

# The Nanostructure of Low-CO<sub>2</sub> Concrete for a Sustainable Infrastructure

*A scientific collaboration between Lafarge Center for Research (LCR) and  
Northwestern University (NWU)*

Report on year 1 activities and recommendations for future work

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## **Executive Summary**

The objective of this program is to measure the changes in the properties of the C-S-H gel phase in cement paste as a function of the Ca/Si ratio. The motivation is to better understand the hydration products that form in blended cements with lower Ca/Si ratios than portland cement. The main contribution from Northwestern was to characterize specimens using small-angle neutron scattering (SANS). In particular, a new method of measuring the neutron scattering length density, composition, and mass density of the nanoscale hydration products was employed. For samples made at Lafarge, the general microstructure was characterized with SEM, the degree of hydration was measured with QXRD, and the local Ca/Si of the hydration products was measured using EDX.

This report first provides an overview of the SANS analysis method and the information it provides (Section 1), and then a description of the types of specimens that are discussed in this report (Section 2). Sections 3 and 4 contain results for pastes that are not part of the present project, but are included because they are highly relevant. These are unpublished results that should be treated as confidential. In Section 5, the results from the C<sub>3</sub>S pastes with varying amounts of colloidal SiO<sub>2</sub>, made and characterized by LCR, are summarized. Finally in Section 6 recommendations for further collaborative work are made.

The principal findings of this report are as follows. The hydration of C<sub>3</sub>S in the presence of colloidal silica, while scientifically quite interesting, is not representative of pozzolanic blended cements in general due to the high reactivity of the SiO<sub>2</sub>. The results obtained during the past year shed light on the hydration of C<sub>3</sub>S and on the nanostructure of C-S-H, but also raise important new questions. The main recommendation is to perform similar experiments using silica fume or other pozzolanic materials to control the Ca/Si of the paste and of the C-S-H. These results will be of considerable practical use and will also help interpret the results obtained with colloidal silica.

## 1. Analysis of C-S-H gel and cement paste using SANS

Small-angle neutron scattering (SANS) is a powerful and versatile technique for investigating the nanostructure of disordered wet materials such as cement paste. Stated briefly, a monochromatic neutron beam passes through a thin specimen, and a fraction of the neutrons are scattered through interactions with micro- and nanostructural features. The intensity of the scattering is measured as a function of the scattering vector (proportional to the angle of scatter), and this data can be analyzed to reveal a variety of quantitative and qualitative features. During the last decade, SANS measurements on cement paste in its normal, water-saturated state have revealed that the nanometer-scale structure consists of solid particles of C-S-H that are packed randomly to form a continuous phase through the paste, binding the cement particles together. The particles and associated water are shown schematically in Fig. 1(a).

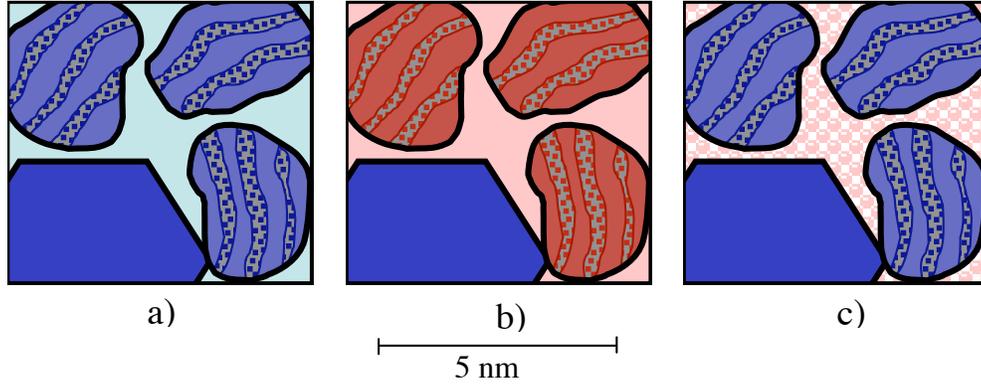
From analysis of the general scattering response of saturated cement paste, much has been learned, including the characteristic size of the particles (4 - 5 nm), their fractal arrangement and packing density, and the specific surface area. The application of SANS to cement was recently reviewed [1]. In addition, a novel method of measuring the water content and density of the nanometer-scale “building block” particles of C-S-H gel in cement paste was recently developed [2]. This technique, which involves SANS measurements of specimens that are exposed to different fluids, has provided important information about the C-S-H phase in OPC and tricalcium silicate ( $C_3S$ ) pastes. As this method is an important aspect of the work performed for this project, it is discussed in more detail later in this section.

Figure 2 shows SANS data for hydrated  $C_3S$  paste made with and without  $CaCl_2$ , plotted as  $IQ^4$  vs.  $Q$ , where  $I$  is the normalized scattered intensity and  $Q$  is the scattering vector. Note that as  $Q$  increases, the size of the features causing the scattering decreases. SANS data from cement paste generally exhibit three scattering regimes associated with surface fractal, volume fractal, and single-particle scattering (see Fig. 2). At lower  $Q$  values, the deposition of hydration product onto the cement particles creates a rough surface that generates surface fractal scattering. At intermediate  $Q$  values, scattering is dominated by a volume fractal structure with a scaling exponent between 2.5 and 2.7 created by the random agglomeration of the fundamental C-S-H particles. At

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<sup>1</sup> A. J. Allen and J. J. Thomas, "Analysis of C-S-H gel and cement paste by small-angle neutron scattering," *Cem. Concr. Res.*, **37**, 319-324 (2007).

<sup>2</sup> A.J. Allen, J.J. Thomas, H.M. Jennings, "Composition and density of nanoscale calcium-silicate-hydrate in cement," *Nature Materials* **6** (2007) 311-316.



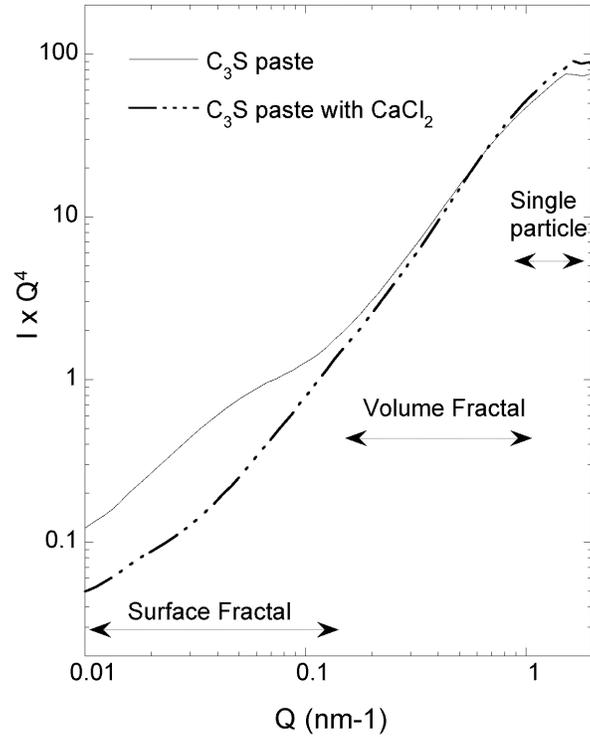
**Figure 1:** Schematic diagram of nanoscale hydration product in cement paste, consisting of layered C-S-H particles and  $\text{Ca}(\text{OH})_2$  crystals surrounded by pore fluid, after. Three fluid exchange scenarios are shown. Phases containing only hydrogen are blue, while phases containing deuterium are red. The black lines indicate the scattering interface between the solid phases and the pore fluid. a) Normal saturated paste with  $\text{H}_2\text{O}$  in the pores. Due to its small volume fraction, scattering from nanoscale  $\text{Ca}(\text{OH})_2$  is almost negligible compared to that from C-S-H. b) A  $\text{D}_2\text{O}$ -exchanged paste. The C-S-H exchanges with  $\text{OD}^-$  groups to become C-S-D, while the  $\text{Ca}(\text{OH})_2$  is unchanged. Compared to case (a), the scattering between  $\text{Ca}(\text{OH})_2$  and the pore fluid is much stronger, while scattering between C-S-D and the pore fluid is much weaker. Experiments with  $\text{D}_2\text{O}$  exchange allow the volume fraction of nanoscale  $\text{Ca}(\text{OH})_2$  to be determined. c) A paste exchanged with d3-methanol ( $\text{CD}_3\text{OH}$ ). Since the fluid does not contain  $\text{OD}^-$  groups, only the pore phase changes. These experiments provide the scattering length density of the overall C-S-H/  $\text{Ca}(\text{OH})_2$  nanoscale solid phase. Combined analysis of the three cases shown here allows the composition and mass density of the solid C-S-H nanoparticles to be determined.

high  $Q$  values, single-particle scattering applies and the characteristic size of the basic particles can be determined. At the highest  $Q$ -values shown in Fig. 1, Porod's law can be applied to calculate the total internal surface area of the specimen per unit specimen volume,  $S_v$ :

$$S_v = \frac{C_p}{2\pi|\Delta\rho|^2} \quad (1)$$

where  $C_p$  is the constant of proportionality for the Porod scattering and  $|\Delta\rho|$  is the difference in the neutron scattering length density (SLD) of the two phases causing the scattering. At this length scale of a few nm, the scattering is dominated by interfaces between solid C-S-H and liquid water.

As can be inferred from Eq. (1), the intensity of the scattering at a given scattering vector,  $Q$ , depends not only on the amount of structure in the associated size range, but is



**Figure 2:** SANS data for C<sub>3</sub>S paste made with and without CaCl<sub>2</sub>.

also directly proportional to the square of the difference in the SLD of the scattering phases, a factor called the scattering contrast. If the chemical composition and mass density of a phase is known, its SLD can be calculated precisely. This is the case for well-defined phases such as H<sub>2</sub>O and Ca(OH)<sub>2</sub>, but is not the case for the C-S-H gel: the unknown water content and density of solid C-S-H is a longstanding issue of importance in cement science that also hinders a full interpretation of scattering data. The problem of an unknown solid phase can often be solved by varying the SLD of the liquid phase by replacing it with a deuterated fluid, in this case by exchanging the pore H<sub>2</sub>O with varying amounts of D<sub>2</sub>O (heavy water), which has a much higher SLD. By noting the matchpoint where the contrast drops to zero, the solid SLD and solid-H<sub>2</sub>O contrast can in principle be calculated directly.

Two problems with this approach arise for cement-based materials. The presence of a small amount of nanoscale Ca(OH)<sub>2</sub> intermixed with C-S-H means that a zero-intensity contrast matchpoint does not exist, since Ca(OH)<sub>2</sub> has a matchpoint quite different from that of C-S-H. More important, solid C-S-H undergoes full H/D exchange to become C-S-D (see **Figure 1(b)**), adding an additional level of complexity. The

volume fraction of  $\text{Ca}(\text{OH})_2$  in various types of cement paste can be determined by analyzing the contrast variation parabolas (plotted as curves of scattered intensity versus  $\text{D}_2\text{O}$  fraction). The scattering contribution from  $\text{Ca}(\text{OH})_2$  can then be subtracted, leaving a self-consistent C-S-H contrast curve for  $\text{H}_2\text{O}/\text{D}_2\text{O}$  contrast experiments (e.g. see Fig. 3). The remaining problem is that this curve is actually for C-S-H/D as D exchanges for H, where both the solid and liquid SLD are changing, and no unique solution is possible if both the composition and density of C-S-H are unknown.

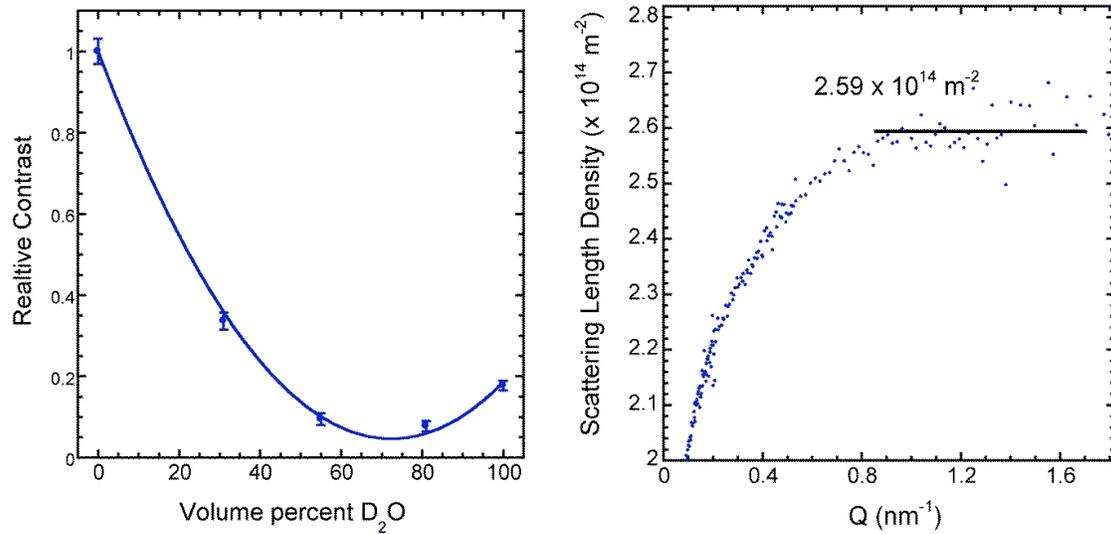
This problem is solved by obtained SANS contrast data using  $\text{CH}_3\text{OH}/\text{CD}_3\text{OH}$  (methanol/ $d_3$ -methanol) exchange – since  $\text{CD}_3\text{OH}$  does not contain OD groups the OH groups in solid C-S-H remain OH and only the fluid phase exchanges (see Fig. 1(c)). Thus, the SLD for the combined C-S-H/ $\text{Ca}(\text{OH})_2$  nanostructure can be calculated from the ratio of the SANS intensities in  $\text{CH}_3\text{OH}$  and in  $\text{CD}_3\text{OH}$  (e.g. see Fig. 3). For the C-S-H phase in cement and  $\text{C}_3\text{S}$  pastes, which has a calcium/silicon (C/S) molar ratio of 1.7, the combined analysis of the SANS data described above yields the molar water content,  $\text{H/S} = 1.80 \pm 0.03$ , and physical density  $(2604 \pm 0.022) \times 10^3 \text{ kg m}^{-3}$  [2]. These values apply to the solid C-S-H particles themselves, and do not include any adsorbed water outside the particles.

While the initial published results provide an important baseline value for calibrating and developing models of C-S-H gel at longer length scales, it is also critical to understand how these values are affected by the composition of the starting cement and other variables. This is the goal of this project.

## 2. *Specimens*

During the past year, SANS analysis, in particular the fluid exchange method discussed above, was applied to cementitious materials for which the C-S-H product would be expected to be different in either chemical composition or structure. Results from the following three paste types will be discussed here:

- i.  $\text{C}_3\text{S}$  paste made with 2 wt% of a common hydration accelerator ( $\text{CaCl}_2$ ). The C-S-H gel that forms in this paste is presumed to have a Ca/Si ratio close to 1.7 as in normal  $\text{C}_3\text{S}$  paste.
- ii. An alternative type of cement made from alkali-activated blast furnace slag (AAS). The slag used was a commercial ground slag (NewCem, Lafarge) and the accelerator was a sodium silicate solution. The overall Ca/Si of the pastes (including both slag and accelerator) is  $\text{Ca/Si} = 1.1$ .



**Figure 3:** Left: Contrast exchange parabola for a  $C_3S$  paste accelerated with 2 wt%  $CaCl_2$ , in which the SANS intensity from the same specimen is measured as a function of the  $D_2O$  (heavy water) content in the specimen. The line is a fit to the data points representing the sum of two parabolas corresponding to C-S-H gel and to calcium hydroxide, each of which has a minimum value of zero. Right: The scattering length density of the same paste, plotted as a function of the scattering vector,  $Q$ . This is calculated from the ratio of the intensities with the pore fluid exchanged with methanol and with d3-methanol ( $CD_3OH$ ). The line represents a statistically constant SLD value for the nanoscale hydration product.

- iii.  $C_3S$  pastes made with varying amounts of colloidal  $SiO_2$  (Levasil 6832 suspension). Because the pastes were fairly mature at the time of analysis ( $> 3$  months old) it was presumed that they would be nearly fully hydrated, so that the Ca/Si of the C-S-H would be close to the global Ca/Si of the mix design. However, later analysis of the degree of hydration by LCR showed that this was not the case. Details are given in Table 1.

Paste types (i) and (ii) were made at NWU, while paste type (iii) was made at LCR. Because the latter specimens ( $C_3S + SiO_2$ ) were designed to hydrate fully to form nearly pure C-S-H with known Ca/Si ratios, they were expected to form the centerpiece of the results. However, as the results from these specimens were unexpected and somewhat difficult to interpret, they are discussed last.

SANS analysis was performed using the 30-m SANS instruments at the National Center for Neutron Research in Gaithersburg, MD (USA).

**Table 1:** Mix design of the specimens made with  $C_3S$  and colloidal silica, along with the degree of hydration ( $\alpha$ ) measured by QXRD and the average Ca/Si of the C-S-H phase determined from EDX. Mixing and analysis performed by LCR. The low degree of hydration of the pastes made with colloidal  $SiO_2$  caused the C-S-H Ca/Si to be lower than the global Ca/Si.

Global Ca/Si	wt $SiO_2$ /wt $C_3S$ (%)	water/solids	$\alpha$	C-S-H Ca/Si
3	0	0.60	0.95	1.7
1.6	23.0	0.60	0.74	1.2
1.4	30.1	0.60	0.66	0.86
1.2	39.5	0.60	0.65	0.80

### 3. Analysis of accelerated $C_3S$ paste made with $CaCl_2$ (confidential unpublished work)

The effect of  $CaCl_2$  on the general SANS response of  $C_3S$  paste is shown in Fig. 2. The results are similar to those previously observed for OPC paste [1]. The intensity at higher  $Q$  values is increased, indicating more volume-fractal scattering, while the intensity at lower  $Q$  values is decreased, such that the surface-fractal regime is apparent only at the lowest  $Q$  values sampled. This is consistent with the formation of a greater amount of fine (nanoscale) C-S-H gel hydration product that fills the (micrometer-size) capillary pore space, leaving relatively little room for a distinguishable surface-fractal interfacial morphology on the capillary-pore walls. The total surface area is increased by the addition of  $CaCl_2$ , the calculated values are  $S_v = 122 \text{ m}^2/\text{cm}^3$  for the  $C_3S$  paste and  $S_v = 151 \text{ m}^2/\text{cm}^3$  for the  $C_3S + CaCl_2$  paste.

While the SANS data in Fig. 2, as well as other published work on the effects of  $CaCl_2$ , clearly indicate that there are morphological effects at the micron scale, it had not been established whether the chemical composition of the C-S-H, in particular the water content ( $H_2O/SiO_2$  ratio) and mass density, are affected by  $CaCl_2$ . The fluid exchange method of analysis was therefore applied (see Fig. 3). The contrast parabola obtained from the  $H_2O/D_2O$  exchange is quite similar to those previously obtained for neat  $C_3S$  paste. The intensity contribution from nanoscale  $Ca(OH)_2$  scattering is 2.1 %. The SLD value for solid nanoscale product is  $2.59 \times 10^{14} \text{ m}^{-2}$ , statistically identical with the previous result for  $C_3S$ . The combined analysis also yields a composition and density that is nearly identical to that of  $C_3S$  (see Table 2). Therefore it can be concluded that the chemical structure of the C-S-H gel phase is not greatly affected by the addition of  $CaCl_2$ , and that the observed differences in the SANS response are associated with differences in

**Table 2:** Measured C-S-H composition and mass density in different pastes, as determined by the SANS fluid exchange technique.

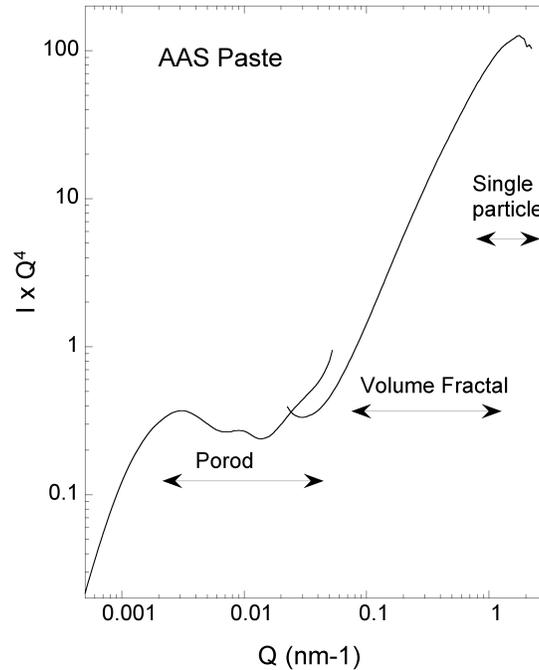
Paste	C-S-H Ca/Si	H <sub>2</sub> O/SiO <sub>2</sub>	Density (kg/m <sup>3</sup> )
Normal OPC or C <sub>3</sub> S [2]	1.7	1.80	2604
C <sub>3</sub> S + 2% CaCl <sub>2</sub>	1.7	1.75	2620
Alkali-activated slag	1.1	0.97	2760
C <sub>3</sub> S + 23% colloidal SiO <sub>2</sub>	1.2	1.55	2800

the arrangement and possibly the shape of the fundamental C-S-H particles, rather than their intrinsic composition.

#### 4. Analysis of alkali-activated slag (AAS) paste (confidential unpublished work)

Ground granulated blast furnace slag is a latently hydraulic material that can be activated by the pore solution of a Portland cement paste (to form blended cement) or by the addition of alkalis to form alkali-activated slag (AAS) paste. The role of the alkalis is to raise the pH of the pore solution to increase the solubility and rate of dissolution of the glassy phases in the slag. Because the Ca/Si ratio of slag is much less than that of Portland cement (generally close to 1), no calcium hydroxide is expected to form, and the Ca/Si of the C-S-H phase is expected to have a similarly low value. The C-S-H phase formed by slag hydration also has the potential for significant aluminum substitution. While this is an important consideration when analyzing the chemical structure, the substitution of Al for Si does not significantly affect the SANS analysis as these elements have similar neutron scattering lengths.

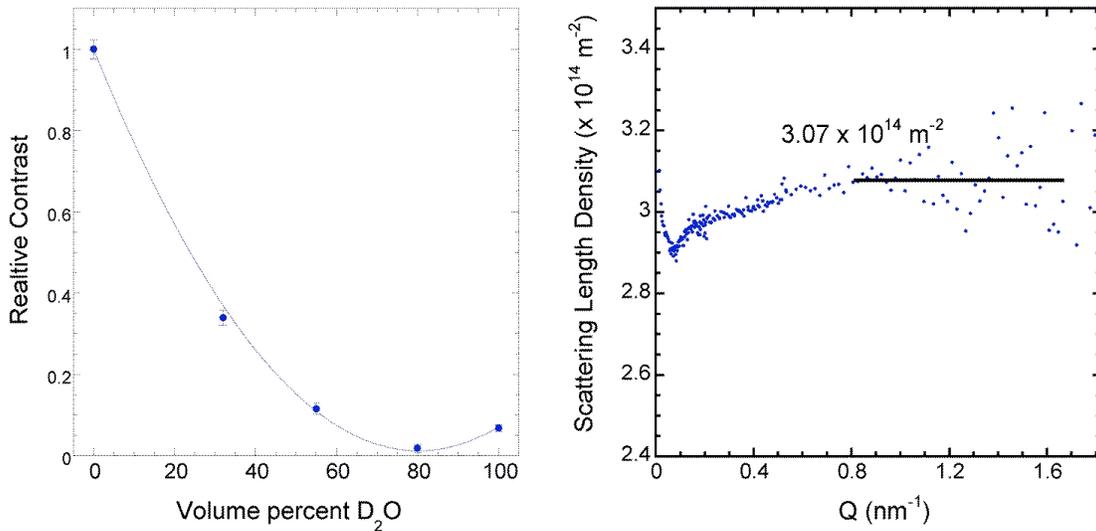
Figure 4 shows the SANS response of an AAS paste as a function of  $Q$ . In comparison with the typical response of a cement paste, the data indicate a volume fractal regime corresponding to the C-S-H phase, along with Porod scattering at high  $Q$  arising from a high specific surface area. At lower  $Q$  values, instead of surface fractal scattering (or a continued drop in intensity as observed with CaCl<sub>2</sub> acceleration), a second Porod scattering range is observed that arises from much larger features than the nanoscale C-S-H particles. This regime can be interpreted as scattering from the unhydrated cores of the slag particles. The sharp transition between volume fractal and low- $Q$  Porod scattering indicates that the C-S-H gel hydration product has grown out into the pore space away from the particles, leaving a sharp transition region in the microstructure between the



**Figure 4:** SANS data for alkali-activated slag paste mixed at  $w/s = 0.5$  and hydrated for 3 months at  $20^\circ\text{C}$ . The data indicate a volume fractal regime corresponding to C-S-H at higher  $Q$  values and Porod scattering associated with the cores of unreacted slag particles at lower  $Q$ . The low- $Q$  data was obtained using a different instrument (USANS).

dense slag particles and the porous hydration product. The specific surface area of the AAS paste is  $147 \text{ m}^2/\text{cm}^3$ , about 20% higher than that of neat portland cement or  $\text{C}_3\text{S}$  paste hydrated under similar conditions.

The  $\text{H}_2\text{O}/\text{D}_2\text{O}$  contrast curve is shown in Fig. 5. The parabolic contrast curve has a minimum at zero intensity, indicating that only one nanoscale phase is present in the paste (C-S-H). The SLD value (Fig. 5, right) has less variation over the entire  $Q$ -range than is observed for cement or  $\text{C}_3\text{S}$  paste. This can be attributed to the lack of  $\text{Ca}(\text{OH})_2$  in the AAS paste.  $\text{Ca}(\text{OH})_2$  occurs primarily as micron scale crystals, so that when it is present its overall contribution to the scattering increases sharply as  $Q$  decreases, causing the SLD value to decrease. The fitted value of the SLD for nanoscale hydration product in the AAS paste ( $3.07 \times 10^{14} \text{ m}^{-2}$ ) is considerably higher than that measured for cement and  $\text{C}_3\text{S}$  pastes, indicating that the C-S-H phase is indeed quite different. As shown in Table 2, the full analysis bears this out: in addition to having a lower Ca/Si ratio, the water content is lower and the mass density is higher. These values are not unexpected, as the water content of solid C-S-H (primarily present as Ca-OH and Si-OH groups) is known to decrease with the Ca/Si ratio. In general, these results



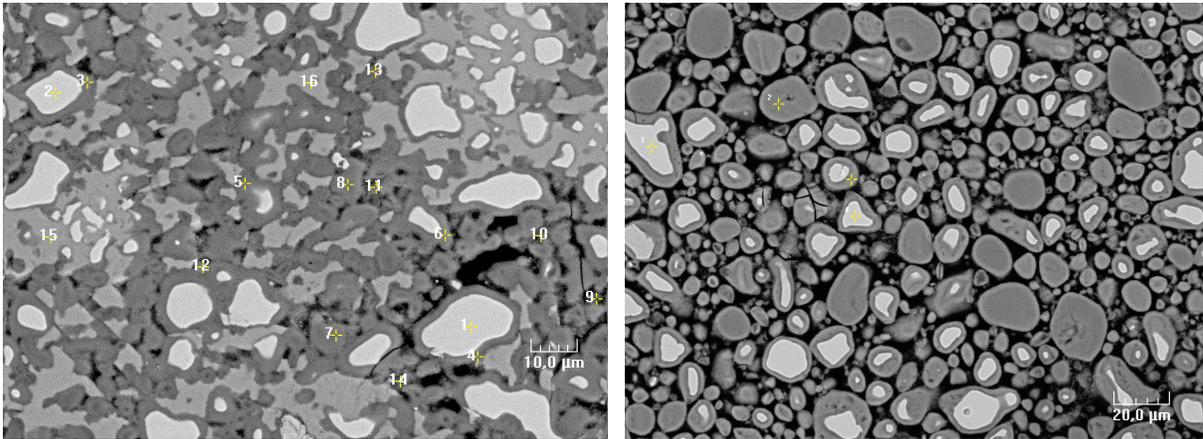
**Figure 5:** Contrast exchange parabola (left) and SLD value (right) for an alkali-activated slag (AAS) paste. See caption to Fig. 2 and text for more details. Note that the parabola at left has a minimum of zero intensity, indicating a single nanoscale phase in this paste (C-S-H).

indicate that the fluid exchange technique is robust enough to be applied to entirely different systems than portland cement.

##### 5. Analysis of pastes made with $C_3S$ and colloidal $SiO_2$

Because colloidal silica is highly reactive, and will readily react with calcium ions to form C-S-H, it was assumed that after three months of hydration the pastes made with  $C_3S$  and colloidal silica would be nearly fully reacted (as is the control with no silica). In fact, the addition of colloidal silica is known to accelerate the early hydration rate of cement and  $C_3S$  by providing additional nucleation sites. However, as shown in Table 1, the measured degree of hydration ( $\alpha$ ) after more than 3 months of hydration actually decreased significantly with the addition of the  $SiO_2$ . Because the rate of hydration at longer hydration times depends on the rate at which reacting ions can diffuse through the layer or hydration product (i.e. C-S-H) around the  $C_3S$  particles, it can be hypothesized that in the presence of colloidal  $SiO_2$  the product layer that forms is less permeable such that the  $C_3S$  particles are effectively sealed off from the liquid in the pore space, stopping hydration.

As shown in Fig. 6, backscattered SEM images of the microstructure reveal significant differences in the product morphology between a pure  $C_3S$  paste (left image)

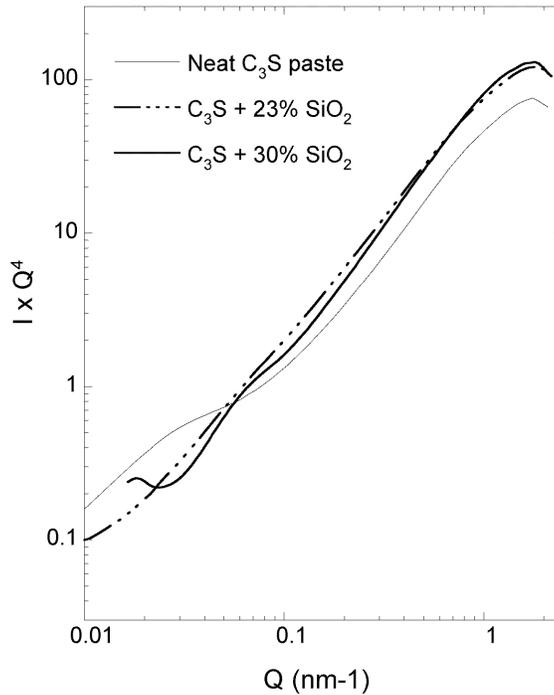


**Figure 6:** Backscattered electron micrographs (LCR). Left: Pure  $C_3S$  paste. Right:  $C_3S$  with colloidal silica, global  $CaO/SiO_2$  ratio of 1.6. The measured  $Ca/Si$  ratio of the C-S-H gel in this paste is 1.2. This value is less than 1.6 because all of the colloidal  $SiO_2$  has reacted but only 74% of the  $C_3S$ .

and a  $C_3S$  paste with colloidal  $SiO_2$  (right image). In the neat  $C_3S$  paste, the C-S-H (dark grey) and  $Ca(OH)_2$  (light grey) effectively fill the pore space creating what appears to be a continuous matrix phase. In the paste made with  $SiO_2$ , a discrete layer of hydration product surrounds each  $C_3S$  particle, leaving large amounts of pore space between the particles. This strongly supports the hypothesis made above that colloidal  $SiO_2$  decreases the degree of hydration by generating a dense, impermeable product layer.

This unexpected result may be attributed to the high reactivity of the colloidal  $SiO_2$  with calcium. After initial mixing, the calcium released by  $C_3S$  dissolution may immediately react with the colloidal  $SiO_2$ , creating C-S-H with a very low  $Ca/Si$  ratio near or on the particle surfaces. The minimum  $Ca/Si$  for C-S-H is believed to be about 0.6. It has previously been shown [3] that when the initial C-S-H that forms during  $C_3S$  hydration has a low  $Ca/Si$ , the degree of hydration at later times is lower. As  $C_3S$  continues to dissolve, the newly released calcium will either react with  $SiO_2$  or will be incorporated into previously formed low  $Ca/Si$  C-S-H, and the average  $Ca/Si$  of the C-S-H will slowly increase with time toward the global  $Ca/Si$  of the paste. However, because a significant amount of  $C_3S$  remained unhydrated at the time of analysis, the  $Ca/Si$  of the C-S-H remained lower than the global  $Ca/Si$  (see Table 1).

<sup>3</sup> S. Garrault and A. Nonat, "Hydrated layer formation on tricalcium and dicalcium silicate surfaces: Experimental study and numerical simulations," *Langmuir*, **17**, 8131-8138 (2001).



**Figure 7:** SANS data for  $C_3S$  pastes made with varying amounts of colloidal silica (See Table 1). For clarity, the SANS data for the paste with 40%  $SiO_2$  is not shown, as it is very similar to that of the paste with 30%  $SiO_2$ .

It should be noted that the above hydration scenario is significantly different from the hydration of a paste containing a pozzolanic material such as silica fume. In the latter case, the reactivity of the added silica is much lower. As a result, the initial hydration of the  $C_3S$  or cement proceeds normally, forming high Ca/Si C-S-H and  $Ca(OH)_2$ , and only at later times does the pozzolanic reaction consume the  $Ca(OH)_2$  to form additional C-S-H and perhaps lower the Ca/Si of the already-formed C-S-H gel.

The SANS response of the  $C_3S + SiO_2$  pastes is shown in Fig. 7. While it might have been anticipated from the above discussion that the lower degree of hydration and the apparently higher density hydration product would lead to less volume fractal scattering and a lower specific surface area, it can be seen that the opposite is the case. The Porod constants, measured solid SLD values, and resulting specific surface area values calculated using Eq. 1 are listed in Table 3. Addition of  $SiO_2$  increases  $S_v$  by 35 – 75% over that of the neat  $C_3S$  paste, despite the lower degree of hydration.

To put these values in context, it is useful to estimate how much C-S-H is present in each  $cm^3$  of paste, to see if the specific surface area of the C-S-H phase itself is

changed by the addition of SiO<sub>2</sub>. The amount of C<sub>3</sub>S hydrating in each paste is taken to be the measured degree of hydration listed in Table 1. For the neat C<sub>3</sub>S paste, the C-S-H is assumed to form with Ca/Si = 1.7 with the remaining calcium going to form Ca(OH)<sub>2</sub>. In the pastes with SiO<sub>2</sub>, all of the silica is assumed to react with the C<sub>3</sub>S to form C-S-H. This gives a calculated value for the Ca/Si of the C-S-H, listed in Table 3. These values are slightly higher than the measured values listed in Table 1, but show the correct trend. In calculating the amount of C-S-H per unit volume, chemical shrinkage is ignored and 1 mole of C-S-H corresponds to 1 mole of SiO<sub>2</sub>, regardless of the amounts of CaO and H<sub>2</sub>O. On this molar basis, the amount of C-S-H increases with the addition of colloidal SiO<sub>2</sub>, and the specific surface area of the C-S-H remains within a rather narrow range of about 27 – 30 m<sup>2</sup>/mmol. This indicates that the nanoscale morphology of the C-S-H may not be greatly different in the pastes made with SiO<sub>2</sub>, an observation also supported by the roughly parallel slopes in the volume fractal region (see Fig. 7).

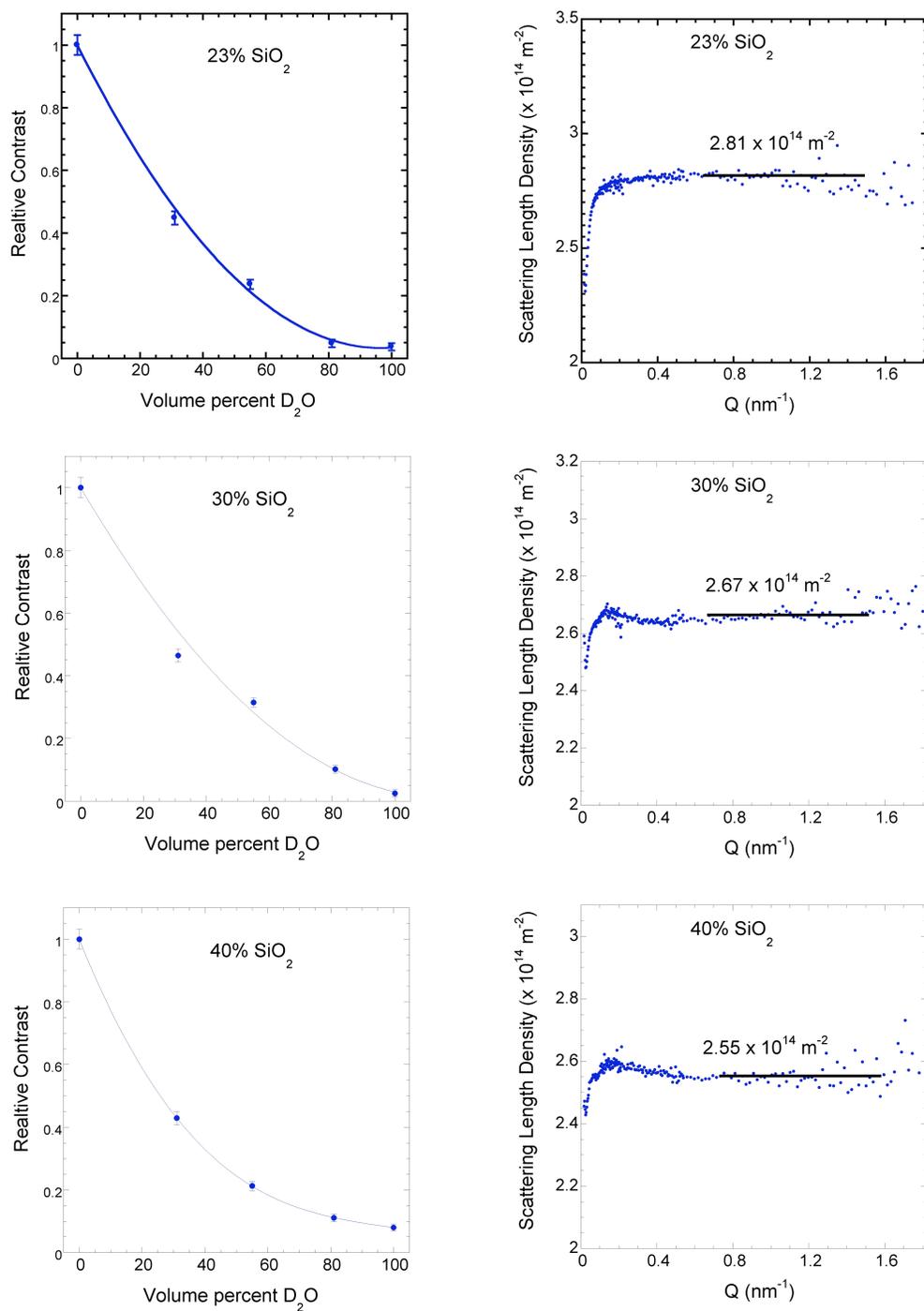
The results of the fluid exchange experiments on the C<sub>3</sub>S + SiO<sub>2</sub> pastes are shown in Fig. 8 (left side). The contrast curves for these pastes are different from all contrast curves we have previously obtained for any cementitious material. This includes pastes made with OPC and silica fume, and C<sub>3</sub>S pastes with low Ca/Si ratios following chemical decalcification [4]. Instead of a minimum near 80% D<sub>2</sub>O, these pastes appear to give contrast minimums close to 100% D<sub>2</sub>O (23% SiO<sub>2</sub>) or to the right of 100% D<sub>2</sub>O (30% and 40% SiO<sub>2</sub>). This indicates that the C-S-H phase in these specimens has a different chemical structure and density than has been previously measured.

**Table 3:** Specific surface area (SSA) values for the specimens made with C<sub>3</sub>S and colloidal silica. For this calculation, 1 mole of C-S-H corresponds to C<sub>x</sub>-S-H<sub>y</sub> (1 mole of SiO<sub>2</sub>).

Ca/Si (Global)	$C_p$	Solid SLD (x 10 <sup>14</sup> m <sup>-2</sup> )	Paste SSA ( $S_v$ ) (m <sup>2</sup> /cm <sup>3</sup> )	C-S-H Ca/Si <sup>a</sup>	C-S-H amt (mmol/cm <sup>3</sup> ) <sup>a</sup>	C-S-H SSA (m <sup>2</sup> /mmol)
3 (no SiO <sub>2</sub> )	76.3	2.59	122	1.7	4.56	26.8
1.6	117.7	2.81	165	1.38	6.11	27
1.4	128.4	2.67	196	1.10	6.41	30.5
1.2	129.5	2.55	212	0.91	7.09	29.9

<sup>a</sup> Calculated from the stoichiometry of C<sub>3</sub>S hydration and the measured degree of hydration,  $\alpha$ .

<sup>4</sup> J. J. Thomas, J. J. Chen, A. J. Allen and H. M. Jennings, "Effects of decalcification on the microstructure and surface area of cement and tricalcium silicate pastes," *Cem. Concr. Res.*, **34**, 2297-2307 (2004).



**Figure 8:** Contrast exchange curves (left) and SLD values (right) for  $C_3S + SiO_2$  pastes. See caption to Fig. 2 and text for more details.

The measurements of the solid SLD values obtained from the methanol/d-methanol exchange experiments are also shown in Fig. 8 (right side). In this case, the results are less surprising. The SLD value is fairly constant across a wide range of  $Q$ , as expected for a paste with a single nanoscale phase, and the fitted SLD values (indicated by the horizontal lines) are not too different from the value obtained for normal C-S-H gel. The SLD values (listed in Table 3) decrease with increasing SiO<sub>2</sub> content. It should be noted that the fact that the SLD values for the neat C<sub>3</sub>S and the paste with the highest SiO<sub>2</sub> loading are similar does not imply that the C-S-H phase itself is similar, as there are many combinations of composition and density that will give the same SLD value (this is why the results of the H<sub>2</sub>O/D<sub>2</sub>O exchange must also be used).

Although the unusual contrast curve results make the results tentative, it is possible to calculate the C-S-H composition and density for the paste with 23% SiO<sub>2</sub> by assuming a matchpoint close to 100% D<sub>2</sub>O (see Table 2). Compared to the results for the AAS paste (which has a similar Ca/Si ratio) this paste has a higher water content (H<sub>2</sub>O/SiO<sub>2</sub> = 1.55 vs. 0.97) and also a slightly higher density (2800 kg/m<sup>3</sup> vs. 2760). As the addition of water to C-S-H should in general make the density decrease, this result suggests a very different chemical structure in the C-S-H.

## 6. Suggested future work

The original motivation for this project was to study the lower Ca/Si C-S-H phases that form in blended cements made from pozzolanic materials. As the system C<sub>3</sub>S + colloidal SiO<sub>2</sub> appears to not be representative of blended cement systems in general, the obvious next step is to test blended cements directly. To facilitate the analysis, the best way to do this is with blends of C<sub>3</sub>S and silica fume, as this remains within the CaO-SiO<sub>2</sub>-H<sub>2</sub>O system. The combination of the SANS analysis by the NWU team with the characterization of degree of hydration and C-S-H Ca/Si ratio by LCR should allow a full and definitive characterization of the C-S-H phase for this system that would likely apply to other blended cements. In addition, these experiments will make a fascinating comparison with the C<sub>3</sub>S + colloidal SiO<sub>2</sub> results discussed above, possibly resulting in a more definitive interpretation.