A Thermodynamic and Kinetic Model for Paste-Aggregate Interactions and the Alkali-Silica
Reaction

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16 **Abstract**

17 A new conceptual model is developed for ASR formation based on geochemical
18 principles tied to aqueous speciation, silica solubility, kinetically controlled mineral
19 dissolution, and diffusion. ASR development is driven largely by pH and silica gradients
20 that establish geochemical microenvironments between paste and aggregate, with
21 gradients strongest within the aggregate adjacent to the paste boundary (i.e., where ASR
22 initially forms). Super-saturation of magadiite and okenite (crystalline ASR surrogates)
23 occurs in the zone defined by gradients in pH, dissolved silica, Na⁺, and Ca²⁺. This model
24 provides a thermodynamic rather than kinetic explanation of why quartz generally behaves
25 differently from amorphous silica: quartz solubility does not produce sufficiently high
26 concentrations of H₄SiO₄ to super-saturate magadiite, whereas amorphous silica does. The
27 model also explains why pozzolans do not generate ASR: their fine-grained character
28 precludes formation of chemical gradients. Finally, these gradients have interesting
29 implications beyond the development of ASR, creating unique biogeochemical
30 environments.

1. Introduction

Expansion due to reaction between cement and aggregate has been recognized for over 70 years as a cause of premature degradation in concrete [1]. Although various deleterious reactions have been observed, the alkali-silica reaction (ASR) remains the most infamous, forming an alkali-rich silica gel that swells on hydration and that is associated with cracking tied to premature degradation of the concrete. ASR has a worldwide distribution [2], occurring over time in concretes that contain both available alkali (sodium and/or potassium) and certain types of silica-rich aggregates [3, 4].

For the almost sixty years since its presentation, the conceptual model of Powers and Steinour [5, 6] for ASR has remained the basis for most interpretations of the mechanisms by which the reaction proceeds. Although some aspects of the model have been refined by subsequent studies, the model remains largely intact [7].

A central tenet of the Powers and Steinour (P&S) model is that ASR initiates by an attack of silica-rich phases (such as opal, chert, strained quartz, volcanic glass) by alkalis in the pore fluids from the cement paste: specifically, alkali cations and hydroxyl anions diffuse into the silica-rich phase, disrupting the silica framework to form what is termed “ASR gel”. In this model, the dissolution kinetics of these reactive silica phases generates silica gel whereas unstrained quartz is unreactive. This model successfully explains many observations of ASR, including the following two:

- Often, gel forms initially within the bounds of the aggregate, producing the darker reaction rim on the aggregate that is one characteristic of ASR as well as forming gel in fractures that transect the aggregate.

- Gel within the bounds of the aggregate is enriched in alkalis and depleted in calcium, despite the fact that calcium dominates the chemistry of the hydrated paste outside the bounds of the aggregate.

In this study, we offer an alternative conceptual model for ASR based on geochemical principles and tools that have evolved since the Powers and Steinour model was introduced. Our conceptual model is based on dissolution and precipitation driven by an acid-base disequilibrium across the cement-aggregate interface; this disequilibrium establishes a chemical gradient that drives dissolution and transport processes on both sides of the interface. The net result is the formation of a geochemical microenvironment defined by an accumulation of aqueous silica and alkali within the aggregate boundary and by a gradients in pH and aqueous silica species, ultimately resulting in the super-saturation and precipitation of ASR gel.

In developing this conceptual model, we rely on calculations from reactive-transport simulations [8, 9], focusing on simple, well-documented physical processes: dissolution, precipitation, equilibrium aqueous speciation, and diffusion. We introduce the conceptual model by focusing on the simplified cement system $\text{CaO-SiO}_2\text{-H}_2\text{O}$. The use of a simplified system allows us to explore quantitatively a few key processes that will occur in both the simple and full systems. Additional components (Na^+ , Cl^- , HCO_3^- , and SO_4^{2-}) are added to the simplified reference-case to develop the conceptual model with respect to other solid phases and fluid species. In developing the model, we directly evaluate the impact of two key uncertainties: dissolution rate (including reactive surface area) and C-S-H solubility (including both Ca:Si ratio and differences in published solubility products). Although the lack of thermodynamic information on ASR gels precludes addressing the formation of gels

directly, conceptual aspects of gel formation are explored using saturation of crystalline surrogates for ASR gel and considering mechanisms of silica gelation. We do not, however, consider other possible crystalline surrogates for ASR gel (such as analcime [10] or erionite [11]), which have also been reported as crystalline products associated with ASR; these would require adding an additional chemical complexity to the system (e.g., Al^{3+}).

Like the original model of Powers & Steinour [5, 6], the geochemical model presented here is able to explain the two key observations of ASR described above. In addition, it provides a sound physical basis for explaining the roles of silica mineralogy (i.e., amorphous silica vs. unstrained quartz) and of grain size (e.g., problematic siliceous aggregate vs. beneficial, fine-grained siliceous pozzolans), as well as for understanding the impact of lithium on gel formation. Importantly, our model has distinct differences in the driving mechanisms for ASR gel formation, which, we hope, will lead to new insights on predicting and controlling ASR. More specifically, dissolution occurs on both sides of the cement-aggregate interface, stressing the role of reactions in the paste in the development of ASR gel, particularly the role of dissolution of calcium-silicate-hydrate paste. An outcome of this is that pH is buffered in the paste, allowing a gradient to develop inside the aggregate. Although the acid-base disequilibrium between paste and aggregate has been noted widely in ASR research, its implications for the mechanisms of ASR have not been fully explored. In our model, this gradient has numerous implications, including the establishment of silica gradients that drive diffusion, the shifting of aqueous (alkali-) silica species across the cement-aggregate boundary, and the development of stability fields within the aggregate for ASR reaction products. In general, this pH gradient drives the development of unique geochemical environments at the boundary between paste and

99 aggregate that could have implications beyond the formation of ASR (including, for
100 example, the formation of microbial niches, as discussed briefly below).

2. Methods

2.1 Modeling Approach

Pan et al. [12] present a comprehensive review of computational modeling that has been applied to ASR. Although several studies have attempted to couple the chemical and mechanical effects in order to explain both the reaction and the associated expansion, most have followed the basic chemical mechanisms of Powers and Steinour [5] and Dent Glasser and Kataoka [3], assuming the diffusion of alkali and hydroxyl to the reacting silica-rich particle.

We follow a different approach in this study, simulating well-established chemical and transport phenomena. Our basic hypothesis is that ASR gel forms from precipitation of dissolved constituents in response to thermodynamic solubility, so our focus on chemistry and transport explores what can occur when fluids are present in a porous or fractured medium, allowing an in-depth analysis of potential reaction mechanisms. We further simplify the analysis by focusing on dissolution and diffusion, highlighting the impacts that result from these two fundamental phenomena. Although we allow kinetically controlled precipitation of cement and aggregate phases, we do not address the precipitation of ASR gel directly: a rigorous treatment of ASR-gel precipitation would require better thermodynamic data on solubility of ASR gels, additional assumptions on processes (such as water evaporation), and a comprehensive treatment of silica polymerization in the fluid. Nevertheless, in the discussion, we explore potential precipitation pathways of ASR using surrogates that simulate a range of ASR gel compositions: magadiite $[\text{Na}_2\text{Si}_7\text{O}_3(\text{OH})\cdot 3\text{H}_2\text{O}]$, okenite $[\text{CaSi}_2\text{O}_5\cdot 2\text{H}_2\text{O}]$, and silica gel. (Okenite has been observed as a crystallization product from some ASR gels [13].) As detailed in Section 4.1, magadiite and okenite were

used as crystalline proxies due to the similarities in composition to low-calcium and high-calcium ASR gels, respectively, and due to the lack of published solubility products for kanemite, which has been argued to be the best crystalline surrogate for low-calcium ASR gel [2]. The use of crystalline proxies was not intended to suggest that ASR gel is crystalline; rather, it allowed the evaluation of saturation state for crystalline phases that are close in composition to ASR gels. In general, non-crystalline phases have a higher solubility than their crystalline compositional equivalents, so magadiite and okenite provide measures for the minimum saturation state that must be achieved for ASR formation. Silica gel precipitation from a sol is discussed as another ASR surrogate, based largely on models presented by Iler [14].

Reactive-transport calculations were used to simulate the dissolution and diffusion phenomena that occur when an aqueous fluid phase interacts with phases in hydrated cement paste and silica-rich phases in the aggregate. Reactive-transport modeling is used extensively in the geochemical community to simulate the interactions of fluids with solids (e.g., see reviews by [8, 9]). It combines equilibria among the aqueous species with dissolution and precipitation reactions that depend on the solution chemistry relative to the solubilities of the solid phases. In this effort, the calculations included the effect of diffusion of aqueous species in the fluid phase as well as kinetically controlled mineral dissolution and precipitation.

The continuum-scale conceptual model consisted of a one-dimensional grid of 500 nodes, each coinciding with the center of a representative elementary volume (REV). The first half of the REVs represented cement paste, and the second half of the REVs represented aggregate. The overall linear dimension of the simulation was 1 cm, so each

REV corresponded to a linear dimension of 20 μm . Table 1 details model conditions, and Table 2 gives the initial properties assigned to the two types of REV.

The simulation code PFLOTRAN was used to perform all calculations [15, 16]. PFLOTRAN is an open source, state-of-the-art massively parallel subsurface flow and reactive transport code that solves partial differential equations describing multiphase, multicomponent and multiscale reactive flow and transport in porous materials. Our simulations focused only on diffusion and reaction (i.e., we did not include advection). The code was run in isothermal mode at 25°C with boundary conditions given in Table 2. Initial compositions for each fluid species were defined by setting them to a small non-zero value, allowing them to evolve in response to kinetically controlled dissolution of the phases. In other words, the simulations essentially probed a scenario where the cement and aggregate system reacted with pure water.

Simulations considered three processes: equilibrium aqueous speciation, diffusion in the aqueous phase, and kinetically controlled mineral dissolution–precipitation. Aqueous phases were allowed to reach equilibrium at each time step according to the speciation reactions given in Table 3. For silica, only monomeric species were included in the calculations; thus, we did not account for the formation of larger polymeric silica phases nor for the formation of sols, due to lack of appropriate thermodynamic data. Their inclusion would have raised the value of silica concentration in the fluid (particularly at higher pH). The saturation state was determined at each time step using activity coefficients calculated from an extended Debye-Hückel formulation and the solubility product constants (K_{sp}) for solid phases as given in Table 4. Ionic strengths of solutions in the paste regions exceeded the limits of applicability for an extended Debye-Hückel

formulation (approaching values of 0.5), which may limit the accuracy of values calculated in the simulations. However, our purpose was not to provide a detailed quantitative analysis of the chemistry but instead to focus on geochemical trends that illustrate reaction pathways. Finally, diffusion was modeled according to Fick's law, assuming a species-independent specific diffusion coefficient of $10^{-5} \text{ cm}^2\text{s}^{-1}$.

Simulations were run with a single continuum. In other words the results could apply to processes along a fracture or within a porous medium, but we did not attempt to differentiate phenomena that occur when both operate simultaneously. Simulated time for most cases was 0.5 days (10^6 time steps); this could correspond to, for example, a period of wetting (e.g., after a rain). Tortuosity was chosen to allow diffusion and reaction fronts to establish over a length of several millimeters on either side of the paste-aggregate interface, and the simulated length was chosen to ensure that unaffected paste and aggregate remained at each end. Non-reactive aqueous species (K^+ , Rb^+ , I^- , and Br^-) were included as tracers for diffusion-only; their concentrations were set to be about 10^{-4} of those for the reacting species to minimize impact on ionic strength. Porosity was set to 10% for both paste and aggregate. Our choice of 10% was somewhat arbitrary; it was not intended to match a specific matrix porosity in cement (which can typically be much higher) or a specific porosity in aggregate (which could be much higher or much lower). The simulations were intended to provide insight into reactions in either the matrix or fractures, so porosity was simply a proxy for fluid-occupied space. A uniform porosity was chosen to remove porosity as a variable in the analysis. In these simulations, porosity's primary impact was on the degree of dissolution that could occur prior to the fluid approaching equilibrium with the dissolving phase; in other words, increasing porosity

would have the affect of allowing more dissolution and at a faster rate in cases close to equilibrium.

2.2 Thermodynamic Data

The solubility product constants for solid phases and aqueous species were taken from the PFLOTRAN database [16], augmented with a several values taken from other sources as noted in Tables 3 and 4 [17-23]. Solubility products for C–S–H were taken from several sources in order to evaluate the impact both of Ca:Si ratio and of uncertainty in the solubility products (as reflected in the various studies) [17, 19-21]. In order to facilitate comparison, solubility products from the various studies were converted to a common basis set (H_4SiO_4 , H^+ , Ca^{2+}) and to a formula unit based on a stoichiometry of one Si (Table 4).

The range in solubility products for C–S–H results in a range of predicted values for key species in the fluid. Figure 1 shows calculated values for silica concentration and pH (two key parameters investigated below) as a function of both Ca:Si in C–S–H, assuming equilibrium with C–S–H and portlandite. As can be seen, the wide range in values had a small impact on calculated values of pH for these conditions (Fig. 1a). However, the calculated values for dissolved silica varied significantly for both Ca:Si and among the various studies (Fig. 1b), with a particularly large range in calculated silica concentrations for Ca:Si ~ 0.7 – 1.2 . Consequently, we investigated the impact of these variations on geochemical conditions in the zone of ASR precipitation. As a reference case, we use C–S–H with Ca:Si of 1.70 and a K_{sp} as reported in Carey and Lichtner’s thermodynamic model of C–S–H [17] (listed as C–S–H (A) in Table 4). We then compare predictions for other values of K_{sp} over the range of Ca:Si.

The calculations only considered monomeric aqueous silica species, omitting both polymeric species and sols due to lack of appropriate thermodynamic data. As noted in Iler [14], monomeric silica can polymerize into oligomers at neutral to basic conditions, owing in part to the higher pK_a for monosilicic acid ($pH=9.9$) relative to the pK_a 's for polysilicic acids (which can approach $pH\sim 6.7$); these oligomers can grow to colloidal size, with the rate of formation increasing in basic conditions. The inclusion of polymeric species in the calculations would primarily have resulted in higher calculated total dissolved silica concentrations in the high pH regions of the paste and in the region around the paste-aggregate boundary. As will be argued below, with respect to impacting saturation state for ASR gel, total dissolved silica is less important than the concentration of the species H_4SiO_4 , which would not be impacted by the exclusion of polymeric silica species in the model once the solution reached equilibrium with the dissolving silica phase. A detailed analysis of precipitation of ASR gel from a sol, however, would require the inclusion of polymeric species.

2.3 Kinetic Data

Mineral dissolution was modeled as a kinetic process using a simple transition-state rate-law formulation:

$$r_i \text{ (mole s}^{-1}\text{)} = A_i \text{ (cm}^2\text{)} \cdot k_i \text{ (mole cm}^{-2} \text{ s}^{-1}\text{)} \cdot \left(1 - \left(\frac{Q}{K_{sp}}\right)_i\right) \quad (1)$$

where r_i is the release rate of components dissolved from mineral i , A_i and k_i are the mineral's surface area and dissolution rate constant (respectively), and $(Q/K_{i, sp})$ describes the saturation state of the fluid with respect to mineral i . In the analysis, we monitor the saturation state by the saturation index ($SI=\log[Q_i/K_{i, sp}]$).

In general, ionic solids (such as portlandite, gypsum, or alkali sulfates) have significantly higher dissolution rates than silicates such that they are not likely to be rate limiting in the system studied. The dissolution rate and surface area for portlandite ($7.2 \times 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}$ and $6 \times 10^3 \text{ cm}^2 \text{ g}^{-1}$, respectively) were based on Bullard et al. [24]. The dissolution rate for gypsum ($1.6 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$) was taken from Palandri and Kharaka [25]; surface area was set to that used for portlandite ($6 \times 10^3 \text{ cm}^2 \text{ g}^{-1}$).

Dissolution of the silica-rich phases (C–S–H, amorphous silica, and quartz) is likely to be rate limiting in the development of ASR, and the dissolution rates for these phases are less well constrained than for ionic solids. Hence, we considered them to be uncertain parameters, probing each over a large but reasonable range to determine how the observed phenomena were impacted.

Dissolution rates for C–S–H were based on rates reported in Palandri and Kharaka [25] for other Ca–Si phases. Based on its somewhat comparable structure and composition, prehnite ($\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$) is the closest C–S–H surrogate in the Palandri and Kharaka database. This was used to define a lower limit for the dissolution rate of C–S–H of $1 \times 10^{-16} \text{ mol-Si cm}^{-2} \text{ s}^{-1}$ (Fig. 2 and Table 5). Two anhydrous Ca–Si phases are also shown for comparison—wollastonite (CaSiO_3) and grossular ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$)—both of which have lower polymerization of Si tetrahedra and, hence, likely higher dissolution rates than C–S–H. Nevertheless, we considered a conservative upper limit for the dissolution rate of C–S–H to be $1 \times 10^{-13} \text{ mol-Si cm}^{-2} \text{ s}^{-1}$ (roughly consistent with wollastonite). As a mid-point value, we selected a rate of $3 \times 10^{-15} \text{ mol-Si cm}^{-2} \text{ s}^{-1}$, which is the average of the log values of high and low.

Dissolution of the silica-rich aggregate was based on the dissolution of amorphous silica. Figure 2 shows a typical dissolution rate for amorphous silica as summarized in Palandri and Kharaka [25], based on studies at near-neutral pH [26]. Although experiments by Icenhower and Dove [26] were at higher T (40–250°C), they reported an Arrhenius relationship for amorphous silica in water based on both their data and data from four other studies [27–30]. This relationship— $\log[k(\text{mol cm}^{-2} \text{s}^{-1})] = -3.17809 - 3892.3/T(\text{K})$ —results in a value for $\log[k_{25^\circ\text{C}}]$ of -16.2 ($6 \times 10^{-17} \text{ mol-Si cm}^{-2} \text{s}^{-1}$). This was taken as a lower limit for the dissolution rate of amorphous silica (Table 5).

In our model, we did not directly incorporate a rate dependence for Na^+ or H^+ into the rate equation. Instead, we chose to capture the impact of these factors by choosing a broad range for dissolution rate in our sensitivity analysis. Although direct incorporation would have provided a more accurate spatial representation of variations in dissolution rate, there is insufficient information for some silica phases (e.g., C–S–H) to justify adding this level of sophistication to the model. Hence, we focused on general trends reflected in the sensitivity analysis.

Icenhower and Dove [26] observed an increase in dissolution rate with alkali (Na^+) concentration with rates beginning to level off at concentrations of ~ 0.05 molal. At these concentrations, they observed a ~ 22 -fold increase in dissolution rate for amorphous silica [their Fig. 5]. This effect has also been reported for Ca^{2+} and other alkali and alkaline-earth ions in the context of quartz dissolution. Thus, the presence of Na^+ , K^+ , and Ca^{2+} in ASR systems would likely increase silica dissolution rates over those found in deionized water by an order of magnitude or more.

Various studies have also shown a pH dependence for quartz dissolution. Specifically, under basic conditions, OH⁻ catalyzes quartz dissolution, causing a significant increase in dissolution rate. Although Palandri and Kharaka [25] do not provide a dissolution model for amorphous silica in basic solutions, they do provide a relationship for quartz, which can be used to provide general insight into the likely pH effects for amorphous silica (Fig. 2). At pH's of 10 and 12, the dissolution rate for silica increases by ~10-fold and ~100-fold, respectively, over rates observed at neutral pH. As will be shown in the simulations, most of the aggregate dissolution occurs in pH conditions near neutral pH, but close to the boundary with hydrated paste the pH approaches 12. Based on all of these observations, we considered a conservative upper limit for the dissolution rate of amorphous silica to be 1×10^{-13} mol-Si cm⁻² s⁻¹. As a mid-point value, we considered a rate of 2×10^{-15} mol-Si cm⁻² s⁻¹, which is the average of the log values of high and low. However, we opted to use the same mid-point value used for C-S-H (3×10^{-15} mol-Si cm⁻² s⁻¹) such that the reference case would use equivalent dissolution rates for the two rate-limiting phases.

Surface area was also considered to be an uncertain parameter due both to potential variability in samples and to uncertainties in defining reactive surface area (e.g., BET areas vs. geometric surface areas). For C-S-H, the upper value for surface area— 2×10^6 cm² g⁻¹—was based on N₂ BET values for a cement with a water:cement ratio of 0.35 as reported by Thomas et al. [31], and the lower value was based on converting BET value to an equivalent geometric surface area assuming a roughness factor of ~200. The mid-point value was set to 1×10^5 cm² g⁻¹, which is the average of the log values of the high and low. For amorphous silica, the lower value for surface area—300 cm² g⁻¹—was based on the geometric surface

305 areas for silica glass as reported by Wolff-Boenisch et al. [32, 33]. The upper value for
306 surface area— $2 \times 10^6 \text{ cm}^2 \text{ g}^{-1}$ —was based on $\sim 100 \text{ \AA}$ effective diameter reported for opal
307 spheres by Jones and Segnit [34]. The mid-point value was set to the value used for C-S-H
308 in order to result in equivalent values for $k \cdot A$ in the reference case.

3. Observations

3.1 Dissolution and Diffusion for Reference Case

The reference case scenario examined the evolution of the system when the rates of moles released for each phase ($k \cdot A$) are equivalent for the two rate-limiting phases (C–S–H and amorphous silica) and for the case of Ca:Si=1.70 for C–S–H. The stoichiometry for these phases was set such that both had one mole of silica per mole of mineral (i.e., the silica release rates are equivalent); however, the molar volumes for the two phases differ significantly ($124.1 \text{ cm}^3\text{mol}^{-1}$ for C–S–H (A); $29 \text{ cm}^3\text{mol}^{-1}$ for amorphous silica), resulting in differing rates of volume change for the two phases. Kinetic parameters for the reference case coincided with the mid-point values reported in Table 5. The time point shown in the figures was 0.5 days; saturation for the C–S–H and portlandite was reached in the paste by ~15 minutes, whereas saturation for amorphous silica in the aggregate region away from the interface was reached in ~6 hours.

Figure 3 shows the profiles for the aqueous species moving from the paste (left) to the aggregate (right). Over the course of 0.5 days, diffusion caused non-reactive tracers to penetrate ~4 millimeters symmetrically on either side of the boundary (Fig. 3a). In contrast, the pH gradient was asymmetric, remaining constant throughout the paste and decreasing smoothly within the aggregate, reflecting the presence of portlandite and C–S–H in the paste (Fig. 3b). The profile of the pH front was much steeper than the diffusion front for the tracers, dropping to the equilibrium pH of the aggregate interiors in less than 2 millimeters from the boundary. The profile for Ca^{2+} was intermediate between the pH and tracer profiles (Fig. 3b).

The profiles for dissolved silica (Fig. 3c) were also asymmetric. Within the paste region, the primary silica species was H_3SiO_4^- , with a total dissolved silica content of $\sim 10^{-5}$ molal. Within the equilibrium regions of the aggregate (e.g., greater than $\sim 2\text{--}5$ mm from the boundary), the primary silica species was H_4SiO_4 , with a total dissolved silica content of $\sim 10^{-2.7}$. A significant variation in speciation occurred in the aggregate region close to the boundary with the paste (i.e., within ~ 2 mm); in this region, pH was sufficiently high to increase the stability of H_3SiO_4^- , causing a slight increase in the total dissolved silica.

Figure 4 shows the mineral dissolution and precipitation that resulted from acid–base reactions at the boundary of paste and aggregate. Amorphous silica dissolution occurred near the boundary (Fig 4a), causing a significant release of silica (Fig. 4b). Although one might expect this to cause an increase in dissolved silica in the paste due to diffusion, the calculations predicted a precipitation of C–S–H in the paste- and aggregate- regions near the boundary (Fig. 4), maintaining a buffer for dissolved silica in the paste.

The general trends of the acid-base driven reactions at the boundary are:

- (1) Buffering of pH within the paste followed by a steep pH decline in the aggregate, dropping to $\sim \text{pH}=10$ within about 0.25 mm and to the equilibrium pH of the aggregate within about 1.25 mm (Fig. 3b);
- (2) Shifting silica speciation moving from the boundary into the aggregate interior, with H_4SiO_4 becoming the dominant species at greater than ~ 0.25 mm, when pH has dropped below ~ 10 (Fig. 3c);
- (3) Dissolution of amorphous silica within ~ 0.5 mm from the boundary (Fig. 4a);
- (4) Precipitation of C–S–H near the boundary (both in the paste and in the aggregate within ~ 0.25 mm of the boundary) (Fig. 4a).

3.2 Effect of Dissolution Rates and Surface Areas for C-S-H and Amorphous Silica

Sensitivity analysis showed that the general trends observed for the reference case apply over a wide range in dissolution rate (k) and surface area (A) for C-S-H and amorphous silica, except at very low dissolution rates for amorphous silica (Figs. 5 and 6).

In the case of low dissolution rates ($k \cdot A$) for amorphous silica (2×10^{-14} mol-Si/g/s), acid-base driven reactions were too slow to develop any changes in 0.5 days, whereas reactions could be observed at rates of 3×10^{-10} mol-Si/g/s and greater (Fig. 5). These observations illustrate the effect of kinetics in the development of ASR.

In the case of low dissolution rates ($k \cdot A$) for C-S-H (1×10^{-12} mol-Si/g/s), acid-base driven reactions resulted from sufficiently high rates for amorphous silica (Fig. 5). In comparing this effect with the behavior of amorphous silica, recall that the low rate for C-S-H was about 200x faster than the low rate for amorphous silica.

For all cases where reactions occurred, the higher the dissolution rate for the phase, the closer dissolution occurred to the boundary. In other words, for high rates, dissolution was concentrated near the boundary, whereas dissolution was less intense but spread over a larger area for lower rates.

The pH gradient always occurred primarily within the aggregate, even for low dissolution rates for amorphous silica. In the case of high rates for amorphous silica but low rates for C-S-H, the pH buffering capacity of the paste was not sufficiently fast to maintain a constant pH within the paste right up to the boundary (Fig. 6), but the pH gradient remained dominantly within the aggregate.

When the dissolution rate for amorphous silica was high, the pH gradient at the boundary was particularly steep, dropping to ~ 10 right at the boundary for the highest

rates. The concentration of H_4SiO_4 also followed this pattern due to its coupling with pH. For the lowest dissolution rates for amorphous silica, H_4SiO_4 concentration remained low; in fact, for these rates, amorphous silica remained under-saturated even at 10 days. In the longer time-points, pH was eventually lowered by silica dissolution, allowing H_4SiO_4 concentration to increase (approaching equilibrium); however, the pH gradient was very shallow, shifting the increase in H_4SiO_4 to ~ 4 mm from the boundary.

3.3 Effect of Solubility Product and Ca:Si for C–S–H

The solubility product used for C–S–H affected the details of dissolution and precipitation at the paste–aggregate boundary (Fig. 7), but the general trend remained constant across the entire range of Ca:Si investigated and among the various published studies of C–S–H thermodynamics. Specifically, acid-base interactions caused dissolution of amorphous silica in a zone close to the boundary and an accompanying precipitation of C–S–H. Although the simulations used the same kinetic descriptions for C–S–H, the differences in solubility product resulted in variation in distribution of precipitated material, with some values producing a sharper precipitation front—e.g., C–S–H (B) and C–S–H (H)—and others producing a broader front—e.g., C–S–H (L) and C–S–H (M). The dissolution of amorphous silica responded accordingly. The pH gradient (not shown) also responded to this difference in C–S–H precipitation, although the impact was slight.

3.4 Effect of No Portlandite in Paste

The presence of portlandite has been assumed in the Powers and Steinour model as the primary buffer for elevated pH in the paste. Indeed, simulations with no portlandite in the paste did show a slight lowering of the pH (Fig. 8), but, assuming mid-point dissolution rates, C–S–H was found to provide sufficient buffering capacity to maintain elevated pH

even in the absence of portlandite as might occur, for example, in a mix with sufficient pozzolanic material. Thus, a pH gradient from paste into aggregate was maintained, with only a slight extension of the gradient from the boundary into the paste. Importantly, the pH was maintained above ~11 within the paste up to the boundary with the aggregate. Nevertheless, this slight depression in pH within the paste had significant impact on stability of some mineral phases, as will be discussed, for example, in section 4.1.

The root of this buffering capacity lies in the ability of C-S-H to maintain a sufficient equilibrium concentration of Ca^{2+} to maintain a high-alkali condition in paste-fluids. This behavior is consistent with the experimental data of Harris et al. [35] and Chen et al. [36], which show that at high Ca:Si ratios (above ~1.0) C-S-H dissolves incongruently effectively buffering the pH above 12; however, as shown by Baston et al. [37], at lower Ca:Si ratios, pH can be lower, with C-S-H buffering pH~10 at Ca:Si ratios of ~0.2–0.7.

When the dissolution rate of C-S-H was low and the rate for amorphous silica was high, however, the asymmetric pH gradient was not maintained (short-dashed black curve in Fig. 8). Instead, a symmetrical pH gradient developed, with the maximum pH in the paste only reaching ~10.5 at 0.5 days. (C-S-H was not saturated at this point, whereas amorphous silica was.)

These examples illustrate, in general, the origin of an asymmetric pH profile across a paste–aggregate boundary. The buffering capacity of paste from both a thermodynamic and kinetic standpoint (relative to aggregate) maintained a relatively constant pH in the paste, whereas the slower kinetics of silica-mineral dissolution allowed an elevated pH front to propagate into the aggregate.

3.5 Effect of Aggregate Mineralogy

Two scenarios were investigated to assess how different aggregate phases affect the dissolution–diffusion processes: quartz aggregate and calcite aggregate. Both of these aggregate mineralogies impacted the profiles for pH and dissolved silica compared with amorphous silica.

Figure 9a shows the pH profiles for quartz and calcite aggregates relative to the reference case (amorphous silica). Quartz produced a slightly different pH profile from the reference case, with a slightly less steep gradient near the boundary and a slightly higher equilibrium pH in the aggregate. Calcite produced a significantly different pH profile, with a shallower gradient and a much higher equilibrium pH in the aggregate (pH ~10).

Figure 9b shows the corresponding profiles for both total dissolved silica and for H_4SiO_4 . Both minerals produced lower silica concentrations in the boundary region of the aggregate (e.g., 0–1 mm from the boundary with the paste). Likewise, H_4SiO_4 concentration in this boundary region was significantly lower for both aggregates, reaching a maximum of $\sim 10^{-4}$ for quartz and a maximum of $\sim 10^{-7.7}$ for calcite (compared with $\sim 10^{-2.7}$ for the reference case with amorphous silica).

3.6 Effect of Dissolved Sodium on Aqueous Geochemistry

Dissolved sodium impacted the paste-aggregate interactions in at least three ways: adding an additional aqueous silica species ($\text{NaHSiO}_3(aq)$; which elevated the equilibrium total concentration of dissolved silica), altering the amount of dissolution that occurred near the boundary between paste and aggregate, and increasing the pH in the paste.

Figure 10 shows the profiles for total dissolved silica and silica species for the reference case (Ca:Si=1.70) and for a case with a C–S–H having Ca:Si=0.67, each having 0.5

molal Na_2SO_4 added to the paste region. (This scenario is equivalent to having ~ 2.5 weight % thenardite present as a contaminant in cement for a water:cement ratio of 0.35.) This addition resulted in an increase in the equilibrium pH in the paste (to 12.80 from 12.37 in the reference case). This pH increase impacted the total dissolved silica: as can be seen in Figure 10a, the total dissolved silica in the paste increased from $\sim 10^{-5}$ to $\sim 10^{-3.4}$. For a lower Ca:Si cement, the level of total dissolved silica paste was even higher ($\sim 10^{-2.2}$). This latter level resulted in a higher concentration of silica in the paste than in the aggregate, shifting the direction of net diffusion. However, in both cases, the addition of sodium increased the total dissolved silica in the zone immediately adjacent to the boundary (~ 0 – 0.5 mm). These increases were tied to the formation of the aqueous species NaHSiO_3 (aq).

Importantly, however, the presence of sodium did not have a significant impact on the silica speciation in the aggregate region at >0.5 mm from the boundary, where the pH had dropped sufficiently to allow H_4SiO_4 to be the dominant silica species, despite that Na^+ had diffused well into the aggregate at this time point.

When Cl^- was added as a charge-balancing ion (i.e., 1.0 molal NaCl) the equilibrium pH in the paste dropped slightly from the reference case (to 12.25 from 12.37). Despite the lowering of pH, the addition of NaCl increased the total dissolved silica in the paste relative to the reference case (to $\sim 10^{-3.9}$). The pH gradient and the nature of the H_4SiO_4 profile, however, were similar to what was observed for sodium sulfate.

When OH^- was added as the anion (i.e., 1.0 molal NaOH), the profiles of silica speciation and pH were similar to what was observed for sodium sulfate.

4. Discussion

The basic geochemical model presented here entails an acid–base reaction between the aggregate and the paste, resulting in dissolution and precipitation at the boundary between the two regions. In general, the acidic silica phases in the aggregate react with the basic phases in the paste (C–S–H and portlandite) through diffusion in the fluid within fractures and/or pores.

The two regions have equilibrium pH's that are distinct: fluids in equilibrium with the paste have pH >12, whereas fluids in equilibrium with the aggregate have a pH~6–6.5. This disequilibrium in the fluids drives diffusion from paste into the aggregate and aggregate into the paste, resulting in dissolution–precipitation reactions in both the paste and aggregate. In the paste, pH is buffered by rapid dissolution of portlandite and, to a lesser but significant extent, by dissolution of C–S–H. In the aggregate, dissolution of silica minerals also occurs, but the rate (relative to diffusion) is insufficient to buffer the pH in the region close to the boundary. The net result is a pH gradient along the margins of the aggregate.

The acid–base reactions and the resulting pH gradient are robust over a range in uncertain and variable parameters in the system. Provided the dissolution rate of the silica minerals is sufficiently high (e.g., likely greater than $\sim 10^{-11}$ or 10^{-12} moles Si per gram per second), the reactions proceed and the gradient forms. Similarly, the reactions proceed and the gradient forms over a the large range in solubility for C–S–H (encompassing both variation in Ca:Si and uncertainty reflected in the range of values reported in the literature). The reactions and gradient occur whether portlandite is present in the paste or not. Finally, the reactions and gradient occur when Na^+ is present regardless of whether

the compensating anion is SO_4^{2-} , Cl^- , or OH^- . (Although not shown, simulations of Na^+ originating in the aggregate region similarly produced the acid–base reactions and the pH gradient.)

In addition to forming a pH gradient, the acid–base reactions form a gradient in silica concentration. The nature of this gradient depends on both the type of silica mineral in the aggregate and the characteristics of C–S–H in the paste. Amorphous silica in the aggregate results in a higher total silica concentration than quartz. In some cases (low Ca:Si), C–S–H may result in a higher dissolved silica concentration than in the aggregate regions, but in most cases the concentration is lower.

Variation in silica speciation due to the pH gradient is an important characteristic of the boundary region. In particular, the concentration of H_4SiO_4 varies significantly, becoming the dominant species once pH drops below ~ 10 . The concentration of H_4SiO_4 when it is the dominant species is determined by the solubility of the silica mineral, with amorphous silica producing a concentration about 20x greater than quartz.

4.1 Precipitation of ASR Gel

In the absence of nucleation barriers, precipitation of a phase reflects solution concentrations at or above saturation for that phase (i.e., at values above the solubility product constant, K_{sp}). Several processes can cause this to occur, including mixing of fluids (by diffusion or advection), dissolution of another phase that causes solution concentrations to raise sufficiently high, changes in temperature, and de-watering of the solution (e.g., by evaporation or freezing).

We explored the possible mechanism of ASR-gel formation by considering both precipitation and gelation of a sol in the context of the first two of these processes (i.e.,

diffusion and dissolution). Unfortunately, no specific values are available for the solubility products of ASR gels, limiting a rigorous evaluation of precipitation. So, instead, magadiite was chosen as a crystalline surrogate for ASR gel. As reviewed by Broekmans [2], low-calcium ASR gel shares compositional and structural similarities with a family of alkali-silicate hydrates that includes kanemite, makatite, magadiite, and kenyaite (representing an increasing degree of silica polymerization and a decreasing ratio of Na:Si). We chose magadiite as a surrogate for low-calcium ASR gel based on availability of solubility data [18], recognizing that kanemite has been argued as the best ASR surrogate [2, 38]. Nevertheless, magadiite is a good indicator of the solubility behavior of an alkali-silicate hydrate with a low Na:Si ratio; compositionally, the Na:Si ratios for kanemite and magadiite are both consistent with the range of compositions reported for low calcium ASR gels (e.g., see [2]). For a high-calcium ASR gel surrogate, we used okenite, which has been reported as a crystallization product in aged ASR gel [13]. We recognize that this is not a rigorously accurate surrogate for high-calcium ASR gel because it contains no alkalis; however, okenite is an indicator of the solubility behavior for a hypothetical high-calcium end-member of the compositional spectrum for ASR gel. Finally, with respect to gelation, we relied heavily on the conceptual models developed by Iler [14].

The solubility product of magadiite [18] and okenite [19] were used to map the saturation state as a fluid containing a dissolved sodium phase (1 molal Na⁺) reacted with the paste and aggregate (Figs. 11 and 12). Three types of sodium sources were explored: Na₂SO₄ represented sodium introduced as a cement phase [39]; NaOH represented sodium introduced as part of an accelerated ASR test [40]; and NaCl represented sodium introduced, for example, by deicing salt or saline water. Two types of sodium sources were

explored: 0.5 molal Na_2SO_4 and 1.0 molal NaCl . Three types of aggregate were explored with mid-point values of dissolution rates for silica minerals: amorphous silica (AS), quartz (Qtz), and 89.1 volume % calcite plus 0.1 volume % amorphous silica (Cal+AS). Four solubility models for C-S-H were explored: C-S-H(A) with $\text{Ca:Si}=1.70$, C-S-H(B) with $\text{Ca:Si}=1.67$, C-S-H(O) with $\text{Ca:Si}=0.67$, C-S-H(P) with $\text{Ca:Si}=0.67$.

Figure 11 shows the profiles for saturation index and solution chemistry for the reference case of C-S-H(A) in the paste and amorphous silica in the aggregate and assuming sodium sulfate as the source of sodium. As shown in Fig. 11a, the reaction of a fluid containing Na_2SO_4 with paste and amorphous silica aggregate, coupled with diffusion, resulted in the super-saturation of magadiite (i.e., $\text{SI}>0$) in a zone within the aggregate region close to the boundary with the paste. Okenite was also super-saturated within the aggregate, but its stability field was closer to the boundary with the paste than that for magadiite. Super-saturation for magadiite occurred at least as early as 1 hour assuming the reference-case values for dissolution of C-S-H and amorphous silica ($k\cdot A$). As can be seen in Figure 11b, the super-saturation for these phases coincided with either total dissolved silica concentration (okenite) or concentration of H_4SiO_4 (magadiite). Although both require sufficient concentrations of Na^+ (magadiite) and Ca^{2+} (okenite), their regions of stability did not coincide with increases in these dissolved constituents (Fig. 11c); rather both phases were super-saturated in regions of a declining gradient in the concentrations of these aqueous species. The pH profile also exhibited a gradient in this region (Fig. 11c); this gradient was critical in determining the speciation of aqueous silica—i.e., as pH dropped below ~ 11 , H_4SiO_4 became the dominant species and magadiite super-saturation occurred.

The profile for magadiite super-saturation was distinctly asymmetric, with a sharp onset of super-saturation next to the boundary with the paste. This asymmetry is consistent with the observation of sharp boundaries between alkali-poor and alkali-rich ASR gels in concrete cores (e.g., [41]).

The general attributes described above for magadiite super-saturation also occurred for other sodium sources where amorphous silica was present in the aggregate. Figure 12a shows magadiite super-saturation in zone within the aggregate and near the boundary occurred for sodium chloride (solid grey curve), albeit the curve was shifted slightly toward the boundary. (The curve for sodium hydroxide overlay the one shown for sodium sulfate.) This shift for sodium chloride primarily reflected the shift in pH (Fig. 13a) and the accompanying shift in stability for H_4SiO_4 (Fig. 13b). Thus, for a 1 molal solution of Na^+ reacting with paste and diffusing into an amorphous silica aggregate, crystalline alkali-silica hydrate became stable in the aggregate region where the pH ranged from ~ 8 – 11 , $[\text{Na}^+]_{\text{total}} > \sim 10^{-3.0}$ molal and $[\text{H}_4\text{SiO}_4] \sim 10^{-3}$ molal.

These general attributes for magadiite super-saturation also occurred for different C–S–H models where amorphous silica was present in the aggregate. Two examples of C–S–H are shown in Figure 12a: $\text{Ca}:\text{Si}=1.7$ and $\text{Ca}:\text{Si}=0.67$. Magadiite remained super-saturated cross the spectrum of $\text{Ca}:\text{Si}$; in fact, the profiles of saturation index for the two cases shown overlaid one another on the figure. This observation was also true for C–S–H models from different studies, across the range of C–S–H (A–P) given in Table 5. This observation can be understood through the aqueous silica profiles shown in Figure 13c: the total dissolved silica and, more importantly, the concentration of H_4SiO_4 were insensitive to the model used to represent C–S–H solubility.

A more dramatic shift in the magadiite and okenite stabilities occurred when the buffering capacity of the paste was lowered. When portlandite was replaced with calcite, the magadiite stability region was more pronounced and shifted toward the boundary with the paste (solid curves Fig. 13b). In addition, the okenite (dashed curves) developed a broad stability region that extended from within the aggregate into the paste. This observation could offer an explanation for transitions in ASR gel distribution and composition that have been reported as ASR evolves over time. Specifically, calcium-rich ASR gels can develop outside of the aggregate as deterioration progresses (e.g., [41]); these gels might reflect a change in paste buffering capacity over time, resulting from, for example, progressive leaching of calcium or carbonation or armoring of C-S-H.

Quartz resulted in a markedly different behavior of magadiite saturation in comparison with amorphous silica. Solutions reacting with quartz aggregate remained highly under-saturated with respect to magadiite at any of the time points investigated (up to 10 days) for all of the 1 molal Na⁺ solutions (e.g., Fig. 12a). This difference in behavior reflects the difference in solubilities for the two silica phases not differences in the kinetics of dissolution: magadiite has a stability field between C-S-H and amorphous silica (Fig. 14a), whereas it has little to no stability in the presence of quartz due to its lower solubility. Sodium clearly plays a role in magadiite (and ASR) stability relative to silica phases: magadiite can precipitate from a fluid in contact with amorphous silica at activities of sodium greater than $\sim 10^{-5}$, but quartz remains stable relative to magadiite under all realistic activities of sodium (Fig. 14b).

The difference in behavior between quartz and amorphous silica can best be understood by comparing the equilibrium concentrations of H₄SiO₄. As shown in Figure

13b, the equilibrium concentration for amorphous silica was $\sim 20\times$ greater than that for quartz, and this coincided with magadiite super-saturation (Fig. 12a). Magadiite became super-saturated in the amorphous silica runs when the saturation of H_4SiO_4 reached $\sim 10^{-3}$ molal. In contrast, in the region within about 0.75 mm of the boundary, total dissolved silica exceeded 10^{-3} molal but magadiite did not precipitate; in fact, the concentration of H_4SiO_4 never exceeded 10^{-4} molal.

Interestingly, simulations for sodium sulfate and an aggregate consisting of 89.9% calcite and 0.1% amorphous silica (representing, for example, an opal-bearing carbonate aggregate) also resulted in magadiite saturation (with a curve overlying those shown for C-S-H (A) in Fig. 12a), despite exhibiting a markedly different pH profile (Fig. 13a).

An alternative pathway for formation of ASR gel is through the precipitation from a sol, which is also consistent with precipitation induced by the pH-gradient within aggregate adjacent to the paste. Iler [14] presents a detailed discussion of gel formation from a sol, noting that gel formation is favored in a few pH conditions with an optimal zone centered around $\sim \text{pH}=6$ (e.g., [14] p. 367), shifting to higher pH in the presence of salts. This optimal pH zone represents a balance between a sufficiently high concentration of OH^- to catalyze gelation yet a sufficiently low negative surface charge on particles to prevent them from repelling. Above $\text{pH}\sim 7$, particles begin to repel one another, stabilizing sols; above $\text{pH}\sim 10.5$, sols dissolve. Hence, conditions for gel formation are optimal around $\text{pH} \sim 6-8$ provided silica concentration is sufficiently high and Na^+ is present. Furthermore, the rates of gel formation are fastest in the same pH region ([14] p. 177), and the rates are enhanced by the presence of sodium or potassium. Interestingly, Li^+ exhibits unique behavior with respect to both sol stabilization and silica dissolution ([14] p. 359); for example, addition of

lithium hydroxide can be used to stabilize sols (and therefore prevent gel precipitation) whereas sodium hydroxide induces coagulation. This unique behavior of lithium with respect to silica sols offers a possible explanation for a role of lithium in ASR treatment or prevention unrelated to any pH effect [42, 43]. Although not directly related to pH and sol precipitation, experiments by Marshall and Warakowski [44] on solubility of silica gels in salt solutions demonstrated that silica solubility decreases significantly in the presence of high salt concentrations, with the effect greater for alkaline earth cations than for alkali cations (i.e., $Mg^{2+}=Ca^{2+}>Li^{+}>Na^{+}>K^{+}$). These experiments suggest that introduction of Ca^{2+} and Na^{+} from the paste to the aggregate could also induce silica precipitation perhaps from a sol.

Changes in temperature and de-watering of the solution are possible additional mechanisms that could shift the geochemical conditions in the concrete system to favor formation of ASR gel. For example, evaporation could serve to increase concentrations of dissolved constituents. Evaporation as a driving mechanism for gel formation is consistent with observations by the authors of gel exudation from cracks in New Mexico sidewalks during the dryout period following afternoon storms.

4.2 Comparison with Model of Powers and Steinour

The Powers and Steinour model focuses on diffusion of alkalis and hydroxyl into a reactive silica aggregate, with the potential of forming ASR governed by the kinetics of dissolution. The alternative model we propose considers diffusion of all species. Unlike Powers and Steinour, our model defines the potential for ASR formation in terms of thermodynamics (solubility) and thus explains the difference in reactivity between quartz

and amorphous silica: (unstrained) quartz is not sufficiently soluble to result in a stability field for alkali-silicate hydrate phases, whereas amorphous silica is.

This alternative model shares some characteristics with the Powers and Steinour model:

- *Diffusion introduces alkalis and OH⁻ from the paste causing their concentrations to rise in the aggregate.* Our assumption is that, in most instances, alkalis are introduced from the paste into the aggregate regions: alkali-sulfates in cements are an important source of alkalis, and introduction of alkalis from external sources (such as deicing salts or saline water) would require alkalis to pass through the cement prior to impacting the aggregate. Thus alkalis, sulfate, and chloride would most likely diffuse from the paste into the aggregate. (In this study, we did not comprehensively consider a source of alkalis from the aggregate itself as might occur, for example, in the case of a rhyolitic aggregate or other aggregates containing alkali-rich minerals.) Similarly, the concentration of OH⁻ in the paste was higher than the aggregate, whereas the concentration of H⁺ was higher in the aggregate; thus, OH⁻ diffused into the aggregate and H⁺ diffused into the paste. However, as shown in Fig. 2, the pH gradient occurred in the aggregate as opposed to symmetrically across the paste–aggregate boundary. This was not an intuitively obvious result, inasmuch as the model had no imposed directionality (i.e., it considered diffusion based purely on concentration gradients). But, the buffering capacity of cement phases (both portlandite and C–S–H) maintained the pH in the paste relatively constant up to the boundary. The net result was a pH gradient within the aggregate.

- *Different silica phases behave differently.* Specifically, fluid in contact with amorphous silica aggregate had lower pH and higher total dissolved silica than fluid in contact with quartz. In the Powers and Steinour model, this phase-specific behavior is ultimately attributed to structural disorder (for example, strained quartz vs. well crystallized quartz), but it is assumed to tie to dissolution rates (which vary depending on structural disorder). In our model, the differences in behavior for amorphous silica and quartz were tied to solubility rather than dissolution rate. Although we recognize that rates for quartz and amorphous silica may differ by an order of magnitude (or more), our simulations assumed equal rates so that we could assess any differences due only to solubility (which also ties to structural state of the material). In this case, we found distinct behavior for amorphous silica and quartz tied only to solubility: H_4SiO_4 concentrations were higher for amorphous silica than for quartz.

This alternative model has several important characteristics that are distinct from the Powers and Steinour model:

- *The development of a geochemical gradient within the boundary of the aggregate is critical in the development of ASR stability.* Although a geochemical gradient is implied in the Powers and Steinour model (arising from the diffusion of alkalis and hydroxide), our model differs in the nature of the gradients: the gradients are more complex chemically, involving aqueous silica; the gradients develop from both diffusion and dissolution (e.g., buffering). Most importantly, in this model, a geochemical gradient is a necessary condition to establish microenvironments necessary for ASR formation.

- *Effectiveness of pozzolans.* The link between a gradient and ASR formation is a likely explanation of the difference in behavior of admixtures relative to their particle size (i.e., pozzolanic vs. deleterious impacts) (e.g., [45]). In other words, a particle must be sufficiently large before a geochemical gradient can be maintained and, hence, ASR gel can develop. Thus our model helps explain why pozzolans do not produce ASR gel.
- *Reactivity of aggregate is based on thermodynamic solubilities.* In principle, the Powers and Steinour model would allow a quartz-bearing aggregate with high surface area to be equally as reactive as an amorphous silica-bearing aggregate with low surface area (e.g., consider a fine-grained, porous sandstone with a great deal of accessible mineral surface and a volcanic glass with almost no surface area beyond the fracture face). The model we present identifies reactive materials based on solubility and suggests an alternative test for reactivity based solely on the silica solubility of aggregate under equilibrium conditions.
- *Explicit role of sodium in the formation and mitigation of ASR.* Alkalis are obviously central to ASR, but our reactive transport model shows explicitly how diffusion of sodium is coupled with silica and the stabilization of sodium-bearing siliceous gels at the paste-aggregate interface. The thermodynamic approach provides a mitigation strategy based on finding compositional additives that destabilize ASR or stabilize a non-swelling alternative.
- *Dynamics of ASR formation and migration.* In our model, the presence of gradients is key to the formation of the gel. While the gel forms at the paste-aggregate boundary, its subsequent mobility is only limited by the fractures generated during swelling.

We expect that over time the ASR-generating gradients are reduced by diffusion and equilibration. Thus the model predicts that ASR growth may be episodic as gradients are re-established during drying/wetting, freeze-thaw, or infiltration by fluids. This type of behavior is observed when fresh ASR gel products appear on map-crack patterned concrete following changes in weather and help explains how local environment conditions may exacerbate or mitigate the impacts of ASR.

4.3 Implications of a Geochemical Microenvironment at Paste–Aggregate Boundaries

The development of geochemical gradients—and particularly a pH gradient—at the boundary between paste and aggregate creates unique geochemical microenvironments with significant implications for the evolution of a concrete system.

First, the development of this microenvironment is a critical aspect of determining the stability of solid phases. As shown in Figures 3 & 4, silica solubility and dissolution are both sensitive to the pH gradient. In addition, as shown in Figures 12 & 13, a suitable pH gradient is essential in developing conditions that promote the stability of alkali-silicate hydrate phases, including gels. In other words, the geochemical gradient impacts both dissolution and precipitation, the key processes necessary for gel formation in this model. However, the nature of the gradient differed for quartz and amorphous silica such that the microenvironments established around quartz aggregates did not produce conditions for stability of alkali-silicate hydrate phases, whereas those around amorphous silica did.

A second implication is the development of conditions that may be suitable for microbial activity. Microbially mediated damage of concrete has been recognized for over 65 years [46, 47]. Conventionally, the high pH of paste is assumed to make concrete inhospitable for most microbes without the formation of thick biofilms as occurs, for

example, in bacterially mediated degradation of wastewater sewage pipes (e.g., [48]). However, the gradient-induced microenvironments result in a range of pH that spans conditions that are compatible with various bacteria, raising the possibility that microbes could exploit the pH gradient associated with the paste–aggregate boundary and with ASR gel.

To explore this possibility, we examined numerous samples of ASR-affected concrete along fractured surfaces from cores taken from pavements and bridge decks in New Mexico. These samples were treated with a ninhydrin solution, which stains protein purple. Many of these exhibited ASR gel with purple stained regions (e.g., Fig. 15), corresponding to biofilms that had developed on top of the ASR gel (as verified by subsequent investigation by scanning electron microscopy). (No attempt was made to ascertain whether organic additives to the mix would also stain positive with ninhydrin, although diffuse purple staining was observed in the paste in some samples.) One particularly interesting case is shown in Fig. 15, where two adjacent aggregates exhibited markedly different characteristics. The rhyolitic aggregate exhibited a biofilm, but the quartzite aggregate showed no indication of the formation of a biofilm. The rhyolitic aggregate additionally show precipitation of an acicular calcium aluminosulfate phase on top of the ASR gel. These observations raise two implications. First, biofilm formation required both a favorable pH condition and some other characteristic associated with rhyolite but not quartzite (such as, perhaps, the presence of iron or another trace metal, an Eh gradient, etc.). Second, precipitation of a calcium aluminosulfate phase in association with ASR may be associated with biofilm formation. We introduce these observations here

763 to underscore the complexities and potential implications of basing our ASR model on the
764 formation of geochemical gradients that form the microenvironments necessary for ASR.

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Figure Captions

Figure 1. Predicted values of (a) pH and (b) $[\text{SiO}_2(aq)]_{\text{total}}$ calculated for equilibrium with C-S-H and portlandite using different reported values of K_{sp} for C-S-H.

Figure 2. Plots of the dissolution rates for various minerals as a function of pH. Rates, taken from Palandri and Kharaka [25], are shown with respect to moles of Si released at 25 °C.

Figure 3. Profiles of aqueous species calculated for the reference case (equal dissolution rates for C-S-H and amorphous silica): a) Tracers. b) pH and $[\text{Ca}^{2+}]$. c) Aqueous silica species.

Figure 4. Profiles of changes in silica phases for the reference case (equal dissolution rates for C-S-H and amorphous silica): a) Volume change for C-S-H and amorphous silica. b) Change in moles of silica for solids and fluid.

Figure 5. Profiles for the change in moles of silica in amorphous silica (solid line) and C-S-H (dashed line) for different relative silica release rates for C-S-H and amorphous silica. Reference case is shown in the center (equivalent to Fig. 4a). Silica release rate for C-S-H increases from bottom (1×10^{-12} moles Si g^{-1}) to top (2×10^{-7} moles Si g^{-1}); silica release rate for amorphous silica increases from right to left. Rates correspond to values detailed in Table 5.

Figure 6. Profiles of the pH (solid line) and concentration of H_4SiO_4 (dashed line) for different relative silica release rates for C-S-H and amorphous silica. Reference case is shown in the center (equivalent to pH curve in 3b and H_4SiO_4 curve in 3c). Rates correspond to values detailed in Table 5. Scale for pH goes from 6 to 14; scale for $[\text{H}_4\text{SiO}_4]$ goes from 10^{-6} to 10^0 .

Figure 7. Profiles for the change in moles of silica in amorphous silica (solid line) and C-S-H (dashed line) for different C-S-H models all assuming the mid-point values for dissolution rates of C-S-H and amorphous silica. Reference case is shown in the upper left (equivalent to Fig. 4a). C-S-H models are labeled according to Table 3.

Figure 8. Profiles for the case with no portlandite present in the paste region, showing change in pH across the paste-aggregate interface. Solid black curve shows reference case dissolution kinetics (mid-point values in Table 5); dashed curve shows case for low dissolution rate for C-S-H and high dissolution rate for amorphous silica.

Figure 9. Profiles for the case with quartz and calcite as the aggregate but all other parameters equivalent to the reference case: a) pH. b) Selected aqueous silica species (total dissolved silica and H_4SiO_4). Note: Horizontal scale is expanded relative to Figs. 3, 4, & 8; also, vertical scale for Fig. 9b is expanded to a minimum of -8 in order to show the H_4SiO_4 profile for calcite.

Figure 10. Profiles of aqueous silica species for two cases that each contain 0.5 molal sodium sulfate. a) Amorphous silica reference-case using C-S-H (A). b) Amorphous silica reference-case using C-S-H (O).

Figure 11. Profiles of saturation index, aqueous silica species, pH, $[\text{Na}^+]$ and $[\text{Ca}^{2+}]$ for the reference-case (C-S-H(A) in paste and amorphous silica aggregate) exposed to 0.5 molal Na_2SO_4 . a) Saturation index for magadiite (solid black line) and okenite (dashed grey line). b) Concentration profiles for $\text{SiO}_2(aq)_{\text{total}}$ (solid black line) and H_4SiO_4 (dashed black line). c) Profiles for pH (solid grey line) and concentrations $\text{Na}^+_{\text{total}}$ (short-dashed black line) and $\text{Ca}^{2+}_{\text{total}}$ (long-dashed black line). Note: the x-axis extends ± 2 mm around the boundary.

Figure 12. Profiles of saturation index for various cases illustrating the impact of aggregate type, cement phases, and sodium-source type. Aggregates include amorphous silica (AS), quartz, (Qtz), and 89.9% calcite plus 0.1% amorphous silica (Cal+AS); sodium sources include 0.5 molal Na_2SO_4 and 1.0 molal NaCl; C–S–H models include C–S–H(A) and C–S–H(O). a) Saturation index for magadiite for cases with various aggregates, C–S–H models, and sodium sources. b) Saturation index for magadiite (solid curves) and okenite (dashed curves) with portlandite present (grey) or absent (black) in the paste; all other conditions similar: C–S–H(A), amorphous silica, and sodium sulfate .

Figure 13. Profiles of pH and aqueous silica species for various cases illustrating the impact of aggregate type, C–S–H type, and sodium-source type. Aggregates include amorphous silica (AS), quartz, (Qtz), and 89.9% calcite plus 0.1% amorphous silica (Cal+AS); sodium sources include 0.5 molal Na_2SO_4 and 1.0 molal NaCl; C–S–H models include C–S–H(A) and C–S–H(O). a) Profiles of pH for various cases. b) Profiles of aqueous silica for various aggregates and various sodium sources. c) Profiles of aqueous silica for various C–S–H models.

Figure 14. Activity diagrams illustrating stability relationships between silica phases, magadiite, and C–S–H. a) Plot of activity of aqueous silica (H_4SiO_4) vs. pH, showing stability for C–S–H, magadiite, and amorphous silica (solid lines), with a dashed line indicating stability for quartz. (Calculated for $a_{\text{Ca}^{2+}} = a_{\text{Na}^+} = 10^{-3}$.) b) Plot of activity of aqueous silica vs. activity of Na^+ , showing stabilities for amorphous silica (solid line), quartz (short dash), and magadiite (long dash). (Calculated for pH = 11.)

Figure 15. Photo of fracture surface in a concrete sample from a highway pavement in New Mexico showing ASR gel both before and after ninhydrin treatment. (A dilute

975 solution of ninhydrin in alcohol was applied to the concrete specimen, which was then
976 heated in an oven at 60°C; under these conditions, ninhydrin reacts with protein to form a
977 purple compound.)

A Thermodynamic and Kinetic Model for Paste-Aggregate Interactions and the Alkali-Silica Reaction
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Tables

Table 1
Simulation Parameters

Cell Size	20 μm
Weighting for Diffusion	Harmonic Average
Activity Coefficients	Extended Debye–Hückel
Temperature Dependence	Isothermal
Porosity	10%
Tortuosity	10 ⁻³
Aqueous Diffusion Coefficient (species independent)	1 × 10 ⁻⁵ (cm ² /s)
Pressure, Temperature	10 ⁵ Pa, 25°C
Time Step	10 ⁻⁶ days (~0.1 s)
Total Simulated Time	10 days (most figures are based on data at 0.5 days)

Table 2

Fluid Chemistry Parameters (at Boundaries and Initial Conditions in Cells)

Parameter	Paste	Aggregate
Ca ²⁺	1×10 ⁻³⁰ molal	1×10 ⁻³⁰ molal
SiO ₂ (<i>aq</i>)	1×10 ⁻³⁰ molal	1×10 ⁻³⁰ molal
H ⁺	Charge balance	Charge balance
SO ₄ ²⁻	not included ^a 1×10 ⁻³⁰ molal ^b 0.5 molal ^c	not included ^a 1×10 ⁻³⁰ molal ^{b, c}
Na ⁺	not included ^a 1.0 molal ^{b, c}	not included ^a 1×10 ⁻³⁰ molal ^{b, c}
Cl ⁻	not included ^a 1×10 ⁻³⁰ molal ^c 1.0 molal ^b	not included ^a 1×10 ⁻³⁰ molal ^{b, c}
HCO ₃ ⁻	not included ^a 1×10 ⁻³⁰ molal ^d	not included ^a 1×10 ⁻³⁰ molal ^d
Rb ⁺ , Br ⁻	1×10 ⁻⁵ molal ^e	1×10 ⁻³⁰ molal ^e
K ⁺ , I ⁻	1×10 ⁻³⁰ molal ^e	1×10 ⁻⁵ molal ^e

^a Reference case and for cases other than those noted.^b Used in the cases with added sodium chloride.^c Used in the cases with added sodium sulfate.^d Used in the cases that included calcite in either the paste or aggregate.^e Used as non-reactive tracers.

Table 3

Speciation Reactions for Secondary Aqueous Species

Reaction	$\log(K_{sp})_{25^\circ\text{C}}$	Molecular Weight (g/mole)	Reference
$\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}$	13.9951	17.0073	[16] ^a
$\text{CaOH}^+ + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{H}_2\text{O}$	12.78	57.0853	[19]
$\text{H}_2\text{SiO}_4^{2-} + 2\text{H}^+ \rightarrow \text{H}_4\text{SiO}_4 + 2\text{H}_2\text{O}$	23.14	94.099	[19, 22]
$\text{H}_3\text{SiO}_4^- + \text{H}^+ \rightarrow \text{H}_4\text{SiO}_4$	9.84	95.1068	[19, 23]
$\text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{SO}_4^{2-} + 2\text{H}^+$	1.0209	98.0795	[16] ^a
$\text{HSO}_4^- \rightarrow \text{SO}_4^{2-} + \text{H}^+$	-1.9791	97.0715	[16] ^a
$\text{CaSO}_4(\text{aq}) \rightarrow \text{Ca}^{2+} + \text{SO}_4^{2-}$	-2.1111	136.1416	[16] ^a
$\text{CaH}_3\text{SiO}_4^+ + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{H}_4\text{SiO}_4$	8.83	135.15	[19, 23]
$\text{NaHSiO}_3(\text{aq}) + \text{H}^+ \rightarrow \text{Na}^+ + \text{H}_4\text{SiO}_4 + \text{H}_2\text{O}$	8.3040	100.0814	[16] ^a
$\text{NaOH}(\text{aq}) + \text{H}^+ \rightarrow \text{Na}^+ + \text{H}_2\text{O}$	14.7948	39.9971	[16] ^a
$\text{NaSO}_4^- \rightarrow \text{Na}^+ + \text{SO}_4^{2-}$	-0.8200	119.0534	[16] ^a
$\text{HCl}(\text{aq}) \rightarrow \text{H}^+ + \text{Cl}^-$	-0.6700	36.4606	[16] ^a
$\text{CaCl}_2(\text{aq}) \rightarrow \text{Ca}^{2+} + 2\text{Cl}^-$	0.6436	110.9834	[16] ^a
$\text{CaCl}^+ \rightarrow \text{Ca}^{2+} + \text{Cl}^-$	0.6956	75.5307	[16] ^a
$\text{NaCl}(\text{aq}) \rightarrow \text{Na}^+ + \text{Cl}^-$	0.7770	58.4425	[16] ^a
$\text{CaCO}_3(\text{aq}) + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^-$	7.0017	100.0872	[16] ^a
$\text{CaHCO}_3^+(\text{aq}) \rightarrow \text{Ca}^{2+} + \text{HCO}_3^-$	-1.0467	101.0951	[16] ^a
$\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HCO}_3^-$	-6.3447	44.0098	[16] ^a
$\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-$	10.3288	60.0092	[16] ^a
$\text{NaCO}_3^- + \text{H}^+ \rightarrow \text{Na}^+ + \text{HCO}_3^-$	9.8144	82.9990	[16] ^a
$\text{NaHCO}_3(\text{aq}) + \text{H}^+ \rightarrow \text{Na}^+ + \text{HCO}_3^-$	-0.1541	84.0069	[16] ^a

^a Thermodynamic data from the PFLOTRAN database [16] are available at <http://www.pflotran.org/>.

Table 4. Dissolution Reactions[§]

Reaction	$\log(K_{sp})_{25^\circ\text{C}}$	Molecular Weight (g/mole)	Molar Volume (cm ³ /mole)	Reference
$\text{Ca(OH)}_2 \text{ (portlandite)} \rightarrow \text{Ca}^{2+} + 2\text{OH}^-$	22.5552	74.0927	33.0560	[16] ^a
$\text{SiO}_2 \text{ (am)} + 2\text{H}_2\text{O} \rightarrow \text{H}_4\text{SiO}_4$	-2.7136	60.0843	29.0000	[16] ^a
$\text{SiO}_2 \text{ (quartz)} + 2\text{H}_2\text{O} \rightarrow \text{H}_4\text{SiO}_4$	-3.9993	60.0843	22.6800	[16] ^a
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \text{ (gypsum)} \rightarrow \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	-4.4823	172.1722	74.6900	[16] ^a
$\text{CaCO}_3 \text{ (calcite)} + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^-$	1.8487	100.0872	36.9340	[16] ^a
$\text{NaSi}_7\text{O}_{13}(\text{OH})_3 \cdot 3\text{H}_2\text{O} \text{ (magadiite)} + \text{H}^+ + 9\text{H}_2\text{O} \rightarrow \text{Na}^+ + 7\text{H}_4\text{SiO}_4$	-14.3	532.55	234.603	[18]
$\text{CaSi}_2\text{O}_5 \cdot 2\text{H}_2\text{O} \text{ (okenite)} + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{H}_4\text{SiO}_4$	9.18	194.24	94.77	[19]
$\text{Ca}_{1.70}\text{SiO}_{3.70} \cdot 1.70\text{H}_2\text{O}_{\text{C-S-H (A)}} + 3.40\text{H}^+ \rightarrow 1.70\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + 1.40\text{H}_2\text{O}$	30.63	186.246	94.397	[17]
$\text{Ca}_{1.67}\text{SiO}_{3.67} \cdot 2.10\text{H}_2\text{O}_{\text{C-S-H (B)}} + 3.34\text{H}^+ \rightarrow 1.67\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + 1.77\text{H}_2\text{O}$	29.42	191.534	78.	[20]
$\text{Ca}_{1.60}\text{SiO}_{3.60} \cdot 2.58\text{H}_2\text{O}_{\text{C-S-H (C)}} + 3.20\text{H}^+ \rightarrow 1.60\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + 2.18\text{H}_2\text{O}$	28.00	196.248	84.68	[19] ^b
$\text{Ca}_{1.50}\text{SiO}_{3.50} \cdot 1.50\text{H}_2\text{O}_{\text{C-S-H (D)}} + 3.00\text{H}^+ \rightarrow 1.50\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + 1.00\text{H}_2\text{O}$	26.10	171.225	89.230	[17]
$\text{Ca}_{1.50}\text{SiO}_{3.50} \cdot 2.50\text{H}_2\text{O}_{\text{C-S-H (E)}} + 3.00\text{H}^+ \rightarrow 1.50\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + 2.00\text{H}_2\text{O}$	24.899	189.200	80.56	[21]
$\text{Ca}_{1.33}\text{SiO}_{3.33} \cdot 2.17\text{H}_2\text{O}_{\text{C-S-H (F)}} + 2.66\text{H}^+ \rightarrow 1.33\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + 1.50\text{H}_2\text{O}$	21.850	173.853	75.630	[21]
$\text{Ca}_{1.25}\text{SiO}_{3.25} \cdot 2.75\text{H}_2\text{O}_{\text{C-S-H (G)}} + 2.50\text{H}^+ \rightarrow 0.67\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + 2.00\text{H}_2\text{O}$	20.155	179.680	71.925	[21]
$\text{Ca}_{1.22}\text{SiO}_{3.22} \cdot 1.22\text{H}_2\text{O}_{\text{C-S-H (H)}} + 2.44\text{H}^+ \rightarrow 1.22\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + 0.44\text{H}_2\text{O}$	20.01	150.644	82.149	[17]
$\text{Ca}_{1.20}\text{SiO}_{3.20} \cdot 2.06\text{H}_2\text{O}_{\text{C-S-H (I)}} + 2.40\text{H}^+ \rightarrow 1.20\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + 1.26\text{H}_2\text{O}$	19.30	164.456	71.95	[19] ^b
$\text{Ca}_{1.00}\text{SiO}_{3.00} \cdot 1.00\text{H}_2\text{O}_{\text{C-S-H (J)}} + 2.00\text{H}^+ \rightarrow 1.00\text{Ca}^{2+} + \text{H}_4\text{SiO}_4$	15.28	134.178	76.482	[17]
$\text{Ca}_{1.00}\text{SiO}_{3.00} \cdot 2.00\text{H}_2\text{O}_{\text{C-S-H (K)}} + 2.00\text{H}^+ \rightarrow 1.00\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + 1.00\text{H}_2\text{O}$	14.266	152.160	63.416	[21]
$\text{Ca}_{0.83}\text{SiO}_{2.83} \cdot 1.30\text{H}_2\text{O}_{\text{C-S-H (L)}} + 1.66\text{H}^+ \rightarrow 0.83\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + 0.13\text{H}_2\text{O}$	11.08	130.026	59.	[20]
$\text{Ca}_{0.80}\text{SiO}_{2.80} \cdot 1.54\text{H}_2\text{O}_{\text{C-S-H (M)}} + 1.60\text{H}^+ \rightarrow 0.80\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + 0.34\text{H}_2\text{O}$	11.05	132.664	59.29	[19] ^b
$\text{Ca}_{0.79}\text{SiO}_{2.79} \cdot 0.78\text{H}_2\text{O}_{\text{C-S-H (N)}} + 1.58\text{H}^+ + 0.43\text{H}_2\text{O} \rightarrow 0.79\text{Ca}^{2+} + \text{H}_4\text{SiO}_4$	10.87	118.302	66.249	[17]
$\text{Ca}_{0.67}\text{SiO}_{2.67} \cdot 0.67\text{H}_2\text{O}_{\text{C-S-H (O)}} + 1.34\text{H}^+ + 0.66\text{H}_2\text{O} \rightarrow 0.67\text{Ca}^{2+} + \text{H}_4\text{SiO}_4$	8.52	109.48	67.985	[17]
$\text{Ca}_{0.67}\text{SiO}_{2.67} \cdot 1.50\text{H}_2\text{O}_{\text{C-S-H (P)}} + 1.34\text{H}^+ \rightarrow 0.67\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + 0.17\text{H}_2\text{O}$	8.123	124.467	55.420	[21]

^a Thermodynamic data from the PFLOTRAN database [16] are available at <http://www.pflotran.org/>.

^b Stoichiometry for C-S-H as given in [19] was not charge balanced; formula presented here were derived from oxide data provided in [19].

Table 5

Range of Dissolution Rates and Surface Areas

Phase		Dissolution Rate, k (moles-Si cm ⁻² s ⁻¹)	Surface Area, A (cm ² g ⁻¹)	$k \cdot A$ (moles-Si g ⁻¹ s ⁻¹)
Amorphous Silica	High Value	1×10^{-13}	2×10^6	2×10^{-7}
	Mid Value	3×10^{-15}	1×10^5	3×10^{-10}
	Low Value	6×10^{-17}	3×10^2	2×10^{-14}
C-S-H	High Value	1×10^{-13}	2×10^6	2×10^{-7}
	Mid Value	3×10^{-15}	1×10^5	3×10^{-10}
	Low Value	1×10^{-16}	1×10^4	1×10^{-12}

Figure02

Figure03

Figure04

Figure05

Figure06

Figure08

Figure09

Figure10

Figure11

Figure12

Figure13

Figure 14

Figure15

quartzite aggregate

rhyolite aggregate

ASR gel with ninhydrin stain
(purplish hue)