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Determination of the Neutron Scattering Contrast of Hydrated Portland Cement Paste using H_2O/D_2O Exchange

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Accurate measurements of the surface area of cement based materials using small-angle neutron scattering (SANS) require determination of the neutron scattering contrast between the C-S-H gel and H_2O. Because the C-S-H gel has a poorly understood structure and a variable composition, calculated values of the C-S-H:H_2O neutron scattering contrast based on an assumed C-S-H chemical composition and density are subject to error. The C-S-H:H_2O neutron scattering contrast was determined experimentally by measuring the change in apparent surface area as the H_2O in a hydrated cement specimen was replaced with D_2O, resulting in a new value of 6.78×10^{28} m^{-4}. This new contrast value increases some previously reported SANS surface area values by 21%. The results also confirm that C-S-H interlayer water should be included in the solid phase whereas gel pore water should be excluded. ADVANCED CEMENT BASED MATERIALS 1998, 7, 119–122. *© 1998 Elsevier Science Ltd.*

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Small-angle neutron scattering (SANS) is a powerful technique for characterizing the microstructure of colloidal or porous materials. A coherent beam of neutrons passes through a thin specimen, and a small fraction of the beam is scattered out of the incident beam direction by interfaces between the microstructural phases, including pores. The resulting scattering curve, which consists of the normalized scattered intensity as a function of scattering angle, can be analyzed to determine such parameters as microstructural size distributions, the pore volume, and the surface area.

SANS is particularly useful for measuring the surface area of cement paste because it is noninvasive and can be performed on saturated specimens. By avoiding the drying treatment required for gas sorption surface area measurements, the C-S-H[1] gel, which contains much of the surface area of cement paste, is probed in its natural, fully saturated state. Previous SANS experiments conducted on cement have resulted in reported surface area values in the range from 100 to 150 m^2 cm^{-3} for 28-day-old OPC [1]. Although this is perhaps 50% higher than values obtained from nitrogen gas sorption measurements [2], it is about three times lower than the lowest values reported from small-angle X-ray scattering (SAXS) [3].

In a two-phase specimen, the total internal surface, S_V, between the two phases as determined from small-angle scattering can be written [1] as:

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

where C_P is the Porod constant and $|\Delta\rho|^2$ is the scattering contrast. For isotropically scattering microstructures, the Porod constant is determined from the circularly averaged scattering data (about the incident beam direction) at high scattering angles. In this so-called Porod regime, the scattered intensity varies as C_P/Q^4, where Q is the scattering vector given by $(4\pi/\lambda)\sin(\phi_s/2)$, ϕ_s is the angle of scatter, and λ is the neutron wavelength.

The scattering contrast is a parameter that measures the intrinsic strength of the neutron scattering interaction between the two phases. For cement based materials, the surface area is almost entirely that between the C-S-H gel and the pore H_2O; therefore, for a saturated specimen the neutron scattering contrast can be written as:

$$|\Delta\rho|^2 = (\rho_{csh} - \rho_{h_2o})^2 \quad (2)$$

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[1] Cement chemistry notation: C = CaO, S = SiO_2, H = H_2O, D = D_2O.

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where ρ_{csh} and ρ_{h_2o} are the neutron scattering length densities of C-S-H and water. These parameters can be calculated from the average chemical composition and density of each phase using published tables for the strength of the neutron interaction [4]. This approach is satisfactory for well-defined phases such as water, but it presents a problem for the C-S-H gel, which has a variable composition and a poorly defined structure.

A particular problem with the composition of C-S-H gel is that it is not clear how much water should be included for the purpose of calculating ρ_{csh}. Some of the water in C-S-H is chemically bound into the structure, while there is additional water that is loosely bound in the interlayer spaces and within the gel pores. The formula and density that should be assigned to C-S-H for the purposes of calculating ρ_{csh} depend on how much of this water interacts with the neutrons as if part of the solid C-S-H phase, which is not known *a priori*. Since the calculated value of ρ_{csh} is strongly sensitive to the amount of water assigned to C-S-H, it is important to establish this value accurately. The value of ρ_{csh} used in many published SANS results [1] was calculated using a C-S-H formula of $C_{1.5}SH_{2.5}$ and a density of 2.18 g cm^{-3}, which are average values commonly quoted in the literature. In recent years, an improved understanding of the nature of the C-S-H gel has led to the proposal of new formulae and densities, with variations predicted for different moisture conditions within the sample [5].

In principle, the correct neutron scattering contrast for cement can be determined experimentally by taking advantage of the large difference in neutron scattering length density between H_2O and D_2O (heavy water). Previous experimental studies of the change in the scattering contrast with D_2O content (which utilized the above C-S-H formula and composition) [6] have established that, when a hydrated cement paste is placed into D_2O, the D_2O exchanges fully with both the pore water and the water in the C-S-H gel, including structural water existing as OH^- groups, which greatly alters the scattering contrast. We now report new, more accurate, contrast variation measurements, based on varying the H_2O/D_2O ratio. The aim was to select the appropriate C-S-H formula and density scenario from those now available and thereby to infer a more correct value of the contrast to use in eq 1 than has been used in previous SANS studies.

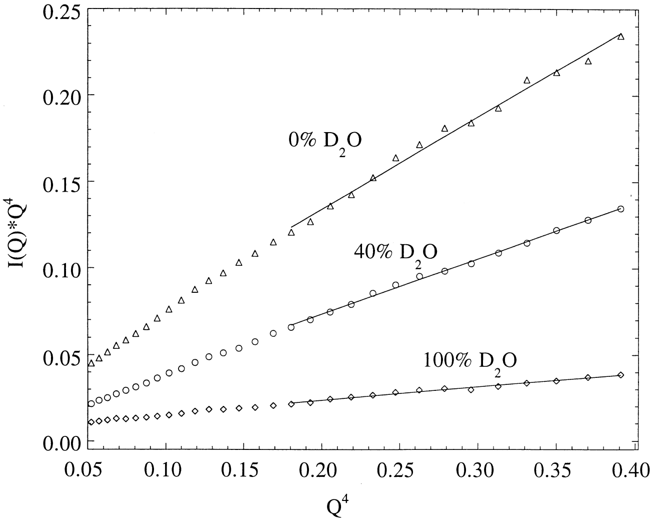

FIGURE 1. SANS data for the 0% D_2O (no exchange), 40% D_2O, and 100% D_2O specimens, plotted as I × Q^4 vs. Q^4, where *I* is the normalized scattering intensity and *Q* is the scattering vector. The lines are linear fits used to calculate the Porod constants.

Experimental

A 28-day-old ordinary Portland cement (OPC) paste with a water/cement ratio of 0.35 was used for this experiment. Six 1-mm-thick coupons with cross-sections of 10 mm × 20 mm were cut from the specimen using a diamond wafering blade, a standard procedure for preparing hydrated cement specimens for SANS. Each coupon was placed into one of six separate mixtures of H_2O and D_2O containing 0%, 20%, 40%, 60%, 80%, and 100% D_2O on a molar basis. Each fluid volume was 10 ml, enough to ensure that the H_2O in the specimen did not significantly alter the overall H_2O/D_2O ratio. The specimens remained in the mixtures for 24 hours, allowing both the pore fluid and C-S-H gel to reach the same H_2O/D_2O ratio as in the surrounding mixture. Previous experiments have indicated that full exchange in a thin cement specimen occurs in a matter of hours [1,6].

Each specimen was sealed into a quartz optical cell along with a small amount of the exchange fluid to ensure that it remained saturated. Then the neutron scattering data were obtained using a neutron wavelength of 0.8 nm. These experiments were conducted using the NIST/NSF[2] 30 m SANS instrument at the National Institute of Standards and Technology Center for Neutron Research, Gaithersburg, Maryland. For each specimen, the Porod constant, C_P, was obtained. Figure 1 shows the experimental SANS data plotted as I(Q) × Q^4 vs. Q^4 for the 0% D_2O, 40% D_2O, and 100% D_2O specimens, along with linear fits to the Porod regime data. The Porod constant, C_P, is the intercept of the linear fit at $Q^4 = 0$.

Since the specimens all had the same surface area, normalizing the Porod constants to the value obtained from 100% H_2O allowed the relative scattering contrast

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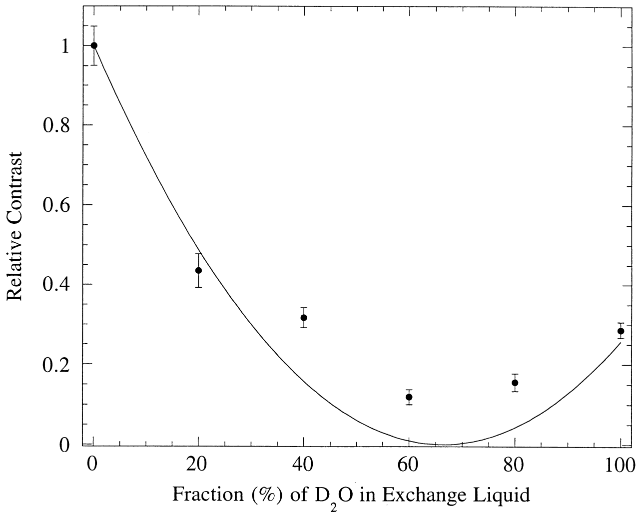

FIGURE 2. Relative neutron scattering contrast as a function of the amount of D_2O in the exchange liquid. The solid circles are the experimental data and the line is the predicted contrast curve obtained from case 3 shown in Table 1. Estimated standard uncertainties are shown for each data point.

as a function of D_2O content to be obtained. These six experimental data points are plotted in Figure 2.

Results and Discussion

To determine the correct C-S-H:H_2O scattering scenario, the relative scattering contrasts for the various chemical compositions and densities of C-S-H were calculated as a function of D_2O replacement, giving predicted contrast variation curves that could be compared with the experimental data.

Table 1 lists the composition, density, and neutron scattering length density of the phases used in the calculations. Case 1 represents the C-S-H used to calculate the previously used contrast value. Cases 2–4 represent experimentally determined values for C-S-H in mature OPC paste under different humidity conditions, as provided by Taylor [5]. Case 2 is C-S-H in a fully saturated paste, for which the water in the gel pores is considered to be part of the C-S-H structure. Case 3 represents C-S-H dried to 11% relative humidity (RH), at which point it is assumed that the gel pores have been emptied of water but all the interlayer water remains. Case 4 represents C-S-H that has been D-dried, the standard drying procedure used for preparing cement specimens for gas sorption. D-drying removes not only the water in the gel pores but also some of the water bound into the interlayer spacings. The neutron scattering length densities of the liquid and of the C-S-H gel phase at D_2O contents between 0% and 100% were calculated using the rule of mixtures. The scattering contrast between C-S-H and water, and between C-S-D and D_2O, is also listed in Table 1 for each case. Note the large variation in the C-S-H:H_2O contrast as a function of C-S-H water content.

For each C-S-H composition, the predicted contrast curve as a function of D_2O content is a parabola with a minimum value of zero, which occurs when $\rho_{\text{liquid}} = \rho_{\text{csh}}$. The quality of the agreement between the calculated curves and the experimental data was analyzed by comparing the positions of the contrast minima and the relative contrast values at 100% D_2O. It should be noted that the experimentally measured contrast never goes to zero because scattering contributions from other cement phases such as CH become non-negligible at intermediate levels of D_2O. The results of the experimental and predicted fits are listed in Table 2. The best agreement based on these criteria is clearly for case 3: C-S-H with the water removed from the gel pores. The predicted contrast variation for case 3 is shown with the experimental data in Figure 2.

The new contrast value of 6.78×10^{28} m^{-4} is 21% lower than that obtained previously using the case 1

TABLE 1. Calculated neutron scattering length density and contrast values

	Phase	Formula	Density (g/cm^3)	Neutron Scattering Length Density [4] ($\times 10^{14}$ m^{-2})	Neutron Scattering Contrast ($\times 10^{28}$ m^{-4})
	Liquid	H_2O	1.00	−0.560*	—
		D_2O	1.11	6.339	—
Case 1	Average C-S-H	$C_{1.5}SH_{2.5}$	2.15	2.283	8.083†
		$C_{1.5}SD_{2.5}$	2.18	4.299	4.162
Case 2	Saturated C-S-H	$C_{1.7}SH_4$	1.90	1.353	3.660
		$C_{1.7}SD_4$	1.97	5.549	0.624
Case 3	11% RH C-S-H	$C_{1.7}SH_{2.1}$	2.18	2.043	6.776
		$C_{1.7}SD_{2.1}$	2.23	5.018	1.745
Case 4	D-dried C-S-H	$C_{1.7}SH_{1.4}$	2.70	2.813	11.377
		$C_{1.7}SD_{1.4}$	2.74	5.430	0.826

*Note the negative scattering length density for H_2O.

†This value is slightly different from that previously quoted (8.35×10^{28} m^{-4}) due to updates in international neutron scattering tables.

TABLE 2. Fit parameters for experimental and predicted contrast curves

Contrast Curve	Type of C-S-H	Position of Contrast Minimum (% D_2O)	Relative Contrast at 100% D_2O
Experimental	(28-day-old OPC paste)	68	0.287
Case 1	Average	58	0.515
Case 2	Saturated	71	0.170
Case 3	11% RH	66	0.258
Case 4	D-dried	79	0.073

scenario in Table 1. This implies an associated 21% increase in the values of cement surface areas obtained from SANS, which is some two to three times the statistical uncertainty associated with independent SANS measurements. Even with this adjustment, SANS surface area values remain much lower than reported SAXS surface areas, which, after conversion to the standard units used for SANS, range from around 400 $m^2\ cm^{-3}$ [3] to over 900 $m^2\ cm^{-3}$ [7,8]. It should be noted that the X-ray scattering contrast is not altered by exchange with D_2O, so the contrast variation technique cannot be used to obtain the SAXS contrast. In practice, SAXS surface area values for cement have been calculated using a different method of data analysis that avoids using the scattering contrast by making different assumptions concerning the total scattered intensities. Although more affected than SANS by uncertainties in the moisture conditions, SAXS data can be analyzed in a similar way to SANS. The corresponding SAXS contrast for the proposed case 3 scenario is $92.16 \times 10^{28}\ m^{-4}$.

While the cements studied were in a saturated condition with the H_2O/D_2O pore fluid flooding the pore system, the C-S-H gel formula and density giving the best agreement with the experimental contrast curve were obtained for solid C-S-H excluding any gel pore water, equivalent to 11% RH drying. Since most of the SANS surface area consists of the interface between solid C-S-H and its gel pores, one would not expect to find that the gel pore water should be included in the solid C-S-H phase (as with case 2). Also, since SANS is insensitive to features as small as the C-S-H interlayer spacings (~0.1 nm), it is to be expected that all the interlayer water should be included in the solid C-S-H and not excluded as in case 4.

Summary

The change in relative neutron scattering contrast of a hydrated OPC specimen was measured as a function of D_2O replacement. The resulting contrast curve was consistent with a C-S-H gel phase with composition $C_{1.7}SH_{2.1}$ and a density of 2.18 $g\ cm^{-3}$. These values are obtained when the interlayer water is included in the solid C-S-H phase but the gel pore water is not. The new C-S-H:H_2O neutron scattering contrast is $6.78 \times 10^{28}\ m^{-4}$, which is 21% lower than a previously assumed value based on an "average" C-S-H formula and density.

References

1. Allen, A.J.; Oberthur, R.C.; Pearson, D.; Schofield, P.; Wilding, C.R. *Phil. Mag. B* **1987,** *56*, 263–288.
2. Rarick, R.L.; Bhatty, J.I.; Jennings, H.M. In *Materials Science of Concrete IV*; Skalny, J.; Mindess, S., Eds.; American Ceramic Society: Westerville, OH, 1994; pp 1–36.
3. Beddoe, R.E.; Lang, K. *Cem. Concr. Res.* **1994,** *24*, 605–612.
4. Sears, V.F. *Neutron News* **1992,** *3*, 26–37.
5. Taylor, H.F.W. *Cement Chemistry*; Academic Press: San Diego, CA, 1990.
6. Allen, A.J.; Baston, A.H.; Wilding, C.R. *Mater. Res. Soc. Symp. Proc.* **1989,** *137*, 119–125.
7. Winslow, D.N.; Diamond, S. *J. Am. Ceram. Soc.* **1974,** *57*, 193–197.
8. Winslow, D.N.; Bukowski, J.M.; Young, J.F. *Cem. Concr. Res.* **1994,** *24*, 1025–1032.