

USAXS studies of calcium-silicate-hydrate gel in cement

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Introduction

Over the past 25 years, various small-angle x-ray scattering (SAXS) and small-angle neutron scattering (SANS) studies have been carried out to characterize and quantify the microstructures of complex cementitious materials [1-7]. Both SAXS and SANS data are dominated by the microstructure of the main cement hydration product, amorphous calcium-silicate-hydrate (C-S-H) gel. The exact composition and density of C-S-H remain uncertain, but the formula is assumed to be of the form $x(\text{CaO}) \cdot y(\text{SiO}_2) \cdot z(\text{H}_2\text{O})$, denoted $\text{C}_x\text{S}_y\text{H}_z$ in cement notation, with x around 1.7 and the density dependent on the number of molecules of water, z , associated with the C-S-H solid phase [7]. The solid/pore C-S-H gel structure is observed to be fractal over a wide range of length scales [2,4], but there is considerable disagreement between SAXS and SANS in quantifying the amount of C-S-H as a function of hydration time [6]. Evaluation of the total surface area, an important parameter influencing both the rheology and permeability of concretes, has proven particularly difficult to reconcile. Reported SAXS values [1,3,4] for the surface area of Portland cement (PC) have been two to six times higher than the equivalent SANS values [2,5,6]. Previous SAXS results usually have been obtained from slit-smear experiments by applying the “scattering-invariant” technique to uncalibrated scattered intensity data and assuming an overall volume fraction of porosity for the scattering phase. SANS studies have assumed a scattering contrast between solid C-S-H and the pore space to extract results from pinhole geometry data calibrated against a scattering standard. In either case, one challenge has been to subtract out the large flat background in order to expose the true small-angle scattering at Q values up to 0.2 \AA^{-1} and beyond.

Double-crystal Bonse-Hart ultrasmall-angle x-ray scattering (USAXS) instruments offer a primary absolute intensity calibration with respect to the incident beam, provided that the detector has linear sensitivity over sufficient dynamic range. Unfortunately, until recently USAXS instruments have not possessed a sufficiently flexible double-crystal geometry to obtain SAXS data beyond about 0.05 \AA^{-1} . This situation has changed with the commissioning of the new USAXS facility at UNI-CAT on the Advanced Photon Source (APS) sector 33-ID [8]. Third-generation synchrotron brilliance, combined with a flexible measurement geometry that allows the analyzing crystals to be moved close to the sample position, has increased the maximum Q to about 0.25 \AA^{-1} for slit-smear absolute-calibrated USAXS data arising from 0.5 mm thick coupons of cement. After desmearing, these data can be compared directly with SANS studies on equivalent samples.

Methods and Materials

Hydrated PC coupons were prepared with thicknesses between 0.38 mm and 0.52 mm and studied by USAXS at hydration times ranging from 14 days to two months. In addition, coupons of hydrated tricalcium silicate (the most active component within Portland cement, denoted C_3S) and a few other cement variations previously studied by SANS were also measured. All samples were studied wet, inside sealed liquid sample cells to ensure that the pore system was saturated with water and a C-S-H: H_2O scattering contrast could be assumed. The objectives of the USAXS experiments were: (i) to compare desmeared USAXS and SANS absolute-calibrated data over an extended Q -range and determine whether the two techniques interrogate the same microstructure; (ii) to determine possible formulae and densities for the C-S-H solid phase that give consistent quantitative results for SAXS and SANS; (iii) to evaluate total surface area values that are consistent between the two techniques; and (iv) to exploit the USAXS capability at ultrasmall Q to extend the microstructural characterization of hydrating cements to coarser length scales than previously studied.

USAXS measurements were carried out using the UNI-CAT USAXS facility with Si(111) optics, 10 keV x-rays (wavelength = 1.24 \AA), and a six-reflection geometry both within the collimating channel-cut crystal before the sample and within the analyzing pair of independent crystals after the sample. The analyzing crystal pair was rocked to give a measured Q -range from 0.00015 \AA^{-1} to 0.25 \AA^{-1} . This large maximum Q value was attained by moving the analyzer monolith close to the sample position so that the distance from the sample to the first analyzer reflection was only 30 mm. This had the effect of ensuring that all of the scattered-beam reflections remained within the analyzer crystal system as it was rocked without intensity spilling over the front or back of either crystal. The slit-smear USAXS data were corrected for background scattering and multiple scattering at low Q , calibrated against an empty-cell blank run, and desmeared using the Lake desmearing program. Correction for multiple scattering effects at low Q was made by integrating the sample and empty-cell data out to Q -values beyond which multiple scattering from the sample was negligible, and using the ratio of these integrals to correct the incident beam normalization. This increased the minimum Q -value, for data with no significant multiple scattering, to 0.0005 \AA^{-1} , still considerably less than the minimum Q in the SANS studies.

Results

Figure 1 shows the absolute-calibrated desmeared USAXS data for a typical 28 day-old PC, together with absolute-calibrated SANS data for comparison. On a log-log scale, the SAXS and SANS data are virtually parallel to each other throughout most of the Q-range of overlap, indicating that for both techniques, the scattering originates from the same microstructural features. The SAXS data are more than a magnitude more intense due to the x-ray scattering contrast being much stronger than that for neutrons. Slight deviations between the datasets can be attributed to relatively greater SAXS intensity arising from microstructural components other than C-S-H gel, particularly at lower Q values from coarse calcium hydroxide crystals (CH in cement notation), the other principal cement hydration product. Nevertheless, the USAXS data indicate that the surface-fractal scattering, observed by SANS, extends to lower Q, and hence to coarser scale lengths than measured previously.

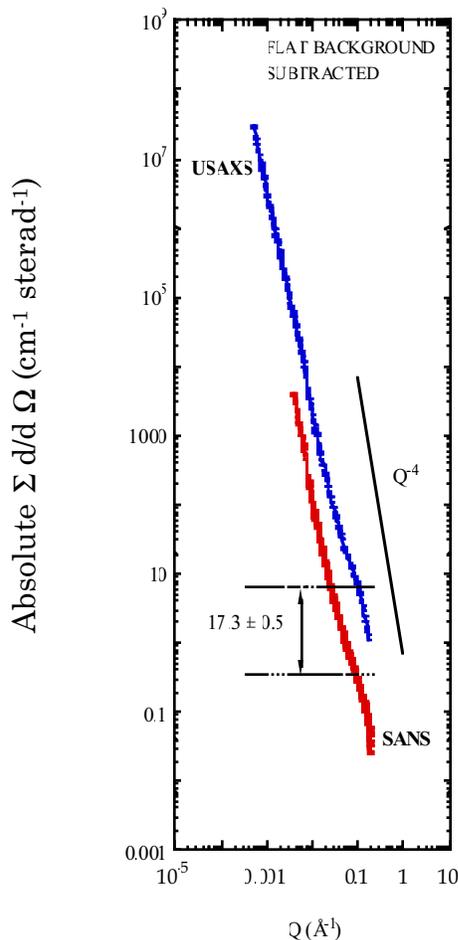


Figure 1: Absolute-calibrated USAXS and SANS data.

A comparison of the SAXS data at high Q with the SANS data, for the various cement studied, indicates a ratio of SAXS/SANS intensities of 17.3 ± 0.5 . This compares with a theoretical ratio of 13.6 for a previously proposed solid

$C_{1.7}S.H_{2.1}$ phase having a density of 2.18 g cm^{-3} [7]. This implies that the surface area, obtained by applying the Porod scattering law at high Q ($0.14 - 0.20 \text{ \AA}^{-1}$) with the x-ray and neutron scattering contrasts for this C-S-H phase in water, will be 27% higher for SAXS than for SANS. A slightly greater C-S-H density and/or slightly less water in the structure would account for this discrepancy. Either way, application of Porod's law for USAXS or SANS indicates a total surface area per unit volume of $\sim 150 \text{ m}^2\text{cm}^{-3}$ for 28 day PC paste, which is $\sim 95 \text{ m}^2\text{g}^{-1}$ for so-called "D-dried" cement. This is within the range of previously reported SANS surface areas, and is significantly less than the reported SAXS values that range from 200 to $600 \text{ m}^2\text{g}^{-1}$ for D-dried cement.

Discussion

Absolute determination of a representative solid $C_xS.H_y$ phase depends on evaluating three unknowns: x, y, and the density. Unfortunately, a comparison of USAXS with SANS, together with SANS H_2O/D_2O contrast variation studies, are insufficient to determine these unknowns because both the free (pore) and bound water are readily exchangeable in such experiments, and the incremental density of the bound water component of C-S-H appears not to be greatly different from 1 g cm^{-3} . The situation is further complicated by differences in the contrast results for PC, C_3S , and other cement types, which have revealed the presence of small amounts of finely divided nonexchanging CH within the C-S-H structure. Thus, absolute determination of the C-S-H phase must await a CH_3OH/CD_3OH contrast exchange study, together with a corresponding SAXS/SANS comparison to ensure that the methanol-saturated C-S-H structure remains the same as the water-saturated one. Calculations suggest that such studies will have little sensitivity to the CH phase, but should succeed in discriminating among the possible $C_xS.H_y$ phases.

The absolute-calibrated USAXS experiments have removed the apparent discrepancy between SAXS and SANS surface areas for cement, giving values well within the previously reported SANS range. Why were the previous SAXS surface areas, based on using scattering invariant methods, so much higher? One issue may arise from the " $Q^2I(Q)$ " integral evaluated in the scattering invariant method [where $I(Q)$ is the desmeared scattered intensity]. The integral must be evaluated over all Q, not just in the Q-range measured. Extrapolation of the present data suggests that half of the final integral value arises from the extrapolation rather than from the actual measured data. Underevaluation of this integral would result in a proportionate overestimate of the surface area. Also, the scattering invariant method requires an estimate of the total porosity, and it is not clear, *a priori*, how much of the open C-S-H structure should be included.

While the final surface area values may be adjusted as a result of the remaining experiments, it is clear that USAXS and SANS surface areas for cement are close to those obtained using nitrogen BET measurements, whereas the higher values previously reported for SAXS are close to

those given by NMR or water sorption measurements [7]. Small-angle scattering appears to interrogate the solid/pore microstructure defined by the interface between solid $C_xS_yH_z$ and free pore H_2O . SAXS and SANS are insensitive to the internal C-S-H structure that is probed in water sorption and NMR studies. Thus, SAXS, SANS, and nitrogen BET surface areas should be those controlling permeability and rheological properties, while a comparison with water-sorption and NMR studies should provide further insights into the nature of C-S-H gel.

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