Effects of decalcification on the microstructure and surface area of cement and tricalcium silicate pastes

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Abstract

Thin coupons of white portland cement (WPC) and tricalcium silicate paste were decalcified by leaching in concentrated ammonium nitrate solutions, resulting in calcium-to-silicon molar ratios (C/S) ranging from 3.0 (control) down to 0.3. The microstructure and surface area were measured using both small-angle neutron scattering (SANS) and nitrogen gas sorption. The intensity in the SANS data regime corresponding to the volume fractal C-S-H gel phase increased significantly on leaching, and the total surface area per unit specimen volume measured by SANS doubled on leaching from C/S = 3.0 to near C/S = 1.0. The nitrogen BET surface area of the WPC pastes, expressed in the same units, increased on decalcification as well, although not as sharply. The primary cause of these changes is a transformation of the high-density “inner product” C-S-H gel, which normally has a low specific surface area as measured by SANS and nitrogen gas sorption, into a morphology with a high specific surface area. The volume fractal exponent corresponding to the C-S-H gel phase decreased with decalcification from 2.3 to 2.0, indicating that the equiaxed 5 nm C-S-H globule building blocks that form the volume fractal microstructure of normal, unleached cement paste are transformed by decalcification into sheetlike structures of increasing thickness.

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1. Introduction

Decalcification of cement paste is closely associated with various types of concrete deterioration. Important examples include leaching by exposure to flowing fresh water or weak acids, which removes calcium from the paste altogether, and external sulfate attack, which reorganizes the cement paste in such a way that the calcium in portlandite [Ca(OH)2 = CH1] and in C-S-H gel is transferred to gypsum and ettringite. The addition of mineral admixtures, such as silica fume and blast furnace slag, to cement paste causes a similar reorganization, with a lower Ca form of C-S-H gel forming at the expense of CH and the typical high-Ca form of C-S-H gel. In recent years, the kinetics of calcium leaching [1,2] and the effects of decalcification on the mechanical properties of cement paste [3–6], the solubility of C-S-H phases [7], and the chemical structure of C-S-H [8–10] have been studied and modeled. What is missing at present is a full understanding of the effects of decalcification, or changes in the calcium-to-silicon ratio (C/S), on the morphology and nanometer-level structure of C-S-H. This paper reports results of small-angle neutron scattering (SANS) and nitrogen gas sorption experiments on tricalcium silicate (C3S) and white portland cement (WPC) pastes leached to different C/S.

An experimental difficulty with leaching studies is the very long time required to leach in fresh water. Leaching cement pastes in concentrated solutions of NH4NO3 can reduce leaching times from weeks or months to hours. The increased rate of calcium dissolution in NH4NO3 can be attributed to a significant increase in the equilibrium calcium solubility. For example, Heukamp et al. [5] have estimated that the equilibrium calcium concentration of a solution saturated in CH increases from 0.022 mol/l in...
pure water to approximately 2.9 mol/l in a 6-mol/l solution of NH$_4$NO$_3$. The dissolution of CH in the latter solution follows [5]:

$$\text{Ca(OH)}_2 + 2\text{NH}_4\text{NO}_3 \rightarrow \text{Ca}^{2+} + 2\text{OH}^- + 2\text{H}^+$$

$$+ 2\text{NH}_3 + 2\text{NO}_3^- \rightarrow \text{Ca(NO}_3)_2 + 2\text{NH}_3(\text{g})$$

$$+ 2\text{H}_2\text{O}$$

(1)

The removal of NH$_3$ from the solution as gas bubbles drives the reactions in Eq. (1) to the right, allowing large amounts of calcium to dissolve without approaching equilibrium. Previous work has established that the effects on the microstructure of leaching in NH$_4$NO$_3$ are similar to the effects of leaching in water or weakly acidic solutions [7,12]. The primary difference, other than the kinetics, is that NH$_4$NO$_3$ leaching preferentially removes calcium from the C-S-H even at very low C/S, whereas water leaching removes increasing amounts of silicon as the C/S falls below 1. The preservation of the Si structure allows very low C/S (near 0.1) to be reached while maintaining the integrity of the specimen.

In this study, thin (0.8 mm thick) coupons of paste were leached to various C/S. The use of thin specimens reduced the gradients in C/S across the specimen, and allowed the average C/S to be used to characterize the entire coupon. SANS was used to measure the specific surface area and the microstructure of saturated coupons, and nitrogen gas sorption was used to measure the surface area of dried companion specimens. Changes in the solubility [7] and chemical structure [7,10] as a function of C/S are reported elsewhere. Those results indicate that the leaching process of a cement or C$_3$S paste can be divided into three slightly overlapping regimes: (1) dissolution of CH, (2) removal of Ca–OH groups from the C-S-H gel (C/S = 1.7 to 1.2), and (3) removal of calcium associated with Si–O–Ca bonds in the interlayer spacings of C-S-H at C/S < 1.2. Step 3 is accompanied by a rapid increase in the degree of polymerization of the silicate chains.

2. Application of SANS to cement paste

Small-angle scattering with either neutrons (SANS) or X-rays (SAXS) has been used successfully to characterize the microstructure of cement and C$_3$S pastes [13–17]. In both cases, an intense beam is passed through a thin specimen, and a small component is scattered out of the incident beam direction by interactions with microstructural features within the bulk of the material. The volume of material probed (approximately 25 mm$^3$ in the present study) is large enough to represent a statistical average of the cement paste microstructure where the relevant scale lengths range from 1 nm to 10 μm. Scattering techniques are ideal for characterizing cement paste because specimens can be studied in their natural saturated state, thus avoiding complications associated with drying the C-S-H gel [18]. In addition, small-angle scattering is particularly appropriate for this investigation because it is most effective in probing features in the 1- to 100-nm size range that defines critical aspects of the C-S-H gel structure. In cementitious systems, the scattering is dominated by the interface between the solid C-S-H and the smallest gel pores. However, comparisons of the rate of the SANS surface area development with the rate of heat evolution [16] and with the rate of bound water development [19] show that while SANS and SAXS are sensitive to the open nanoscale gel/pore structure associated with the low-density “outer-product” C-S-H that forms in the water-filled capillary spaces of the paste, they (like nitrogen gas sorption) have little sensitivity to the dense, closed C-S-H structure that forms within the original boundaries of the anhydrous cement particles. A recent model [20] accounts for much of the quantitative data, including surface area values obtained from different techniques, by proposing different structures for high- and low-density C-S-H. Clearly, this distinction is important if the leaching process transforms the high-density morphology of C-S-H into low-density product with a large specific surface area.

Small-angle scattering studies generally report data as a function of the scattering vector, $Q$:

$$Q = \frac{4\pi}{\lambda} \sin \left(\frac{\theta}{2}\right)$$

(2)

where $\theta$ is the angle of scatter and $\lambda$ is the neutron wavelength. The $Q$-independent background scattering is subtracted from the data, and the data are absolutely calibrated using a standard scatterer. The resulting neutron scattering intensity, $I$, decreases strongly with increasing $Q$, and it is generally this loss of intensity that determines the experimental upper limit of $Q$. Note however, that many of the data reported here are plotted as log($IQ^4$) versus log($Q$), and the term $IQ^4$ actually increases with $Q$ (plots of this form allow subtle features in the data to be more readily observed).

Fig. 1 shows the SANS scattering data [here plotted as log($I$) versus log($Q$)] for an ordinary portland cement (OPC) paste measured at 7 h and at 44 h after mixing, illustrating the type of information that can be obtained from SANS. At small $Q$ values, the largest features are probed, which for a young cement paste are the original cement clinker grains. The data at $Q$ values below about 0.2 nm$^{-1}$ can be modeled as a surface fractal regime, with the surface of the clinker grains becoming roughened by the formation of hydration product. Note the decrease in intensity at low $Q$ with hydration time, as the clinker grains are consumed. At higher $Q$ values, smaller features are probed, and the response is dominated by the low-density C-S-H gel. Thus, the intensity increases significantly between 7 and 44 h due to the early rapid hydration reaction. The scattering response
in the $Q$ range of about 0.3–1.0 nm$^{-1}$ exhibits volume fractal behavior [13], such that $I \propto Q^{-3}$, where the scaling exponent, $x$, is close to 2.5. On a log–log plot of $IQ^4$ versus $Q$, this results in a linear region with positive slope $4 - x$. Previous analysis of the data in the volume fractal regime of cement paste has demonstrated that the scattering can be accounted for by a so-called diffusion-limited single-particle aggregate structure consisting of roughly equiaxed C-S-H gel particles about 5 nm in diameter [13]. The 5 nm building block size usually can also be inferred from a brief regime of associated Guinier scattering in the $Q$ range 0.8–1.2 nm$^{-1}$.

At high $Q$, the intensity of the scattering becomes proportional to the total internal surface area of the specimen; this is known as Porod scattering. For mature cement paste, the Porod region begins at about 1.4 nm$^{-1}$ [16]. The surface area of hydrated cement paste arises almost entirely from the C-S-H gel, with only small additional contributions from other phases, such as CH. In a two-phase specimen, the total internal surface between the two phases can be determined from:

$$S_v = \frac{C_P}{2\pi|\Delta \rho|^2} \quad (3)$$

where $S_v$ is the surface area per unit volume, $C_P$ is the Porod constant, and $|\Delta \rho|^2$ is the scattering contrast. The Porod constant is determined from the SANS data in the high scattering angle region of the scattering curve (after the background is subtracted). For data plotted in the form shown in Fig. 2, the Porod constant is the $y$-axis value of the data at highest $Q$.

The scattering contrast is a parameter that measures the intrinsic strength of the neutron scattering interaction at the interface between two phases. For cement-based materials, the dominant scattering contrast is that between C-S-H gel and pore fluid, and the neutron scattering contrast can be written as:

$$|\Delta \rho|^2 = (\rho_{\text{CSH}} - \rho_{\text{H}_2\text{O}})^2 \quad (4)$$

where $\rho_{\text{CSH}}$ and $\rho_{\text{H}_2\text{O}}$ are the neutron scattering length densities of C-S-H and of water. These are material parameters that can be calculated from the average chemical composition and density of the phase, using published tables [21]. This calculation is straightforward for well-defined phases, such as water and CH, but it presents a problem for the C-S-H gel due to its variable composition and poorly defined structure. A particular problem associated with the composition of C-S-H gel is that it is not clear how much water should be included in the solid phase for the purpose of calculating $\rho_{\text{CSH}}$.

Important information about the neutron scattering contrast for cement can be obtained experimentally by taking advantage of the large difference in neutron scattering length density between H$_2$O and D$_2$O (heavy water) [22,23]. When a hydrated cement paste is placed into D$_2$O, the D$_2$O exchanges fully with both the pore water and the water in the C-S-H gel, including structural water existing as OH$^-$ groups, and this greatly alters the scattering.

Fig. 1. SANS data for the same OPC paste after hydration for 7 h and 44 h. As the scattering vector (or angle) increases, scattering occurs from smaller features in the microstructure.

Fig. 2. SANS response of unleached and moderately leached 6-month-old WPC pastes. The decrease in scattering intensity at low $Q$ can be attributed to the removal of calcium hydroxide.
contrast. When the change in the scattering contrast is measured as a function of D$_2$O content, the result for a two-phase system, such as C-S-H and water, is a parabola with a minimum value of zero contrast. The contrast is zero when the neutron scattering length density of the solid and liquid are equal (see Eq. (4)); this is termed the contrast matchpoint.

In a system with more than one solid phase that contributes to the high-$Q$ scattering, the measured contrast variation curve will be the sum of the individual parabolas for the different solid/water systems, resulting in a single parabola that has a minimum value greater than zero. In (unleached) cement paste, the contrast variation parabola does not go completely to zero, due to small scattering contributions from fine CH crystals. The contribution from CH can be subtracted out, because the neutron scattering length density for CH is known, allowing the C-S-H parabola (and contrast matchpoint) to be determined.

Once the contrast matchpoint for C-S-H is known, the neutron scattering length density can be determined if any two of the three relevant physical parameters (C/S, H$_2$O/Si, and density) are known. The neutron scattering length density of the C-S-H gel in normal cement pastes has recently been established to be in the range $2.55-2.90 \times 10^{-14} \text{m}^{-2}$, based on H$_2$O/D$_2$O contrast exchange experiments. This corresponds to H$_2$O/Si in the range of 1.8–1.4, and a scattering contrast between C-S-H and H$_2$O in the range of $(9.7-12.0) \times 10^{28} \text{m}^{-4}$. Further CH$_3$OH/CD$_3$OH SANS contrast experiments and comparisons between SANS and SAXS [23] suggest a contrast value (between C-S-H and H$_2$O) of $10.7 \times 10^{28} \text{m}^{-4}$, which is used in the present study.

The uncertainty in the contrast value for normal cement paste results in systematic uncertainties in the SANS surface area values of about ±10%, but does not affect relative comparisons between different leached samples.

3. Experimental

Decalcification experiments were performed using pastes made from both WPC (US Gypsum) [24] and C$_3$S. The mineral composition by mass of the WPC is 72% C$_3$S, 17% C$_2$S, 5% C$_3$A, 1% C$_4$AF, and 0.7% alkalis. Pure triclinic C$_3$S was made from both WPC (US Gypsum) [24] and C$_3$S. The WPC and C$_3$S powders were mixed at a water-to-cement ratio (w/c) of 0.5 by mass.

Once the contrast matchpoint for C-S-H is known, the CH content in a parallel series of leached specimens can be determined. Quantitative X-ray diffraction was used to measure the CH content in a parallel series of leached specimens with the same geometry, and the CH was found to be completely removed when the bulk C/S reached 1.4 [10].

To determine accurately the calcium and silicon contents of the pastes (i.e., the C/S), approximately 0.1 g of specimen was interground with LiB$_4$ flux and heated to 1000 °C in a graphite crucible, vitrifying the sample. The glassy sample could then be completely dissolved in dilute HCl. The elemental Ca and Si concentrations of the resulting aqueous solutions were measured using ICP-AES with appropriate standard reference solutions. Tests conducted using a standard OPC showed that this procedure was accurate to within 1%. The bound water contents of the pastes were calculated by first vacuum drying a specimen of coarsely ground paste over water at the temperature of dry ice (D-drying) and then measuring the mass loss after ignition at 1000 °C.

Two separate SANS experiments were performed using the 30-m SANS instruments [25] at the National Center for Neutron Research in Gaithersburg, MD. During the first experiment, 6-month-old C$_3$S and WPC pastes, including all of the contrast variation experiments, were conducted using the NG3 SANS instrument. During the second experiment, 3.5-month-old WPC pastes were measured using the similar NG7 SANS instrument. All SANS measurements were performed on coupons of saturated paste using a neutron wavelength of 0.8 nm. For the WPC paste specimens, three sample-to-detector distances were used, giving an effective $Q$ range of 0.03–2.2 nm$^{-1}$. The C$_3$S pastes were measured only at the shortest distance, so that the lower limit in $Q$ for this case was about 0.3 nm$^{-1}$.

Contrast variation experiments were performed using five coupons of paste at each C/S. The coupons were first analyzed with SANS while saturated with H$_2$O to establish the initial C$_p$. Then, the coupons were placed in H$_2$O/D$_2$O mixtures with D$_2$O mole fractions of 0.2, 0.4, 0.6, 0.8, and 1.0 and allowed to exchange for a period of 24–36 h. They were then analyzed again to determine the new C$_p$, taking care to measure the same location on the coupon so as to minimize the possible effects of any microstructural spatial variation. The contrast variation as a function of D$_2$O content was expressed as the ratio of the second C$_p$ to the first C$_p$ for each coupon.

Surface areas were measured using an automated nitrogen gas sorption unit (Omnisorp 360, Coulter, Hialeah, FL), and the data were analyzed using the multipoint BET method [26]. Specimens were prepared for gas sorption by D-drying for a period of at least 10 days.
4. Results

4.1. SANS response of leached paste

The scattering data for the unleached WPC paste and the WPC pastes leached to C/S of 2.5 and 1.54 are shown in Fig. 2. The overall intensity of the scattering remains fairly constant, but there are changes in the shape of the curves. There is a slight loss of intensity at low \( Q \) values, caused by the dissolution of small (< 1 \text{ nm}) CH crystals, and possibly some loss in the C-S-H surface fractal component, while at higher \( Q \), there is a change in the slope of the volume fractal regime, particularly for the C/S = 1.54 specimen. Fig. 3 shows the scattering response for WPC pastes leached to C/S < 1.0. At C/S = 0.83, there is a significant increase in the scattered intensity in both the volume fractal and Porod regions as compared to the unleached paste. On further leaching to C/S = 0.68, there is significant increase in the scattered intensity across the entire \( Q \) range. While the crossover between the volume fractal and surface fractal regimes remains in roughly the same place (0.2–0.3 \text{ nm}^{-1}), the upper cutoff in \( Q \) for the volume fractal regime moves to the left and the fractal exponent changes, suggesting a coarsening and change in morphology of the fine structure of the leached C-S-H gel. Finally, at C/S = 0.33, the Porod region shifts significantly to the left and the Porod intensity is decreased, indicating either an increase in the size of the fundamental gel particles or a thickening of the sheet structures (discussed below) that result from leaching.

\[ I \propto Q^{-x} \]

Table 1 lists the apparent power law exponents and the range of \( Q \) over which volume fractal behavior is observed in the WPC pastes. The apparent volume fractal slopes are generally less steep than those previously derived from a multicomponent model [13] because that model accounts for the superimposition of the volume fractal and surface fractal components over much of the \( Q \) range measured. However, the breakdown of such models as leaching progresses (at least regarding the volume fractal component) justifies the more empirical observations presented here. Decalcification causes the exponent, \( x \), to change from an initial apparent value of 2.38 to a minimum value of 1.84, and then to increase again to near 2.0. Scattering that follows a \( Q^{-2} \) power law is generally the hallmark of a sheet- or foil-like morphology [27] and thus the present results are in agreement with microscopic evidence that C-S-H gel formed with C/S near 1.0 has a foil-like morphology [11].

As C/S decreases, the upper and lower limits of the volume fractal regime both move to lower \( Q \) values (see Table 1). In cement systems, the observed lower limit of volume fractal scaling generally represents the point where the relative contribution from surface fractal scattering becomes important. The observed slight decrease in the lower \( Q \) limit for the power law scattering therefore reflects an increasing dominance of the volume fractal component of the microstructure over the surface fractal component as leaching progresses. Deviation from \( Q^{-2} \) scattering at the high end of the volume fractal range occurs when the scattering form–factor for the structural building blocks of the volume fractal regime becomes the dominant contribution to the scattered intensity. The \( Q \) value where this occurs is inversely proportional to the size of the building blocks. Thus, the decrease in the upper limit of the volume fractal regime with leaching suggests that either the C-S-H gel globules increase in size with leaching, or that the sheets formed on leaching become thicker as leaching progresses. The shift in the curves to lower \( Q \) values shown in Fig. 3 indicates that for C/S = 0.33, the sheets have thickened to roughly a double layer of the original 5 nm gel globules.

The data shown in Figs. 2 and 3 indicate that as the C/S decreases, roughly equiaxed 5 nm C-S-H particles transform into larger sheetlike structures. This is in good agreement with the known increase in the average linear silicate chain length with decreasing C/S, and with the well-established (e.g., Ref. [28]) similarity of C-S-H phases with C/S near 1 to the layered mineral tobermorite (C/S = 0.83). The significantly higher C/S of C-S-H gel in normal cement pastes causes the structure to become highly disordered, so that no layered structure exists on length scales greater than a few nanometers. As calcium is removed from this structure, the silicates can rearrange into longer chains and this allows for a significant increase in long-range order. \(^{29}\)Si NMR analysis of leached C\(_3\)S pastes (reported in detail elsewhere, [7]) shows that the average chain length begins to increase rapidly with
decalcification at C/S < 1.2, and that at C/S near 0.3, there are significant amounts of Q₃ and Q₄ groups (where Qₙ indicates a silicate bonded to n other silicates) indicating a shift toward a silica gel structure. The degree of polymerization of the silicates as measured by ²⁹Si NMR has also been shown to be greater in lower C/S pastes made with silica-rich mineral admixtures [29,30].

The Porod constant of the WPC and C₃S pastes as a function of leaching. The Porod constant increases as the C/S decreases, reaching a maximum value at approximately C/S = 1.0, and then decreases again with further decalcification. The WPC and C₃S pastes are in good agreement. This strongly suggests that the measured surface area increases significantly on leaching (see Eq. (3)), although it should be noted that an increase in the scattering contrast between C-S-H and the pore fluid could increase the observed SANS intensity and Cₚ value without any microstructural changes. As is shown in the following section, the contrast increases by only about 10% on decalcification to C/S = 1, so this does not account for the factor of two increase in Cₚ shown in Fig. 4. The effects of leaching on the surface area are discussed further in Sections 4.3 and 5.

4.2. H₂O/D₂O exchange experiments

Fig. 5 shows the SANS data for three of the WPC pastes before and after exchange of the pore fluid with pure D₂O. For the unleached WPC paste, D₂O exchange causes the SANS data to have a very different shape. At high Q, the large decrease in intensity reflects the decrease in the neutron scattering contrast when C-S-H exchanges to form C-S-D. With decreasing Q (representing scattering from larger features) the intensity of the scattering from the D₂O-exchanged paste increases significantly relative to, and eventually surpasses that of, the hydrated paste. Because H₂O/D₂O exchange does not affect the microstruc-
ture, this can only be caused by an increase in scattering contrast caused by increased scattering intensity from coarser phases, such as CH, that do not exchange with the D$_2$O. When C-S-H exchanges to form C-S-D, the scattering contrast with the pore fluid decreases by a factor of more than 10, whereas the contrast between pore fluid and nonexchanging CH increases by a factor of 5. Fig. 5 also shows the same type of plot for the WPC pastes leached to C/S = 1.54 and C/S = 0.83. At C/S = 1.54, exchange with D$_2$O significantly decreases the SANS intensity at all Q values, and at C/S = 0.83, the D$_2$O-exchanged and -unexchanged scattering curves are parallel across the entire Q range sampled, indicating that microstructural features at all length scales exchanged fully with D$_2$O.

Fig. 6 shows the results of three of the contrast exchange experiments conducted on leached WPC pastes. The relative contrast, obtained by normalizing the $C_p$ values obtained after D$_2$O exchange to the initial (pure H$_2$O) $C_p$ values, is plotted against the mole fraction of D$_2$O in the exchange fluid. Similar curves were obtained for C$_3$S pastes. The data for each paste is parabolic, as expected. The shape of the curves verifies that the overwhelming majority of the H$_2$O present in the solid phases that generate the Porod scattering exchanged with the pore fluid. Lack of full exchange would result in contrast minimums to the left of those found and would give significantly more scattering intensity for the fully D$_2$O-exchanged coupons.

The results of the contrast variation experiments are listed in Table 2. For the C/S = 3.0 (unleached) and C/S = 2.5 samples, the minimum in the fitted parabola was slightly greater than zero, indicating a small scattering contribution from fine crystalline CH that does not exchange with the pore fluid [23]. These curves were therefore fit as the sum of two parabolas with minimum values constrained to be zero: one representing CH with a minimum constrained to the known matchpoint value of 32% D$_2$O, and the other with a variable matchpoint representing the C-S-H gel. The resulting percentage of the Porod scattering intensity arising from CH is also listed in Table 2. The measured parabolas at lower C/S all have a minimum very close to zero (see Fig. 6), indicating that the SANS in the Porod regime arises from CH alone. Each of the curves for low C/S was fitted using a single parabola with a minimum relative contrast value of zero, and these contrast variation results confirm the expected removal of CH during the initial stages of leaching.

Fig. 7 shows the C-S-H contrast matchpoint as a function of C/S ratio. The matchpoint remains at roughly 81% D$_2$O during initial leaching, in agreement with previous measurements of unleached pastes, and then moves slightly to the left (lower D$_2$O mole fractions) with leaching at C/S below 1.54. The behavior of the WPC and C$_3$S pastes is similar. The relatively small changes in the position of the contrast minimum with leaching indicate that there are correspondingly minor changes in the C-S-H/H$_2$O contrast. As indicated earlier, once the C/S and the C-S-H contrast matchpoint are known, the scattering length density of C-S-H can be determined if either the H$_2$O/Si or the density is known. As the density is difficult to measure due to the fine gel pore structure [31], the H$_2$O/Si ratio was evaluated by measuring the bound water content as a function of leaching. C$_3$S pastes were used to eliminate the effects of aluminate phases present in cements. As shown in Fig. 8, the H$_2$O/Si of the pastes decreases with decreasing C/S. This is consistent with other published data from synthetic C-S-H [32] and from the C-S-H gel present in blended cement pastes such as OPC with silica fume [30].

Fig. 8 shows that a significant amount of bound water remains in the C-S-H even at C/S as low as 0.2, indicating that the structure is still quite different from that of pure amorphous SiO$_2$. This is in agreement with the contrast matchpoint data plotted in Fig. 7: the calculated contrast

![Fig. 6](image_url)  
Fig. 6. Contrast variation with H$_2$O/D$_2$O exchange, for three of the WPC pastes. The lines are parabolic fits (as explained in the text) and vertical bars indicate computed standard uncertainties for each point.

<table>
<thead>
<tr>
<th>Paste type ratio</th>
<th>Fit type</th>
<th>Fitted intensity from CH (%)</th>
<th>C-S-H matchpoint (%D$_2$O)</th>
<th>H$_2$O/Si ratio</th>
<th>C-S-H:H$_2$O contrast ($\times 10^{-2} \text{m}^{-4}$)</th>
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</tbody>
</table>
The matchpoint for pure silica gel (density = 2.2 g/cm³) is at 57% D₂O, considerably less D₂O-rich than the matchpoint of 72% observed for the C/S = 0.33 specimen. For unleached C₃S paste, the H₂O/Si after D-drying is about 1.4, in agreement with published values [31]. This is slightly lower than the H₂O/Si value of 1.6 assumed for the C-S-H/H₂O scattering contrast of unleached pastes in this study. It should be noted that the C-S-H composition after D-drying would not necessarily be expected to correspond to the solid C-S-H phase probed by neutrons, as D-drying may remove some tightly adsorbed water that behaves as part of the solid phase forming an interface with liquid water, and this may also collapse the structure.

To estimate the scattering contrast for C-S-H with C/S < 1.5, the linear fit to the bound water data shown in Fig. 8 was used to estimate the decrease in H₂O/Si on leaching. These H₂O/Si, and the resulting C-S-H/H₂O contrast values, are listed in Table 2. The contrast value increases slightly with leaching.

### 4.3. Surface area of leached pastes

Fig. 9 shows the surface area of the pastes as a function of C/S, calculated using Eq. (3) and the contrast values listed in Table 2. The surface area does in fact increase significantly with leaching, slightly more than doubling from the initial value to the observed maximum near C/S = 1.0.

To verify this trend, the surface area of 6-month-old WPC paste specimens were measured using nitrogen BET. When reported in the standard specific surface area units of m²/g of specimen, the BET surface area increased dramatically with leaching. However, this resulted in large part from the significant decrease in sample weight with leaching, and is thus misleading. To convert the nitrogen BET values to the intrinsic SANS units of surface area per unit volume.
volume, the density of D-dried WPC pastes was also measured as a function of leaching. The resulting renormalized BET surface area values are also plotted in Fig. 9. The BET values increase with leaching, although not as sharply as the SANS values. The agreement between the SANS and BET values is reasonable, given the rather significant effects of drying on the C-S-H gel, although the BET data do not appear to show the significant increase in surface area between C/S = 1.5 and C/S = 1.0 seen with SANS.

5. Discussion

The amount of C-S-H in a paste, when expressed per mole of SiO$_2$, should not change on calcium leaching, and the size of the C-S-H particles, as determined from Guinier fits and fractal modeling of the SANS data, decreases only slightly on initial leaching and then increases. This suggests that the large increase in the measured surface area with decalcification (see Fig. 9) is caused not by an increase in the specific surface area of the C-S-H particles, as determined from Guinier fits and fractal modeling of the SANS data, decreases only slightly on initial leaching and then increases. This suggests that the large increase in the measured surface area with decalcification is not due to an increase in the specific surface area of the C-S-H, but rather by an increase in the amount of C-S-H with a high specific surface area that is accessible to SANS and nitrogen sorption. The C-S-H gel in cement paste forms with two morphologies, commonly referred to as outer product and inner product, and there is evidence that under normal conditions, only the lower density form has a high surface area as measured by SANS [16] or by nitrogen BET [33]. An obvious explanation for the increase in surface area with decalcification is that the leaching process opens up the high-density C-S-H structure, giving it a high measurable surface area. This hypothesis is well supported by other evidence, as discussed below.

The SANS surface area values should be consistent with the overall microstructural picture generated by the SANS data at different scattering vectors. The latter shows cement paste to be a random fractal structure built up from 5 nm globules. For a solid phase consisting of noncontacting 5-nm-diameter spheres, the surface area per unit solid volume is 1200 m$^2$/cm$^3$. For a mature paste with w/c = 0.5, Constantinides and Ulm [35] reported surface area values of 21.7 and 29.4 GPa and associated volume fractions of 70% and 30%. These volume fractions are in good agreement with the model predictions noted above. Acker [34] reported very similar characteristic stiffness values (20 and 31 GPa) for a high-performance cement paste with w/c = 0.3, indicating that the morphology of the two C-S-H types is to some extent independent of the processing and curing conditions. Ulm et al. [36] then showed that if the two C-S-H types with different stiffnesses are assumed to consist of the same solid phase with different characteristic porosities, then the porosity values must be the same as the values predicted by the Jennings [20] structural model. Constantinides and Ulm [35] also performed nanoindentation on a cement paste after decalcification to C/S = 1, and found that the volume fractions of the two C-S-H types were unchanged, while the characteristic stiffness values decreased significantly. They attributed the stiffness decrease primarily to an increase in the intrinsic porosity of the high- and low-density C-S-H.

All of the above evidence indicates that the high-density C-S-H contributes to the surface area measured by SANS and by nitrogen BET only after it is decalcified. It should be noted that the low-density C-S-H is also strongly affected by leaching, and its contribution to the surface area could increase somewhat as well during initial decalcification when the overall surface area is increasing. Continued leaching below C/S = 1 appears to cause a thickening of the (now sheetlike) fundamental C-S-H units and a consequent decrease in the measured surface area.

6. Summary

Decalcification of cement and tricalcium silicate (C$_3$S) pastes by leaching increased the SANS intensity across the entire volume fractal regime corresponding to C-S-H gel, and the surface area per unit specimen volume, determined from the SANS intensity at the highest scattering vectors, nearly doubled on decalcifying the C-S-H from C/S = 1.7 to C/
S = 1.0. The surface area per unit volume measured by nitrogen gas sorption on dried specimens increased more gradually with decalcification and did not show a sharp maximum near C/S = 1. The best explanation for these results is that the high-density “inner-product” C-S-H gel, which normally has a low specific surface area at low C/S, has a low specific surface area at high C/S. This explanation is supported by recent nanoindentation results indicating that the internal porosity of the high-density form of C-S-H gel is increased by calcium leaching.

Decalcification also changed the apparent volume fractal scaling exponent of the SANS data from 2.3 to about 2.0. This indicates that the equiaxed 5 nm C-S-H globule building blocks (first identified in previous SANS work) that form the volume fractal microstructure of normal, unleached cement paste are transformed by decalcification into sheetlike structures of increasing thickness. This in agreement with the well-established link between low-C/S C-S-H phases and the layered mineral tobermorite.

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References

[24] Information on commercial products is given for completeness and does not constitute or imply their endorsement by the National Institute of Standards and Technology.

