ANALYSIS OF C-S-H GEL BY SMALL-ANGLE NEUTRON SCATTERING

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Abstract
The role of small-angle x-ray and neutron scattering (SAXS and SANS) in the characterization of cement is briefly reviewed. The unique information obtainable from SANS analysis of C-S-H gel in hydrating cement is compared with that obtainable by other neutron methods. Implications for the nature of C-S-H gel, as detected by SANS, are considered in relation to current models.

Keywords
Small-angle scattering; SANS; SAXS; microstructure characterization, Portland cement.

Introduction
The quantitative and statistically-representative characterization and modeling of hydrating cement microstructures using both small-angle neutron and x-ray scattering (SANS and SAXS) has been pursued by groups from around the world, e.g., [1-13]. When a neutron or x-ray beam passes through a material, a component of the beam may be scattered out of the incident beam direction by a small angle due to heterogeneities within the microstructure. The angular profile of the small-angle scattered (SAS) intensity is effectively a Fourier transform of this microstructure. In principle, the angular width, intensity, and the scattering profile can be analyzed to determine the statistically-representative size distribution, volume fraction and form of the scattering features [14]. In practice, the data are interpreted using an appropriate microstructure model, and the microstructure is quantified through the parameters obtained. SAS techniques are particularly useful for investigating calcium-silicate-hydrate (C-S-H) gel structure, given that amorphous C-S-H renders diffraction ineffective. Also, the gel can be affected by sample preparation, requiring great care to be taken for methods such as electron microscopy. By comparison, the sample preparation required for SAS does not disturb the microstructure. Furthermore, the CSH gel structure, which exhibits fractal properties, extends over length scales that are appropriate for SAS.

Quantifying C-S-H structure is complicated by the presence of water (H) in various states ranging from OH groups to trapped liquid in the nanoscale pores. A further complication is the presence of calcium hydroxide (CH) crystals in intimate mixture with C-S-H [15]. This makes it necessary to determine the fine and coarse CH structure at length scales from nanometers to tens of micrometers so that the C-S-H can be unambiguously characterized. SANS studies can address these issues in two ways. The strong isotope effect in neutron scattering enables much information to be gained from H/D contrast variation studies. The recent development of practical ultra-SANS (USANS) instrument configurations provides access up into the 10-micrometer scale regime [16].

The quantitative microstructure analysis of CSH gel by combined SANS and USANS is of particular interest, especially when the results are compared with those of quasielastic neutron scattering (QENS) which can measure the different states of free and bound water [17], and inelastic neutron scattering (INS), which can measure the amount of CH formation [18]. SANS/USANS data from cement exhibit characteristic hallmarks of the C-S-H microstructure from which a picture of the C-S-H gel morphology can be discerned.
Small-angle scattering and the difference between SANS and SAXS

Figure 1 shows a schematic of a SANS experiment together with typical data for a hydrating Portland cement. The data shown are normalized to the incident beam intensity and corrected for both sample absorption and other background scattering effects (including a significant flat background subtraction at high Q for both SAXS and SANS), and have been circularly-averaged about the incident beam direction. The scattering cross-section, $d\Sigma/d\Omega$, is a material property (for x-ray or neutron scattering) and is the probability per unit sample volume of scattering into unit solid angle about a direction corresponding to the scattering vector, Q. The direction of Q bisects the incident and scattered beam directions and has magnitude, $Q = (4\pi/\lambda)\sin\theta$ where $\lambda$ is the neutron or x-ray wavelength and $\theta$ is half the angle of scatter, $\phi_S$. On a log-log plot of $d\Sigma/d\Omega$ versus Q the general shape of the curve is similar for SAXS and SANS. However, SAXS values of $d\Sigma/d\Omega$ are significantly larger than for SANS. SAXS arises due to x-ray photon scattering from whole atoms (or ensembles of atoms) and the scattered intensity varies with the square of the electron number density; SANS arises due to neutron scattering from the atomic nuclei and the scattered intensity fluctuates through the periodic table with some strong isotope effects. In particular the SANS from H or H$_2$O is significantly different to that from D or D$_2$O. Thus, the scattering contrast for hydrating cement can be varied by changing the H/D ratio in the pore water, or other pore fluid.

![SANS Instrument Schematic and Example of SANS Data](image)

Figure 1. SANS experiment schematic and example of SANS data for cement.

**Analysis of SANS data**

Many microstructure models are now available [19], from use of the Guinier approximation for particulate systems to sophisticated size distribution analyses, modeling of coherently ordered microstructures, and characterization of fractal morphologies. Generally, an inverse-Q relationship exists between scattering and scattering size. Typically, the data are analyzed to provide a quantitative measure of a model microstructure based on an interpretation established from microscopy. Occasionally, hallmarks appear in the data, associated with particular morphologies. These include peaks when interference effects occur in an ordered or periodic microstructure, $Q^1$ scattering for long capillary structures, or $Q^2$ scattering for sheets or membranes.
Fractal versus other microstructures for C-S-H gel

It must be stated that the $Q^2$ scattering that would be indicative of a possible sheet-like C-S-H structure has not been observed for cement systems, except where extensive leaching has reduced the overall Ca/Si ratio to less than 1.5 [13]. This does not preclude a sheet structure for C-S-H at the nanometer scale if this is folded up within the observed C-S-H microstructure, but it does preclude an extensive sheet-like morphology. Instead, as Figure 1 indicates, the data can be interpreted using a combination of surface-fractal and mass- or volume-fractal components, together with a building block globule size of diameter 5 nm or less. Mass-fractal structures are characterized by non-integral power law $Q^{-D_v}$ scattering where (usually) $2 < D_v < 3$; surface-fractal structures are characterized by non-integral power law $Q^{-4-D_s}$ scattering where $2 < D_s < 3$ so that the scattering exponent is between 3 and 4. Our general interpretation of the data in Figure 1 is that the gel globules and mass-fractal structure comprise the C-S-H low-density or outer-product structure in hydrating cement, and that the surface-fractal structure arises where this decorates clinker grains or other coarse features. A quantitative model can determine not only the fractal exponents, $D_v$ and $D_s$, but also C-S-H volume fractions, surface areas, and the correlation lengths that define the size regimes for fractal scaling [10]. In recent years, this fractal interpretation has proven useful for following cement hydration in real time, for exploring the effects of cement additives (e.g., silica fume), and for assessing the microstructural results of leaching. However, an absolute determination of the microstructure parameters depends not only on absolute calibration of the SANS or SAXS data but also assumes an accurate knowledge of the scattering contrast for C-S-H gel. This issue remains a challenge due to the uncertain nature of C-S-H, and is a subject of ongoing research by the authors. SANS contrast variation studies are central to such efforts.

Scattering invariant

In principle, scattering theory provides a method to circumvent uncertainties in the C-S-H scattering contrast, through application of the scattering invariant, $Q_{\text{INVARIANT}}$, given by:

$$Q_{\text{INVARIANT}} = 2\pi^2\Phi_t (1 - \Phi_t) |\overline{\rho}|^2 = \int_0^Q Q^2 \frac{d\Sigma}{d\Omega}(Q) dQ$$

(1)

where $\Phi_t$ is either the solid volume fraction or the porosity and $|\overline{\rho}|^2$ is the scattering contrast between the voids and the solid phase. Independent knowledge of the cement porosity, set to either $\Phi_t$ or $(1 - \Phi_t)$ affords a value of $|\overline{\rho}|^2$ if the $Q^2$-weighted SANS or SAXS data are integrated across the Q-range as indicated in equation (1). This approach was taken in early SAXS studies of cement [1]. However, Figure 2 indicates limitations in this method. The integral must be taken over all Q, not just the Q-range measured. This implies that an extrapolation must be made both to $Q = 0$ and to $Q = \infty$ (or at least, $Q = 4\pi/\lambda$). Figure 2 shows how significant parts of the integral fall outside the measured Q-range. If this is ignored $Q_{\text{INVARIANT}}$ can be underestimated, leading to a spuriously high surface to solid-volume surface-area determination if derived from a comparison of the above equation with that for the Porod scattering: $d\Sigma/d\Omega = 2\pi|\overline{\rho}|^2 S_f /Q^4$, where $S_f$ is the surface area per unit sample volume. (The unknown $|\overline{\rho}|^2$ cancels out in the comparison. Difficulties in making the data extrapolation arise from uncertainty in the high values of $d\Sigma/d\Omega$ at low Q, and in the flat background subtraction at high Q (note data are $Q^2$-weighted). Thus, absolute determination of $d\Sigma/d\Omega$ and $|\overline{\rho}|^2$ for both SANS and SAXS is preferred over the scattering invariant method in investigations of hydrating cement.
Distinguishing the calcium hydroxide component

Ultrasmall-angle scattering (USAXS and USANS) instruments apply crystal diffraction optics to obtain SAXS or SANS data to much lower Q values than can be obtained using the conventional geometry shown in Figure 1 [16]. USANS extends the range to particularly low Q, as indicated in Figure 3. By combining SANS and USANS for different H/D blends it has been possible to discern the microstructure of the CH component within cement. This is because the formula and density for CH are well-known, the OH groups do not exchange to become OD, and a contrast match point occurs with the pore water at 32 % D₂O. Such knowledge permits the CH SANS component to be subtracted out, leaving the SANS overwhelmingly associated with C-S-H.

Relationship of SANS to other neutron methods

At wavelengths useful for structural investigation of materials, neutrons have energies close to the thermal energies of molecular vibration (unlike x-rays for which the energies are much higher). Furthermore, the incoherent neutron scattering cross-section for H is particularly high. Thus, inelastic neutron scattering (INS) can measure molecular vibration spectra [18], particularly when H-bonding or OH groups are involved as in C-S-H or CH, and quasielastic neutron scattering
(QENS) can exploit the effects of neutron recoil from protons of approximately the same mass in order to interrogate the free or bound state of water within C-S-H gel, and elsewhere within a cement [17]. INS studies have recently provided significant information on the bonding within C-S-H, as well as on the total CH formation, including nanoscale CH embedded in C-S-H [18]. This contrasts with neutron and x-ray diffraction methods that measure the micrometer scale crystalline CH formation. QENS measurements are particularly valuable in quantifying the changes in the state of the cement pore water as it is incorporated into C-S-H gel and CH during the hydration process. Figure 4 shows the time dependence of the bound water content with hydration time. As with INS data, the QENS time dependence closely follows calorimetric measurements of the hydration reaction heat output. This is to be expected given that both INS and QENS measure changes associated directly with the hydration chemistry. However, while the microstructure changes measured by SANS or SAXS (increase in surface area and in the fractal microstructure development) follow the reaction chemistry through the time of the main hydration peak, this does not continue over more extended periods. The measurable microstructure changes in subtle ways after the first 24 h, but the dense or inner-product C-S-H produced from continued hydration is not obviously visible to SANS or SAXS.

![Figure 4. Time dependences of SANS, reaction heat output and QENS during hydration.](image)

**Issues for further consideration**

SAXS, SANS, INS and QENS studies of hydrating cement systems, and of C-S-H gel in particular, reveal a number of questions for further investigation: How is the C-S-H globule/fractal picture of C-S-H associated with SAXS and SANS to be reconciled with the various other particulate and sheet morphologies associated with characterization methods such as electron microscopy? What is the dense or inner product morphology of C-S-H and why is it virtually invisible to SAXS or SANS? To what extent and under what conditions can inner product and outer product C-S-H transform between each other? Our knowledge and understanding of cements and C-S-H gel are now sufficient that it is timely to consider how such questions might be answered.

**References**