

Determination of the State of Water in Hydrated Cement Phases Using Deuterium NMR Spectroscopy

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Received October 28, 1997

Before hydration, Portland cement consists of a mixture of four clinker phases. Tricalcium silicate (Ca_3SiO_5) is the most abundant, followed in turn by dicalcium silicate ($\beta\text{-Ca}_2\text{SiO}_4$) and the calcium aluminates ($\text{Ca}_3\text{Al}_2\text{O}_6$ and $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$). The hydration reactions of Portland cement are not well understood, due in part to the X-ray amorphous nature of the most important hydration product, calcium silicate hydrate (C–S–H), which has been the material basis for much of human infrastructure in the last 2000 years. To gain more direct insight into the nature of the water in these systems, we have used deuterium (^2H or D) quadrupolar echo and ^2H T_1 measurements to study the hydration reactions in several D_2O /cement phase and D_2O /inorganic phase systems. Our findings indicate that the D_2O undergoes a state change from liquid to solid during the hardening reaction with Ca_3SiO_5 . Before and during the hardening reactions, solid $\text{Ca}(\text{OD})_2$ is also formed. The non- $\text{Ca}(\text{OD})_2$ deuterons in hardened $\text{D}_2\text{O}/\text{Ca}_3\text{SiO}_5$ mixtures experience fast tetrahedral (or higher symmetry) jumps on the NMR time scale, similar to those observed in D_2O ice.¹

Other techniques such as “D-drying” have been used to show that there is excess evaporable water in completely cured Ca_3SiO_5 cement.² ^1H NMR relaxation measurements (T_1 and T_2) have been used to study the nature of the water during the hydration of cement and its constituent phases.^{3–5} However, ^2H NMR line shape and relaxation time measurements yield larger effects with which to trace the fate of hydrogen. ^2H relaxation parameters have been used previously to characterize the hydration of $\text{Ca}_3\text{SiO}_5/\text{D}_2\text{O}$,⁶ but the observations and conclusions differ considerably from ours as shown below.

Deuterium (^2H or D) quadrupole echo NMR spectra and deuterium NMR inversion recovery T_1 measurements at ambient temperature (22 °C) were obtained on-resonance at a Larmor frequency of 45.65 MHz as a function of time after mixing for a sealed sample of Ca_3SiO_5 mixed with D_2O in a 2:1 by weight ratio (1 mol of Ca_3SiO_5 to 5.7 mol of D_2O). Other sealed samples with similar solid-to- D_2O ratios by weight were prepared with $\text{Ca}_3\text{Al}_2\text{O}_6$ (1:7.1 mole ratio), CaO (1:1.8 mole ratio), and SiO_2 (1:1.8 mole ratio). These mixtures and D_2O itself were subjected

Table 1. Deuterium Spin–Lattice Relaxation Times (T_1) and Line Widths ($\nu_{1/2}$) for the Central Signal in Several Solid/ D_2O Systems at Various Times after Mixing

substance	stoichiometry (mole:mole)	time (after mixing)	$\nu_{1/2}$ (Hz)	T_1 (s)
D_2O			60	0.37
$\text{SiO}_2/\text{D}_2\text{O}$	1:1.8	90 min	100	0.21
		3 days	100	0.21
$\text{CaO}/\text{D}_2\text{O}$	1:1.8	3 h	270	0.10
		24 h	270	0.10
$\text{Ca}_3\text{Al}_2\text{O}_6/\text{D}_2\text{O}$	1:7.1	40 min	290	
		60 min	290	0.033
		1 day	280	0.032
		3 days	200	0.093
$\text{Ca}_3\text{SiO}_5/\text{D}_2\text{O}$	1:5.7	1 day	390	0.20
		4 days	750	0.033
		6 days	1050	0.033
		1 month	3200	0.013

to the same experiments as $\text{Ca}_3\text{SiO}_5/\text{D}_2\text{O}$. The room-temperature deuterium spin–lattice relaxation times of the central liquidlike resonances of these samples are given as a function of time in Table 1. Quadrupolar echo NMR spectra were also obtained as a function of temperature from -150 °C to ambient temperature for the $\text{Ca}_3\text{SiO}_5/\text{D}_2\text{O}$ sample.

Single pulse and quadrupolar echo spectra of $\text{SiO}_2/\text{D}_2\text{O}$ and D_2O itself show only a sharp central peak with observed widths at half-height of 100 and 60 Hz, respectively. These narrow peaks had unchanging T_1 values of 0.21 and 0.37 s for $\text{SiO}_2/\text{D}_2\text{O}$ and D_2O , respectively. The $\text{SiO}_2/\text{D}_2\text{O}$ T_1 values are consistent with liquid D_2O in rapid exchange with less mobile liquid-state D_2O that is hydrogen bonded to SiO_2 and silanol groups, similar in nature to the first layers of water adjacent to clay surfaces.⁷ The $\text{CaO}/\text{D}_2\text{O}$ mixture is different. Besides a sharp central peak with peak width at half-height of 270 Hz, it shows the growth of the rigid $\text{Ca}(\text{OD})_2$ deuterium powder pattern. The quadrupole coupling parameters for this signal are $q_{\text{cc}} = 260$ kHz and $\eta = 0$. This value is comparable to the calculated q_{cc} for sodium deuterioxide in mixed $\text{NaOH}\text{--}\text{NaOD}$ of 247.7 kHz at 293 K.⁸ After mixing, the $\text{Ca}(\text{OD})_2$ powder pattern continues to grow at the expense of the central peak, but the central peak does not totally disappear even after several days. The T_1 of the sharp central peak is slightly nonexponential, indicating components with differing T_1 values with the best match at 0.10 s. This T_1 is consistent with liquid-state D_2O in rapid exchange with liquid-state D_2O that is less mobile in the hydrogen-bonded network adjacent to CaO and $\text{Ca}(\text{OD})_2$.

The $\text{Ca}_3\text{SiO}_5/\text{D}_2\text{O}$ mixture took almost 3 days to completely solidify. This is consistent with a previous report which documented the dramatic set-retarding effect when H_2O is replaced with D_2O .⁹ The spectra of the $\text{Ca}_3\text{SiO}_5/\text{D}_2\text{O}$ mixture (Figure 1) also contain a deuterium powder pattern with a quadrupole coupling constant (q_{cc}) of 260 kHz and $\eta = 0$ which is characteristic of $\text{Ca}(\text{OD})_2$. The perpendicular edges or “horns” are apparent even before the mixture is set (Figure 1a,b). Dominating the $\text{Ca}_3\text{SiO}_5/\text{D}_2\text{O}$ spectrum, however, is an extremely large central peak. The width at half-height of this peak is 390 Hz at 1 day, 750 Hz at 4 days, and 1050 Hz at 6 days of hydration. The deuterium T_1 value for the central peak is 0.20 s after 1 day (before setting), but sharply decreases during the setting period to 0.028–0.033 s with slight deviations from single-exponential relaxation. After 1 month the $\text{Ca}(\text{OD})_2$ powder pattern has grown in intensity (Figure 1c), but the central component is still intense and considerably broader than at 6 days with a width at half-height of ~ 3.2 kHz and a T_1 value of 0.013 s.

In previous ^2H NMR studies of a $\text{Ca}_3\text{SiO}_5/\text{D}_2\text{O}$ system, a sharp central signal was also observed, and was assigned to mobile

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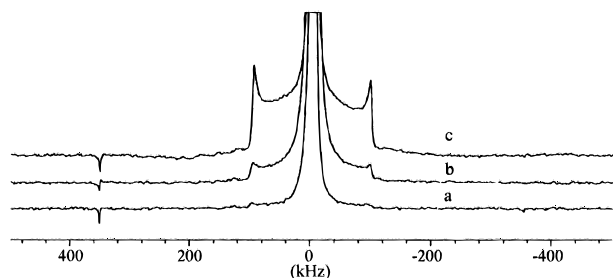


Figure 1. (a) ^2H quadrupole echo $((\pi/2)_x - \tau_1 - (\pi/2)_y - \tau_2 - \text{Acq})$ spectrum of a sealed sample of a 2:1 by weight (1:5.7 mole ratio) mixture of tricalcium silicate (Ca_3SiO_5) and deuterated water ($^2\text{H}_2\text{O}$) at ambient temperature 1 day after mixing, before hardening (on-resonance, $(\pi/2) = 1.8 \mu\text{s}$, $\tau_1 = 30 \mu\text{s}$, $\tau_2 = 20 \mu\text{s}$, repetition time = 60 s, and dwell time = 1 μs). (b) 2 days after mixing, before hardening, same NMR parameters as in (a). (c) 1 month after mixing, after hardening, same NMR parameters as in (a).

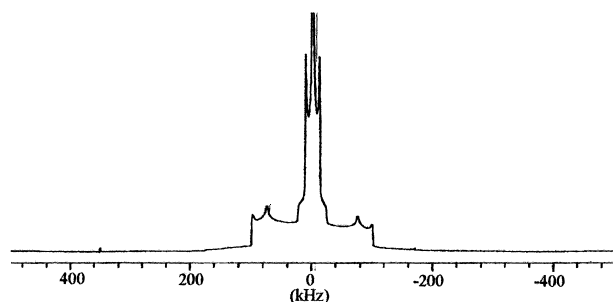


Figure 2. ^2H quadrupole echo spectrum of a sealed sample of a 2:1 by weight (1:7.1 mole ratio) mixture of tricalcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$) and deuterated water ($^2\text{H}_2\text{O}$) at ambient temperature 1 h after mixing, after loss of fluidity, same NMR parameters as in Figure 1a.

(liquid) water.⁶ The ^2H T_1 was reported as a function of the curing time, and similar values were observed. The $\text{Ca}(\text{OD})_2$ powder pattern which we observed both before and after curing at ambient temperature was not reported. After heating the sample for 2 h at 75 °C, the authors did report the appearance of a Pake doublet in the ^2H spectrum and assigned it to water associated with hydrates, although the quadrupolar coupling constant and η were not reported.⁶ Their primary hypothesis was that the sharp central peak and its variation in T_1 were due to liquid-state deuterium nuclei in rapid exchange between bound and free forms, similar to the case observed with water and clay.^{6,7} For bulk D_2O in fast exchange with less mobile liquid D_2O hydrogen bonded to the surface (cement or clay), this model predicts that $1/T_1 = f_b/T_{1b} + f_s/T_{1s}$ (where f_b = bulk liquid fraction, f_s = “surface” liquid fraction, and $f_b + f_s = 1$).⁷ T_{1s} has been determined to be approximately $T_{1b}/5.35 \approx 0.07$ s in the liquid monolayer adjacent to a clay surface in the absence of paramagnetic impurities.⁷ T_{1b} is independent of the magnetic field because the liquid-state isotropic rotational correlation time τ_c (ca. 2.5 ps for $T_{1b} = 0.37$ s¹⁰) fulfills the extreme narrowing condition, $\omega_0^2\tau_c^2 \ll 1$, at room temperature.⁷ The fast exchange model works for the $\text{Ca}_3\text{SiO}_5/\text{D}_2\text{O}$ mixture before hardening ($T_1 = 0.20$ s), for the $\text{SiO}_2/\text{D}_2\text{O}$ mixture ($T_1 = 0.21$ s), and for the $\text{CaO}/\text{D}_2\text{O}$ mixture ($T_1 = 0.10$ s), but no combination of T_{1b} (0.37 s) and T_{1s} (~ 0.07 s) can produce the T_1 observed for the $\text{Ca}_3\text{SiO}_5/\text{D}_2\text{O}$ mixture after hardening ($T_1 \leq 0.033$ s). Liquid-state paramagnetic relaxation could produce such a change in T_1 if there was a sudden increase in the concentration of paramagnetic species during hardening, although there is no evidence to support this.

On the basis of our ^2H NMR data, we have a different hypothesis which we believe is more consistent with the observations: The central peak before setting in the $\text{Ca}_3\text{SiO}_5/\text{D}_2\text{O}$ mixture

is due to liquid-state D_2O in rapid exchange with less mobile liquid-state D_2O . The central peak after setting has a T_1 of ~ 0.03 s or less and is due to *solid-state* D_2O for which the deuterium nuclei or whole D_2O molecules experience jumps of tetrahedral (or higher) symmetry like those observed in D_2O ice between -6 and 0 °C.¹ This includes all of the deuterium in the system that is not in the form of $\text{Ca}(\text{OD})_2$. This type of rapid jump motion produces a sharp central line if $\eta = 0$, and an unresolvable “mini-powder pattern” if $\eta = 0.1$.^{1,11} Nearly linear jumps associated with exchange of a deuterium between two oxygens involved in the same hydrogen bond reorient the quadrupolar axis system by 180° , but do not produce an effect on the powder line shape or on quadrupolar relaxation. However, rapid tetrahedral jumps affect both, and are a natural choice for the excess D_2O in the $\text{Ca}_3\text{SiO}_5/\text{D}_2\text{O}$ mixture since ice has a tetrahedral lattice structure with all four tetrahedral orientations equiprobable.¹ The theoretical relationship between the jump rate and the T_1 relaxation time for the central peak was calculated assuming tetrahedral jumps, $qcc = 216$ kHz, and $\eta = 0.1$.^{1,12} This model yields jump rates of $\sim 2 \times 10^9 \text{ s}^{-1}$ ($T_1 = 0.033$ s at 4–6 days) and 3×10^8 or $2 \times 10^7 \text{ s}^{-1}$ ($T_1 = 0.013$ s at 1 month).

A liquid- to solid-phase transition for D_2O in the $\text{Ca}_3\text{SiO}_5/\text{D}_2\text{O}$ mixture is consistent with several other observations, including the observed hardening of cement which occurs during the same period as the change in relaxation time. Another is the observed heat evolved during the hardening of the $\text{Ca}_3\text{SiO}_5/\text{D}_2\text{O}$ mixture, which we measured in an isothermal calorimeter as 96 cal/g of D_2O , slightly larger than the heat of fusion of D_2O , 76 cal/g of D_2O .¹³ And finally, the variable temperature quadrupole echo spectra (not shown) obtained for the hardened $\text{Ca}_3\text{SiO}_5/\text{D}_2\text{O}$ mixture reveal a large loss in quadrupole echo intensity on cooling below -50 °C as would be expected if the jump rate decreased into the intermediate jump rate regime.¹ The echo intensity recovers at temperatures below -100 °C, and is almost completely recovered at -150 °C, where the jump rate is slow on the NMR time scale. The “horns” of ice-phase D_2O first appear at temperatures below -100 °C. At -150 °C, the powder pattern for rigid ice-phase D_2O is clearly discernible ($qcc = 216$ kHz, $\eta = 0.1$).¹

The $\text{Ca}_3\text{Al}_2\text{O}_6/\text{D}_2\text{O}$ mixture loses its fluidity immediately after mixing but is not as hard as hardened $\text{Ca}_3\text{SiO}_5/\text{D}_2\text{O}$. Its quadrupole echo spectrum contains four types of deuterium signals (Figure 2). As above, the outermost powder pattern with horns at ± 98 kHz corresponds to $\text{Ca}(\text{OD})_2$. The powder pattern with horns at ± 74 kHz and an asymmetry parameter of $\eta \approx 0.1$ is very similar to that observed in rigid D_2O ice¹ and is tentatively assigned to D_2O molecules associated with the hexahydrate $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 6\text{D}_2\text{O}$. The inner axially symmetric powder pattern with horns at ± 11.6 kHz may correspond to “tethered” deuterium undergoing rapid rotational diffusion in a cone,¹⁴ perhaps from $\text{Al}-\text{O}-\text{D}$ or D_2O at the air–solid interface of the hydrated solid. The sharp central peak has a width at half-height of 290 Hz and a T_1 relaxation time of 0.033 s 1 h after mixing which increases to 0.093 s after 3 days, possibly indicating a solid- to liquid-phase transition or large decrease in the solid-state jump rate. The elucidation of this behavior will require further study.

This preliminary investigation shows that it is possible to directly observe the reactions of deuterated water in cement systems with solid-state ^2H NMR techniques. Further applications of these methods promise to reveal a great deal about the complex relationships among cement composition, preparation conditions, and the physical properties of these systems.¹⁵

JA973728X

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