining transparent. These images
 351 show that the hydration products nucleate on the surfaces of the Ca_3SiO_5 particles
 352 and grow outward, which is in qualitative agreement with the experimental obser-
 353 vations in Fig. 3. C–S–H nucleates rapidly on Ca_3SiO_5 , which consumes the driving
 354 force for further nucleation in less than 60 s, as shown in Section 4.2. Its final nucle-
 355 ation density is $6 \mu\text{m}^{-2}$. $\text{Ca}(\text{OH})_2$ nucleates on this C–S–H after about 17 min, while
 356 the C–S–H is still contained within a thin layer around the particles, and continues
 357 to nucleate for 5 min after that. A total of 104 $\text{Ca}(\text{OH})_2$ nuclei have formed before
 358 the driving force for nucleation becomes too low. (see Section 4.2). These $\text{Ca}(\text{OH})_2$
 359 embryos coalesce extensively as they continue to grow, so only one, or at most two,
 360 large domains are visible after 7 h.

361 The simulated microstructure in Fig. 4 is qualitatively consistent with the nCT ob-
 362 servations in Fig. 3. However, the total volume of simulated hydration product (middle
 363 image of Fig. 4) is considerably less than the experiments indicate. Furthermore, the
 364 experiments show that the products are distributed asymmetrically about the parti-
 365 cle, with considerably more being observed at the top and right side of the cluster; the
 366 simulations produce a more even distribution of product.

367 Figure 5 shows the simulated time dependence of the volume of Ca_3SiO_5 , C–S–H,
 368 and $\text{Ca}(\text{OH})_2$ over 10 h of hydration. The figure also shows the volume of Ca_3SiO_5
 369 measured at 0 h and 7 h as solid circles, and indicates that the simulated rate of Ca_3SiO_5
 370 dissolution is consistent with the observed volume of Ca_3SiO_5 consumed over the
 371 same time period.

372 For comparison, the measured volume of the product region at 7 h is also indi-
 373 cated in the plot. The apparent volume of product is more than twice the combined
 374 simulated volumes of C–S–H and $\text{Ca}(\text{OH})_2$ at the same time. At least some of the

observed extra volume of product may be caused by a larger amount of fine porosity within the growing C–S–H than the 70 % assumed in the model, as will now be shown by combining the nCT data with analysis of the nXRF measurements of the same system.

Fig. 6 shows the nXRF data obtained on the system, showing the relative calcium and silicon concentrations [18]. The quantitative analysis of the nXRF data was restricted to a region within 3 μm along the left boundary of the product region where the product is closest to the detector, because signal absorption is related to the path length through the material before reaching the detector. Prior work suggested that < 25 % of the Si and 5 % of the Ca X-rays should be absorbed in that region closest to the detector [61].

nXRF data fused with nCT data, an analysis technique called “nano-Tomography Assisted Chemical Correlation” (nTACCo) [15], can provide an estimate of the mass density of calcium and silicon in the hydration product region shown in Fig. 6. The nXRF signal is collected over the entire depth of the solid intersected by the X-ray beam, giving mass concentrations per unit cross-sectional area rather than per unit volume [18]. For purposes of rough estimation here, the solid intersection depth in the same region is assumed to be (6 ± 2) μm based on the nCT reconstruction in the same region. With that additional assumption, the region highlighted in Fig. 6 has volume averaged mass densities $\rho_{\text{Ca}} = (255 \pm 105) \text{ kg m}^{-3}$ and $\rho_{\text{Si}} = (18 \pm 9) \text{ kg m}^{-3}$. This corresponds to molar densities $n_{\text{Ca}} = (6362 \pm 2620) \text{ mol m}^{-3}$ and $n_{\text{Si}} = (641 \pm 320) \text{ mol m}^{-3}$, respectively [18]. If one assumes that (1) all the Si in the product is part of C–S–H that itself has a molar Ca/Si ratio of x , and (2) the only solid phases in the product region are C–S–H and $\text{Ca}(\text{OH})_2$, then

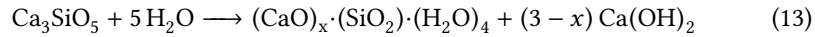
$$n_{\text{C–S–H}} = n_{\text{Si}} = (641 \pm 320) \text{ mol m}^{-3} \quad (11)$$

$$n_{\text{Ca}(\text{OH})_2} = n_{\text{Ca}} - x n_{\text{C–S–H}} \quad (12)$$

where x is the Ca/Si molar ratio of C–S–H, the composition of which has been normalized by the number of SiO_2 formula units for convenience. If $x = 1$, which is at the low end of the range of values reported in the literature, then substituting Eq. (11)

402 into Eq. (12) yields $n_{\text{Ca(OH)}_2} = (5721 \pm 2940) \text{ mol m}^{-3}$. Likewise, if $x = 2$, which is
 403 at the high end of the range of values reported in the literature, then $n_{\text{Ca(OH)}_2} =$
 404 $(5080 \pm 2940) \text{ mol m}^{-3}$. Therefore, at least within the $\approx 3 \mu\text{m}$ thick region of hydra-
 405 tion product highlighted in Fig. 6, the effect of C–S–H composition on the inferred
 406 amount of Ca(OH)_2 is small compared to the uncertainty in the composition mea-
 407 surements. For that reason, the rest of this analysis will simply assume the value of
 408 Ca/Si predicted by the simulation at 7 h of hydration, $x = 1.667$. That assumption
 409 is also reasonably close to the value of $x = 1.7$ that seems to be most often cited in
 410 the literature [42, 43]. In that case, the nXRF measurements imply that the number
 411 of moles of Ca(OH)_2 per unit volume of product is $n_{\text{Ca(OH)}_2} = (5297 \pm 2990) \text{ mol m}^{-3}$.
 412 In terms of mole fractions, X , of solids in the product region, these molar densities
 413 correspond to $X_{\text{C–S–H}} = 0.11 \pm 0.05$ and $X_{\text{Ca(OH)}_2} = 0.89 \pm 0.05$. The implied molar
 414 ratio of Ca(OH)_2 to C–S–H is 8 ± 4 , which is considerably greater than the value of
 415 about 1.34 that would be produced solely by reaction of Ca_3SiO_5 if the Ca/Si molar
 416 ratio of C–S–H is 1.667.

417 The molar densities just estimated can be combined with the total solid volume of
 418 hydration product above the needle measured by nCT to obtain an estimated number
 419 of moles of Ca(OH)_2 and C–S–H at 7 h of hydration. Table 4 compares these values
 420 both with the simulated number of moles and with the moles that would be required
 421 by the net hydration reaction, assuming that $x = 1.667$,



422 From these data, one may also estimate the volume fraction of fine occluded poros-
 423 ity that is evidently contained in the product region. Using a C–S–H molar volume
 424 of $\bar{V}_{\text{C–S–H}} = 1.94 \times 10^{-4} \text{ m}^3$, which is augmented relative to the published value [42]
 425 by the assumed 70 % of intercluster pores as already described, the Si molar density
 426 measured by nXRF implies that the fraction of the solid product region occupied by
 427 C–S–H, including its saturated gel pores, is

$$\phi_{\text{C–S–H}} = n_{\text{C–S–H}} \bar{V}_{\text{C–S–H}} = 0.124 \pm 0.062$$

Likewise, the volume fraction of $\text{Ca}(\text{OH})_2$ in the product region can be estimated as the product of its molar density in the product and its molar volume

$$\phi_{\text{Ca}(\text{OH})_2} = n_{\text{Ca}(\text{OH})_2} \bar{V}_{\text{Ca}(\text{OH})_2} = 0.18 \pm 0.10$$

Therefore, assuming no other solid components in the region of hydration product, the total volume fraction of solids in that region is estimated to be only 0.30 ± 0.16 ; the remaining 70 % of the product region is occluded porosity that is not already accounted as C–S–H gel porosity.

Based on the foregoing analysis, the best estimates of C–S–H and $\text{Ca}(\text{OH})_2$ volumes in the product region at 7 h are shown in Fig. 5 as a filled triangle and a filled square, respectively.

4.2. Aqueous Solution

The composition of the aqueous solution was not monitored as part of the nCT experiments, but understanding of the simulation results can be enhanced by considering its predictions of the solution composition. Figure 7 shows as a solid curve the evolution in the total silicate concentration and total calcium concentration. The individual points on this plot are measurements made by different laboratories as compiled and plotted by Jennings as Curve B [45], which is typically observed during early-age hydration of Ca_3SiO_5 ; additional measurements made at higher calcium concentrations by Bellmann [62] are also shown. Within the first 0.3 s of hydration, the solution composition lies along the data for Curve B, both before and after the precipitation of $\text{Ca}(\text{OH})_2$.

The composition and solubility of the solid solution end members for C–S–H (Table 3) were set by assuming that it is in equilibrium with solutions lying along Curve B [48]. Therefore, the fact that the simulated solution remains close to Curve B implies that C–S–H attains and stays close to equilibrium with the solution. In turn, this implies that Ca_3SiO_5 dissolution controls the rate of hydration over this time scale. In support of this interpretation, Fig. 8 shows the total saturation of C–S–H (Eq. (10)) [47] and the saturation index (*i.e.*, ratio of activity product to solubility product) of Ca_3SiO_5 . The total saturation with respect to C–S–H rapidly spikes to nearly

$\beta_T = 7$ at the beginning of the simulation, but then quickly decreases to $\beta_T < 2$ within 0.5 s as C–S–H nucleates and grows. From about one second until the end of the simulation, $\beta_T \approx 1.3$, which is close to the equilibrium condition of $\beta_T = 1$. The saturation index of Ca_3SiO_5 , in contrast, spends most of the simulation at values less than 0.1.

An earlier simulation study by Bullard and Scherer [36] suggested that the solution of a hydrating Ca_3SiO_5 paste could be significantly undersaturated with respect to C–S–H, so that neither C–S–H nor Ca_3SiO_5 could be near equilibrium throughout the early stages of hydration. However, that previous study used a discrete mixing model of C–S–H composition instead of the more thermodynamically realistic solid solution model [47] used here, and it also assumed component solubilities for C–S–H that were much lower than the ones used here, more closely approximating Jennings Curve A [45] than Curve B. These two results are therefore not inconsistent, but hinge on the assumption of whether the solubility of C–S–H forming at early times more closely resembles that indicated by Curve B or Curve A [45]. This topic is taken up again in the Discussion.

5. Discussion

The similarities and, more importantly, differences between the experimental observations and the simulation provide insights into those aspects of hydration and microstructure development that can be understood—or at least captured—in terms of the the model’s assumptions and those that are not yet well understood. Those aspects that the model does not adequately simulate can be used to sketch a road map for further research.

5.1. Ca_3SiO_5 Dissolution

Mounting experimental evidence indicates that dissolution rates of numerous minerals [63–68], including rapidly dissolving ones such as gypsum [69] and cubic tricalcium aluminate [70], can vary from point to point on the surface at constant undersaturation by a factor of ten or more, being strongly influenced by the local density and type of surface defects such as dislocation outcroppings, stacking faults,

485 and grain boundaries. Dissolution rates for these minerals, and most probably for
486 Ca_3SiO_5 [17, 18], are therefore more properly characterized by a statistical distribu-
487 tion than by a single rate.

488 The rates reported by Nicoleau [28] for dissolution of a dilute suspension of Ca_3SiO_5
489 particles should, therefore, be understood as a statistical average over all exposed sur-
490 faces on all the particles in the suspension. Even these average values exhibit consid-
491 erable scatter, as indicated in Fig. 2. In addition, very few rate measurements were
492 reported at the highest activity products where the dissolution rate is low. Unfortu-
493 nately, the solution in a hydrating Ca_3SiO_5 system spends all but the first few seconds
494 of its time at those higher activity products. A variation by as little as $0.5 \mu\text{mol m}^{-2} \text{s}^{-1}$
495 in this region has major implications for the hydration rate. For example, changing
496 the dissolution rate law from the solid curve to the dashed curve in Fig. 2 reduces the
497 degree of hydration at 7 h from 18 % to < 3 %. Besides these uncertainties, a small
498 cluster of only several particles, such as that examined in this paper, is not a large
499 statistical sampling and cannot be expected *a priori* to dissolve, even on average, at
500 the mean rate for the same undersaturation that otherwise would be observed in a
501 much larger sample.

502 In the absence of more detailed characterization of the local dissolution rates of
503 the particle cluster, we have chosen to retain the form of the average rate law, Eq. (3),
504 applied uniformly across the exposed Ca_3SiO_5 surface. However, in light of the fore-
505 going discussion, the parameters of the rate law have been modified slightly as shown
506 in Fig. 2, still providing a good agreement with the experimental dissolution data while
507 enabling a better match to the measured net volume of Ca_3SiO_5 lost by the cluster after
508 7 h of hydration. Therefore, a mean rate law consistent with prior measurements in
509 the literature appears to be adequate for characterizing the dissolution in this system.
510 However, hydration models could benefit greatly from more experimental research on
511 the statistical distribution of Ca_3SiO_5 dissolution rates as a function of undersatura-
512 tion, and on how those rates are potentially influenced by other dissolved components
513 in solution, such as aluminates and sulfates, that are present in portland cement.

5.2. Hydration Product Quantity

Setting aside for the moment the large amounts of occluded porosity in the region of hydration product, the simulated moles of C–S–H and $\text{Ca}(\text{OH})_2$ at 7 h are 15 % greater and 43 % less, respectively, than observed in the experiment (Table 4). However, the discrepancies in the moles of Ca_3SiO_5 and each of the two hydration products are all within the propagated uncertainties in the measurements. More importantly, both the experiment and simulation exhibit greater amounts of $\text{Ca}(\text{OH})_2$ than can be justified by mass balance when reaction (13) is applied only to the particle cluster at the needle tip. The anomalously high $\text{Ca}(\text{OH})_2$ content is likely caused by hydration of the Ca_3SiO_5 below the field of view. As described in Section 3.1, these simulations assume that ions in solution are homogeneously mixed because the diffusion coefficients are fast enough for diffusion to homogenize the solution within 1 s over the length scales of this simulation [19, 34]. However, a homogeneous distribution of solution components can still lead to an uneven distribution of C–S–H and $\text{Ca}(\text{OH})_2$ products. Recall that an extra layer of Ca_3SiO_5 was placed below the particle cluster in the simulations, which was necessary to mimic the additional Ca_3SiO_5 particles glued to the needle in the nCT experiment. However, this Ca_3SiO_5 layer has only 30 % of the surface area in the simulated system. Therefore, C–S–H nucleation will happen preferentially where the Ca_3SiO_5 surface area is higher, and so more of it will nucleate and grow on the particle cluster than on the layer below. As greater C–S–H surface area forms around the cluster, $\text{Ca}(\text{OH})_2$ will preferentially nucleate and grow there as well. The driving force for growth is constant everywhere because the solution is mixed, so the only variations in product growth are caused by local differences in their surface areas. Only small heterogeneities in surface area are present near the start of hydration, but they are increasingly magnified with time.

Is the use in the simulations of an extra layer of Ca_3SiO_5 below the field of view an adequate way to handle the experimental reality? In the experiments, the powder particles below the field of view are partially embedded in the epoxy that was used to affix them to the needle. Those particles are also arranged more compactly and have significantly more interior porosity than the cluster. It is therefore difficult to determine the exposed surface area of that powder region that can readily exchange dissolved

material with the cluster above. If one assumes that only the exterior surface of the powder mass can exchange dissolved material with the cluster, then the simulated and experimental surface area below the needle may not differ by a great amount. However, if the “communicable” surface area of these particles is significantly greater than assumed in the simulations, or if partially dissolved small particles migrate up to the cluster by convection, then the total amount of hydration product could be considerably greater than in the simulations. But the moles of C–S–H and $\text{Ca}(\text{OH})_2$ formed in the simulations and experiments do not differ by more than the measurement uncertainty, so the simulated Ca_3SiO_5 layer below the needle tip is probably sufficient to capture the major effects of the extra material used in the experiments.

5.3. Hydration Product Morphology and Distribution

5.3.1. C–S–H porosity

The most striking observation from the experiments is the large amount of occluded porosity, about 70 %, that evidently is contained within the hydration product in addition to C–S–H gel porosity. Evidence of this porosity is found in the product texture observed in nCT slices, an example of which is shown in the upper left of Fig. 9. More quantitatively, one can calibrate the observed gray values in the nCT data to the absorption of Ca_3SiO_5 and of air, from which an estimate of the density variations in the hydration product can be made. The lower plot in Fig. 9 shows the gray value of the product regions as a function of distance from the Ca_3SiO_5 surface. This plot indicates a uniform decrease in density (or increase in porosity) away from the Ca_3SiO_5 surface. The effect is pronounced enough that the outer third of the product region has an apparent density approaching that of air. This is clear evidence of a high volume of porosity within the product region.

The large volume of solution surrounding the small collection of particles might encourage a different growth mode more reminiscent of diffusion limited aggregation [71], which could easily produce sparse networks of material containing a large internal porosity. This kind of morphology would be seen only rarely in denser pastes [72] where convection is absent and the available space for growth; the product could begin to densify at earlier times by intergrowth of additional C–S–H after the free space

is exhausted. HydratiCA currently assumes that all solids grow as densely as possible. For C–S–H this assumption means that its gel porosity is an intrinsic part of its internal structure, but that it grows as compactly as possible while retaining that gel porosity. However, this study suggests that such an assumption is not realistic, at least not for C–S–H and probably not for other poorly ordered gel phases.

Gottapu and Biernacki [20] have developed a single particle model of hydration in which C–S–H is assumed to grow rapidly as a “proto-product” with an apparent density of 440 kg m^{-3} that later is assumed to densify more slowly to a maximum density of 2200 kg m^{-3} . The molar volume of $\text{C}_5\text{S}_3\text{H}_{12}$ in Table 2—which includes its gel porosity— corresponds to a density of 910 kg m^{-3} , slightly more than twice that of the low-density form used by Gottapu and Biernacki. Had the molar volume been doubled here to coincide with their low-density form, the simulated volume of C–S–H at 7 h ($1248 \mu\text{m}^3$) would have been approximately doubled. When combined with the simulated volume of $\text{Ca}(\text{OH})_2$ ($265 \mu\text{m}^3$), the total apparent volume of hydration product would coincide with the nCT observations ($2729 \mu\text{m}^3$) to within its measurement uncertainty.

The assumed molar volume of C–S–H end members used in this simulation could be modified to better agree with the low-density form proposed by Gottapu and Biernacki [20], which also had been proposed earlier by Bishnoi and Scrivener [7]. This would immediately produce a closer agreement with the observed product volume in the experiment. However, this low density of C–S–H is probably not a material property but instead is a consequence of its growth mechanism. Therefore, it seems more appropriate to work in the future on a more physically and chemically rigorous growth model for C–S–H that would naturally produce low-density material followed by a gradual in-filling of the occluded porosity as suggested by Fig. 9. Such a growth model, if properly formulated, would also be able to predict the influence on growth morphology of various solution components that have been observed to influence C–S–H growth [73–75]. Unifying the chemistry and physics of C–S–H growth and morphology at this length scale will require more research.

604 5.3.2. C–S–H distribution

605 Aside from the low apparent density of C–S–H, the hydration product region ob-
606 served by nCT is asymmetrically distributed around the original particle cluster, while
607 the simulations produce a more evenly distributed envelope of product around the
608 cluster. Evidently, the simulations fail to capture some physical mechanism causing
609 this asymmetry. One possible explanation is that the Ca_3SiO_5 particles below the field
610 of view are unevenly distributed around the needle, and that their dissolution causes
611 stronger upward convective flow of material on the right side than on the left. The
612 simulation assumed that material dissolved from below the needle is homogeneously
613 mixed throughout the solution, so it was unable to produce such an asymmetric mass
614 transport either by advection or diffusion. In fact, simulating diffusion or advection by
615 HydratiCA currently is accomplished by a biased random walk [76] that, for ions with
616 mobilities in water as great as Ca^{2+} and OH^- , requires exceedingly small time steps
617 on the order of 10^{-5} s. The simulation shown here would have taken approximately
618 three months to complete, which was not feasible with our current computational
619 resources (but may be possible in the future as computational power continues to
620 increase).

621 A second possible explanation for the asymmetric product distribution is that
622 there are a greater density of low-energy nucleation sites for C–S–H on the right and
623 upper portions of the particle cluster. Fig. 3 indicates that Ca_3SiO_5 dissolution hap-
624 pened preferentially in those areas, which suggests that the surfaces may have had
625 higher energy defects to drive that dissolution. According to the derivation leading to
626 Eqs. (8 and (9, for the nucleation rate, the free energy change for forming C–S–H nu-
627 clei at those higher-energy sites would be greater than on lower-energy surface sites.
628 Nucleation rates should therefore be greater at high-energy defects than at other sur-
629 face sites. However, to capture this effect in the simulations would require knowing in
630 advance the distribution and relative energy density of surface defects on the Ca_3SiO_5
631 particle cluster. This information not available from the experimental characterization
632 methods used here.

633 Regardless of the origin of the observed asymmetric distribution of product, the

effect likely would be less pronounced in a typical cement paste because (a) the free space for growth between particles would be so much less and (b) the much greater number and even spatial distribution of Ca_3SiO_5 particles would ameliorate most inhomogeneities in dissolved material sources and favorable nucleation sites.

5.3.3. *C–S–H composition*

The experimental solution composition measurements cataloged by Jennings for “Curve B” were all obtained by sampling the solution during hydration of some form of Ca_3SiO_5 for no more than a few days [45, 77], although at least one set of measurements under nominally the same conditions, reported by Brown *et al.* [56] lied along Curve A. The latter study used colorimetry without treating the solution with a dilute acid, so some additional precipitation could have occurred in the solution to drive it toward Curve A after the Ca_3SiO_5 was removed. With the exception of that study, however, all other data along Curve A, or at least well below Curve B, were reported for experiments during which C–S–H was equilibrated with the solution for much longer periods of time, up to several months [46, 53, 54, 78]. If, as in this simulation, one uses Curve B to define the solubility of C–S–H during hydration at early times, then the dissolution of Ca_3SiO_5 controls the rate of hydration. However, if Curve A defines the C–S–H solubility then neither dissolution nor C–S–H growth fully control the hydration rate [36]. Given the preponderance of data that Curve B characterizes the solution at least until after the main hydration rate peak in the acceleration period, this study has assumed C–S–H end members and solubilities that will generate Curve B. The simulations could have included the possibility of formation of the other C–S–H solid solution that eventually produces Curve A [47] but did not because of computational efficiency and because the majority of prior experimental evidence suggests that Curve A is obtained only at considerably longer times than those simulated here.

5.3.4. *$\text{Ca}(\text{OH})_2$ distribution*

Turning from the overall appearance of the hydration product region, the simulation predicts for $\text{Ca}(\text{OH})_2$ a fairly large mass that is near and rather evenly distributed

about the Ca_3SiO_5 particle cluster. In contrast, Fig. 6 indicates a few higher-density regions in light gray within the product envelope that are probably individual large grains of $\text{Ca}(\text{OH})_2$ [18]. Portlandite is often observed as relatively few large masses even in denser pastes of Ca_3SiO_5 [79], so the current observation of few but large $\text{Ca}(\text{OH})_2$ domains is unlikely to be an artifact of the isolated cluster arrangement. The model assumes classical heterogeneous nucleation rate theory, and there is no experimental evidence that $\text{Ca}(\text{OH})_2$ nucleation is nonclassical. The nucleation work used for $\text{Ca}(\text{OH})_2$ (see Table 3) was estimated from multiple comparisons of HydratiCA simulations to experimental solution composition data during Ca_3SiO_5 hydration, nearly all of which show that the total calcium in solution reaches a maximum concentration of 35 mmol L^{-1} to 40 mmol L^{-1} [35, 36, 39, 56]. Those comparisons were made under the assumption that nucleation first begins in that concentration range but then also happens at a fast enough rate to reduce the calcium concentration at a rate that is also consistent with those experimental data. The values in Table 3 are also in close agreement with the theoretically computed values using the best estimates of the parameters used in Eq. (8).

The current experimental data, however, suggest that the nucleation rate might be considerably lower than in the simulations. Two reasons why the $\text{Ca}(\text{OH})_2$ distribution may be too homogeneous in the simulation are that either the nucleation work is incorrect or the catalog of surfaces on which $\text{Ca}(\text{OH})_2$ can nucleate is incomplete. C–S–H was chosen as a favorable $\text{Ca}(\text{OH})_2$ substrate in the model because C–S–H itself has $\text{Ca}(\text{OH})_2$ -like layers separated by silicate chains. $\text{Ca}(\text{OH})_2$ is allowed to nucleate elsewhere, but the assumed nucleation work on other surfaces is set high enough that it does not happen in the simulations. However, other types of surfaces may be present, at much lower concentrations, where $\text{Ca}(\text{OH})_2$ could nucleate. For example, statistical variations in C–S–H growth structure may produce a few microscopic regions that are relatively rich in $\text{Ca}(\text{OH})_2$ layers and relatively denuded of silicate chains, at which $\text{Ca}(\text{OH})_2$ could more readily nucleate. Once again, however, an effect like this would be exceedingly difficult to confirm with existing experimental characterization methods, and without that kind of confirmation the only available course is to alter either the nucleation work or the pre-exponential fac-

tor in Eq. (7), and perhaps the growth rate constant for $\text{Ca}(\text{OH})_2$, in such a way that fewer supercritical nuclei are produced before growth rates become sufficiently high to reduce the driving force for nucleation below the maximum supersaturation range. Such alterations could only remain consistent with previous experimental measurements [39, 56] if they do not also greatly change the typical simulated calcium concentration time dependence in solution. Trial-and-error parameter modifications are undesirable, though, since the parameters are tied to material properties and physical mechanisms, and could be avoided with the aid of fundamental $\text{Ca}(\text{OH})_2$ nucleation rate measurements in well-characterized supersaturated solutions with a variety of substrate materials.

6. Conclusions

nCT and nXRF observations of a collection of tricalcium silicate (Ca_3SiO_5) particles reacting in a calcium hydroxide solution were used as a test of HydratiCA simulations that model, as nearly as possible, the thermal and chemical conditions of those experiments. At the 7 h point of comparison, the simulated and observed moles of Ca_3SiO_5 , C–S–H, and $\text{Ca}(\text{OH})_2$ agree to within the measurement uncertainty, although both indicate that the moles of hydration product— especially $\text{Ca}(\text{OH})_2$ exceed the amount that can form by hydration of the particle cluster alone. The additional hydration products arrive by migration of ions produced by dissolution of Ca_3SiO_5 below the observation volume.

Measurements of calcium and silicon concentration within a thin sample of the hydration product nearest to the nXRF detector suggest that that region comprises approximately 12 % C–S–H and 18 % $\text{Ca}(\text{OH})_2$, with the remaining 70 % being occluded porosity that is not already part of the gel porosity. This low-density growth morphology is particularly noticeable in these experiments because of the large volume of solution into which growth can easily penetrate, and has approximately the same apparent density as that assumed by Gottapu and Biernacki to rapidly form at early times as low-density “proto-product” which densifies more slowly at later times [20]. However, more research is needed to elucidate the physics and chemistry of C–S–H

723 growth at length scales of 10 nm to 500 nm so that microstructure models can be en-
724 dowed with more realistic C–S–H growth mechanisms that can account for free vol-
725 ume of growth and solution composition. Ultimately, a new random aggregation and
726 densification model that unifies the physics and chemistry should emerge from that
727 work.

728 A more careful refinement of $\text{Ca}(\text{OH})_2$ nucleation and growth parameters must
729 also be undertaken, with the aid of controlled experimental observations, to bring the
730 simulation into better agreement with microstructure observations, here and in typi-
731 cal Ca_3SiO_5 pastes, that $\text{Ca}(\text{OH})_2$ usually forms fewer but larger masses than observed
732 in this simulation. In fact, more direct microscopic measurements of nucleation rates
733 and growth rates (not fits to phenomenological equations) of all the common prod-
734 ucts of portland cement hydration are probably the most important missing data that
735 will be required to improve the predictive capability and microstructure fidelity of
736 computer models of hydration in the future.

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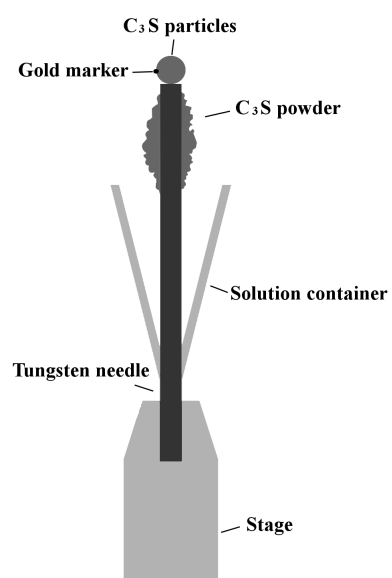


Figure 1: Experimental setup for nCT experiments.

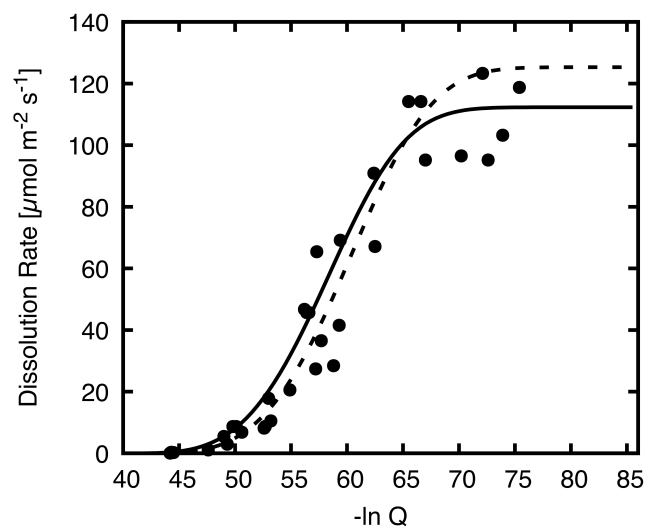


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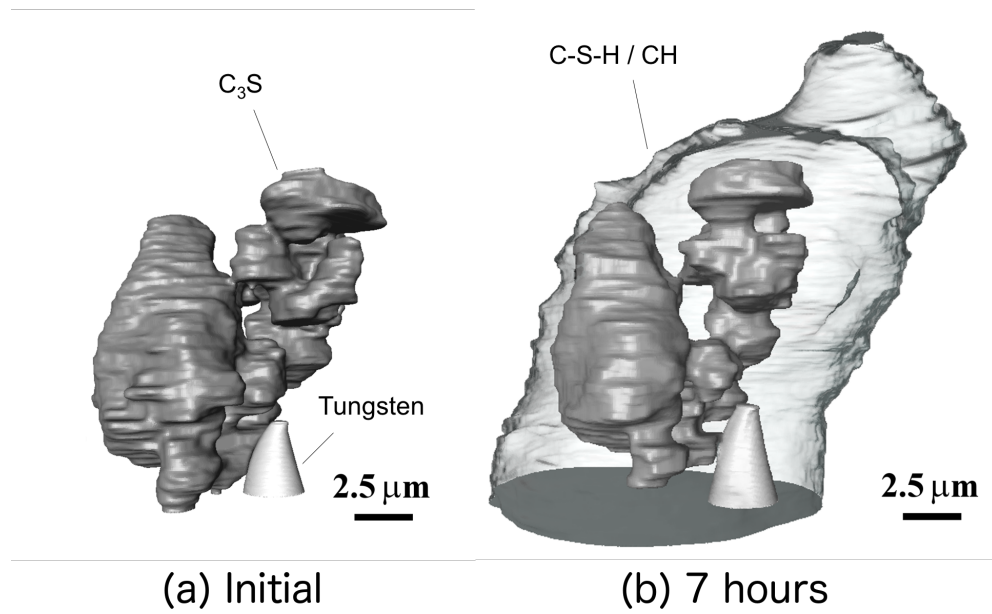


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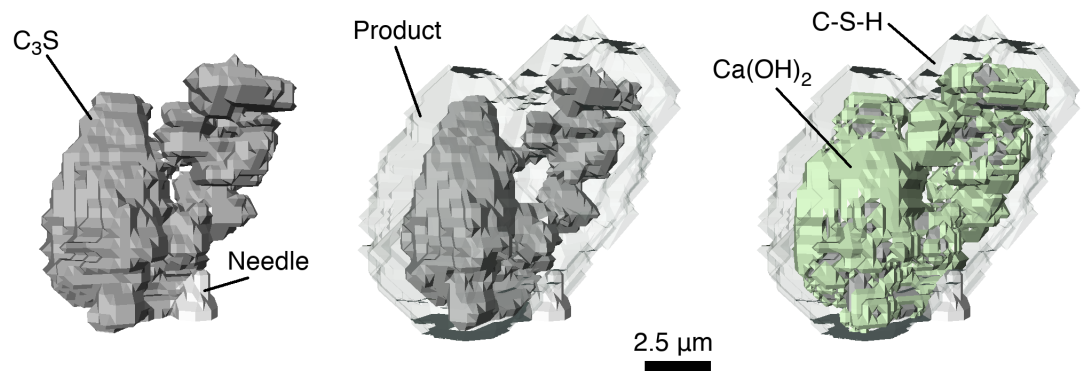


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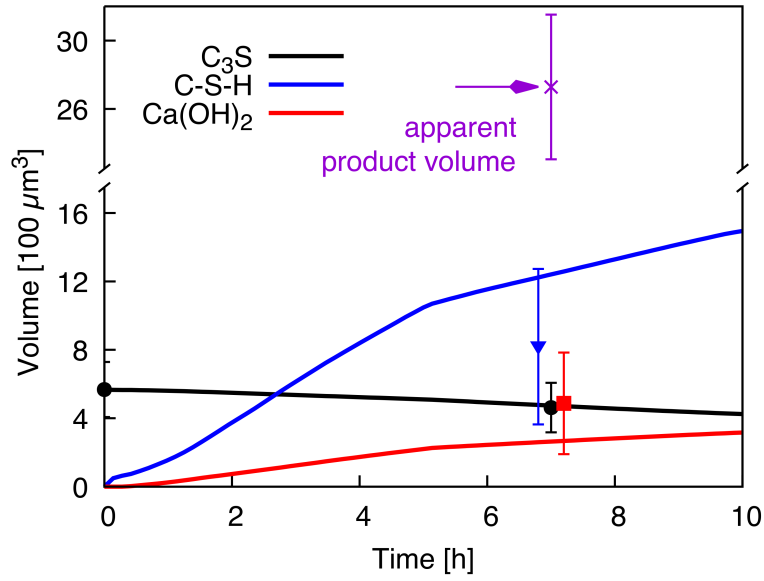


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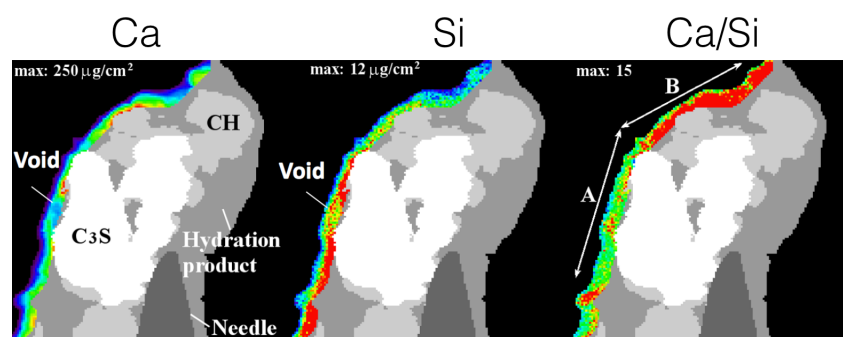


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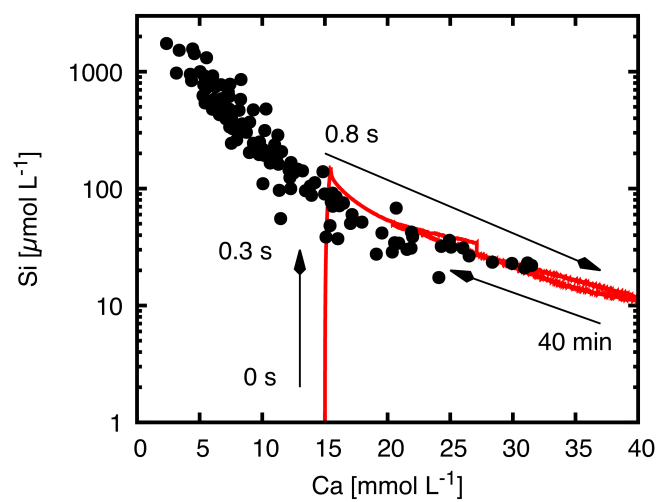


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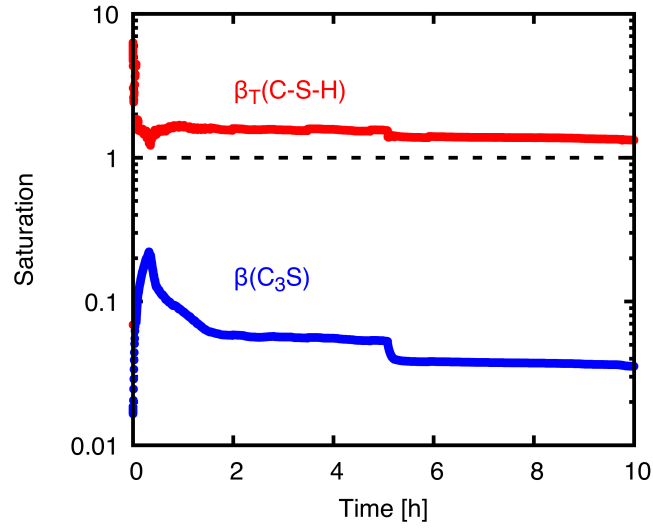


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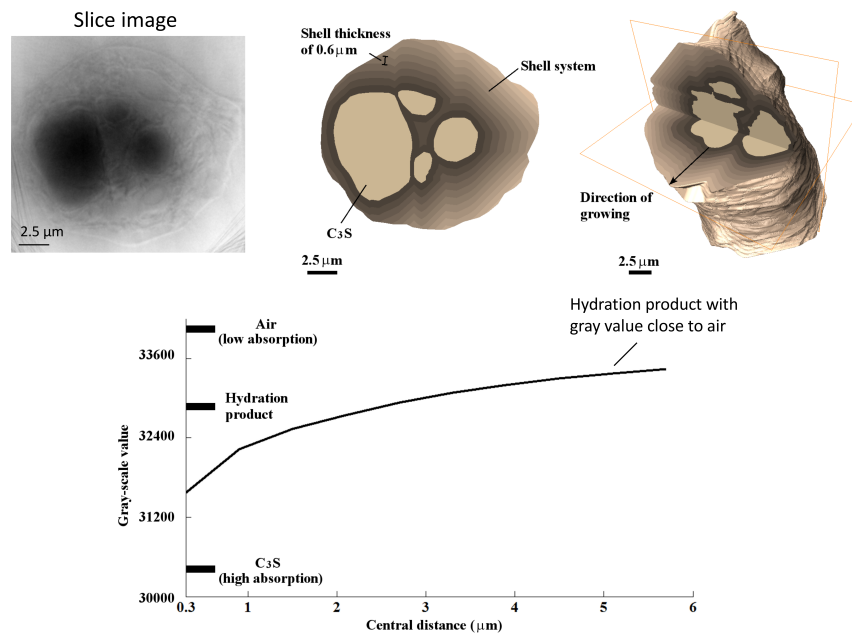


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1029		with the values expected from net reaction (13) based on the <i>measured</i>	
1030		amount of Ca_3SiO_5 dissolved.	52

Table 1: Elemental composition and BET specific surface area of the Ca_3SiO_5 powder. Three replicate measurements of each element concentration were made and typically had a range of ± 2 in the least significant digit. The uncertainty in the surface area is reported as $\pm$ one standard deviation of three replicates.

ICP Elemental Analysis	Al	Ca	Mg	Si	Sr
(mole %)	< 0.2	74.8	< 0.002	25	0.0018
BET surface area ($\text{m}^2 \text{kg}^{-1}$)	1216 ± 3				

Table 2: Properties of material components used in the simulations. V_m is the molar volume, M is the molar mass, σ is the bulk electrical conductivity through the given solid phase, σ_o is the electrical conductivity of the bulk aqueous solution, and D is the ion diffusion coefficient of an ion in the solution at infinite dilution. η and $\phi_{\max}$ are parameters determining the efficacy of C–S–H phases in blocking the access of Ca_3SiO_5 to water and are described further in Eq. (6). Unless otherwise indicated, the values in the table are taken from Reference [36].

Component	$V_m/$ $10^{-6} \text{ m}^3 \text{ mol}^{-1}$	$M/$ kg mol^{-1}	$\sigma/\sigma_o^{(a)}$	$D^{(b)}/$ $10^{-9} \text{ m}^2 \text{ s}^{-1}$	$\eta^{(c)}$	$\phi_{\max}^{(c)}$
H_2O	18.1	0.018 02	1.0			
Ca_3SiO_5	72.4	0.228 33	0.0			
$\text{C}_2\text{S}_3\text{H}_{12}^{(d)}$	633.6	0.5086	0.7		0.75 ^(e)	0.2
$\text{C}_5\text{S}_3\text{H}_{12}^{(d)}$	747.2	0.6768	0.7		0.50	1.0
$\text{Ca}(\text{OH})_2$	33.1	0.074 09	0.0			
Ca^{2+}		0.040 08		0.79		
CaOH^+		0.057 09		0.71		
$\text{H}_2\text{SiO}_4^{2-}$		0.094 10		0.70		
H_3SiO_4^-		0.095 10		0.70		
OH^-		0.017 00		5.28		

^(a) Relative conductivity (*i.e.*, the conductivity divided by that in the bulk solution).

^(b) Ion mobility at infinite dilution.

^(c) See Eq. (6) for the meaning of these terms for coverage of Ca_3SiO_5 .

^(d) Stoichiometric components of an ideal solid solution model for C–S–H [47].

^(e) Reduced from 0.9 based on more simulation studies conducted after Reference [36] at different lattice spacings.

Table 3: Stoichiometry and assumed thermodynamic and kinetic parameters for simulated reactions. Except where noted, the collection of reactions and the parameter values are taken from Reference [36] and references therein. The reactions and solubilities for C–S–H are based on a newer solid solution model in Reference [47], and the kinetic parameter values were chosen to give approximately the same rates of nucleation and growth as simulated in Reference [36].

Reaction	$k_+ /$ $\mu\text{mol m}^{-n} \text{s}^{-1(a)}$	$\ln K$	$I_0^B /$ $\text{m}^{-n} \text{s}^{-1(a)}$	$q /$ K^3
$\text{Ca}_3\text{SiO}_5 + 4 \text{H}_2\text{O} \rightleftharpoons 3 \text{Ca}^{2+} + \text{H}_3\text{SiO}_4^- + 5 \text{OH}^-$	112.5 ^(b)	-39.0 ^(b)		
$\text{C}_2\text{S}_3\text{H}_{12} \rightleftharpoons 2 \text{Ca}^{2+} + 3 \text{H}_3\text{SiO}_4^- + \text{OH}^- + 7 \text{H}_2\text{O}$	1.5×10^{-7}	-37.43	$1.1 \times 10^{27(b)}$	$2.0 \times 10^9(b)$
$\text{C}_5\text{S}_3\text{H}_{12} \rightleftharpoons 5 \text{Ca}^{2+} + 3 \text{H}_3\text{SiO}_4^- + 7 \text{OH}^- + 4 \text{H}_2\text{O}$	1.5×10^{-7}	-80.43	$7.3 \times 10^{26(c)}$	$1.7 \times 10^{10(c)}$
$\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2 \text{OH}^-$	7.2	-11.97	$7.35 \times 10^{26(d)}$	$2.5 \times 10^9(d)$
$\text{CaOH}^+ \rightleftharpoons \text{Ca}^+ + \text{OH}^-$	6×10^5	-2.81		
$\text{H}_3\text{SiO}_4^- + \text{OH}^- \rightleftharpoons \text{H}_2\text{SiO}_4^{2-} + \text{H}_2\text{O}$	1.5×10^7	1.91		

^(a) $n = 2$ or 3 for heterogeneous or homogeneous processes, respectively.

^(b) Based on linear regression of measurements in Ref. [28].

^{(c),(d)} Heterogeneous nucleation on Ca_3SiO_5 and C–S–H, respectively.

Table 4: Measured changes in number of moles of each solid phase in Fig. 3 after 7 h of hydration, compared with predictions from simulations and with the values expected from net reaction (13) based on the *measured* amount of Ca_3SiO_5 dissolved.

Component	ΔN inferred from Measurement [pmol]	ΔN inferred from Reaction (13) [pmol] ^(a)	ΔN simulated [pmol]
Ca_3SiO_5	-1.46 ± 0.50	—	-1.326
C-S-H	1.7 ± 0.6	1.46 ± 0.50	1.957
$\text{Ca}(\text{OH})_2$	14 ± 10	1.95 ± 0.90	7.950

^(a) Based on the measured number of moles of Ca_3SiO_5 dissolved in the second column. This assumes $x = 1.667$ in Reaction (13), which is the Ca/Si ratio predicted by the simulation at 7 h.