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Solid-State Deuterium NMR Spectroscopy of d_5 -Phenol in White Portland Cement: A New Method for Assessing Solidification/Stabilization

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We have developed a new NMR-based procedure for studying waste/cement interactions. This is the first use of deuterium NMR spectroscopy to study waste solidification/stabilization (S/S). The main feature of deuterium NMR spectroscopy is the ability to monitor molecular reorientations over a wide range of reorientation rates. This technique allows one to determine if a particular deuterated organic waste is effectively solidified/stabilized and to determine the lower limit of the bond strength between the waste and the cement matrix. Comparison of the predicted and experimental deuterium NMR spectra show that phenol is mainly dissolved in pore waters and, thus, poorly immobilized by white portland cement, at least for cure times up to 1 year. After evaporation of the pore water from the cement matrix the ^2H line shape and T_1 were measured at 230–360 K; the maximum activation energy for the 180° ring flip process is 5.5 kcal/mol. Hence, the lower limit of the bond strength between phenol and the cement matrix is approximately 5.5 kcal/mol.

Introduction

Recently, solid-state ^{27}Al and ^{29}Si nuclear magnetic resonance (NMR) techniques have been used to monitor immobilization mechanisms in the solidification/stabilization of waste in portland cement (1–5). While this data has been useful for following the curing of waste/cement mixtures, it does not address the matter of microscopic motions of the waste. Our research has applied deuterium solid-state NMR techniques with the goal of addressing the following question: "For the case of low concentrations of organic waste in cement, are the waste molecules loosely or tightly bound to the cement matrix?". The answer to this question is very important in order to evaluate the reliability of the solidification/stabilization process for a particular waste. Phenol is water soluble and representative of organic wastes that are found in organic-inorganic mixed waste systems. It has a functional group that can react under the basic aqueous conditions that exist during cement matrix formation. Presumably for maximum immobilization, one would desire deprotonation of the alcohol function and formation of a rigid, insoluble material with tight binding between the phenoxide anion and the cations of the cement matrix.

Since phenols are common constituents of aqueous waste streams, there have been a number of studies of S/S using phenols as model wastes. Most of these centered on the leachability of the phenol from the matrix, and for cement-stabilized phenols, leaching procedures such as the EP Tox or toxicity characteristic leaching procedure (TCLP) show very high percent recovery, and equilibrium leaching procedures afford large leachability indices (6–9).

Indeed, there is a substantial history of studies of interactions of phenol (PhOH) with cement. It has been

assumed in cement literature that PhOH is converted to calcium phenoxide in contact with cement clinker. Interestingly, a qualitative test for the presence of free lime in clinker involves treatment with PhOH in nitrobenzene and water and microscopic observation of the characteristic long needles of "calcium phenoxide" (10). Phenol and monosubstituted phenols typically have pK_a 's in the range 9–11, and the pH of pore waters in cements is very basic, up to about pH 13. Consequently, the potential for conversion of phenols to their anions exists, but the extent of conversion may depend upon a number of factors controlling the acidity of the phenol and the basicity of the pore waters. The cation present in overwhelming amount is Ca^{2+} , consequently a Ca phenoxide would be expected. It has recently been shown (11) that combination of equimolar quantities of $\text{Ca}(\text{OH})_2$ and PhOH produces PhOCaOH not $(\text{PhO})_2\text{Ca}$, and the latter can only be formed under forcing conditions with continuous removal of water.

In previous work, we have investigated several substituted phenols with respect to both leachability and chemical and physical properties. The following results have been obtained with samples prepared with type I portland cement using a 0.5 water-to-cement ratio and containing 10% by weight of the organic. In the presence of 10% *p*-chlorophenol (*p*CP), setting times are approximately doubled, compared to cement alone, and strength is slower to develop (12). However, the 28-day compressive strength is the same as that of the cement paste without *p*CP. The effects of *p*-bromophenol (*p*BP) are similar, but the setting is slightly slower and the 28-day compressive strength is about 10% lower. We have also investigated these samples using scanning electron microscopy (SEM) and X-ray diffraction (XRD) (13). SEM and XRD do show matrix changes with increasing proportions of organic. There is decreasing crystallinity, as judged qualitatively from SEM and from the increasing background noise relative to sharp peaks in the XRD patterns. Nevertheless, even at 20% by weight phenol, both transmission electron microscopy (14) and XRD (13, 15) show $\text{Ca}(\text{OH})_2$ to still be present in the matrix. XRD shows increasing occurrence of new sharp peaks not present in cement alone. Comparison of XRD patterns of phenol-containing cements with those of Ca salts of phenols prepared separately shows peak coincidences, but enough of the salt peaks are obscured by noise or overlapping strong cement peaks that it is not possible to positively identify the salts in the phenol-cement mixture by XRD alone (13).

It is possible to distinguish ionized from nonionized phenol by solid-state ^{13}C NMR, since the ipso carbon of the aromatic ring shifts upfield by about 7 ppm in either PhOCaOH or $(\text{PhO})_2\text{Ca}$ compared to PhOH (11). In our samples at 10% loading in type I portland cement, PhOH is completely ionized (although some combinations of substituted phenols, cement, and metal salts do show both ionized and nonionized phenol).

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Thus, there is considerable evidence for phenol-cement interactions, despite the fact that phenol is only poorly immobilized toward water leaching. In order to obtain more detailed information about the environment of the phenol in the cement matrix, we have applied solid-state deuterium NMR spectroscopy, which is an excellent probe for obtaining the details of molecular motions in solids. Based on a line shape analysis, reorientation modes, such as methyl group rotation, can be distinguished from 180° phenyl ring flips, and reorientation rates can be measured in the region of 10^3 – 10^6 s⁻¹ (16, 17). Based on T_1 measurements, reorientation rates from 10^6 s⁻¹ to more than 10^{11} s⁻¹ can be determined (18, 20). Solid-state deuterium NMR spectroscopy has been frequently applied to various systems such as proteins, lipids, organometallics, and polymers (16–21).

Herein, we have applied solid-state deuterium NMR spectroscopy to the study of phenol-cement interactions. Two different phenol components were found, both a liquid-like component, presumably phenol dissolved in pore waters, and a rigid form, presumably solid calcium phenoxide. As the sample cures from 1 month to 1 year, the liquid-like component decreases, but still constitutes a significant fraction (≈50%) of phenol at 1 year.

Experimental Section

Sample Preparation. Low iron content white portland cement (Lehigh Cement Co., Waco, TX), about 0.3% Fe₂O₃ by weight, was used to reduce the interference of paramagnetic relaxation upon the ²H NMR spectra. *d*₅-Phenol (98%) was obtained from Cambridge Isotopes Laboratories. The procedure used to make the samples was as follows: All samples were prepared under a nitrogen atmosphere in order to reduce the formation of carbonates on the surface of the cement. To a phenol-cement mixture enough deionized water was added to yield a water-cement ratio of 0.5 by weight. The mixture was stirred in a borosilicate glass vial until apparent homogeneity (ca. 2 min). Some samples were immediately transferred to 5-mm NMR glass tubes while others were allowed to solidify in the glass vials. The latter were broken out of the vials as needed, crushed with a mortar and pestle to a fine powder, and then loaded into NMR tubes. In some cases, the crushed samples were reexamined at a later date.

There were three different loading percentages of waste in the cement: 10% phenol by weight relative to cement (1.0 g of white cement, 0.1 g of *d*₅-phenol, 0.5 mL of deionized water); 1% phenol by weight (10.0 g, 0.1 g, 5 mL); and 0.1% phenol by weight (10.0 g, 0.01 g, 5 mL).

Solid-State Deuterium NMR Spectroscopy. Solid-state deuterium NMR spectra were acquired at 30.7 MHz on a Bruker MSL200 solid-state spectrometer. The basic pulse program was a quadrupole solid echo pulse sequence (22, 23): $90_{x-x} - t_1 - 90_{y-y} - t_2 - \text{acquire}_{x-x}$. The 90° pulse length was 3.0 μs, and t_1 was 25 μs; the second delay, t_2 , was adjusted to the echo maximum. In order to cancel the effects of probe ringing, a two-step phase-cycling routine was used where the phase of the first rf pulse and the receiver phase were alternated between 0° and 180° (24). The relaxation delay between scans was 200 ms. A line-broadening factor of 5000 Hz was used in exponential multiplication to improve the signal-to-noise ratio of the spectrum. Approximately 2000–4000 scans were averaged for each experiment.

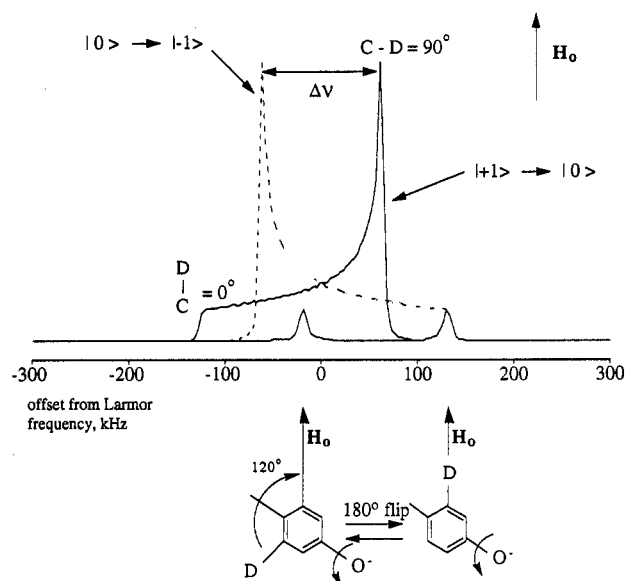


Figure 1. Details of a solid-state deuterium NMR spectrum showing how 180° ring flips can average portions of the deuterium NMR spectrum. Here, $e^2qQ/h = +175$ kHz and $\eta = 0$.

Deuterium spin-lattice relaxation times were measured with the inversion recovery technique. The inversion recovery technique uses the quadrupole echo pulse sequence with a $[180_x - \tau]$ prior to the pulse sequence. The τ is a variable delay period and, typically, 10 different τ delays were used. Experiments at different temperatures were done, but care was taken to adjust the relaxation delay between scans to no less than five times the T_1 at the 90° orientation (see Figure 1) at each temperature. This was done to assure that 99% of the magnetization was recovered before each scan. The T_1 values at the 90° orientation, $T_1(90^\circ)$, were calculated by fitting (simplex algorithm) the spectral intensity at the corresponding frequency, I , to the following equation:

$$I = I_0[1 - A \exp^{-\tau/T_1}] \quad (1)$$

where I_0 , T_1 , and A are the intensity at equilibrium, corresponding relaxation time, and measure of the efficiency of the 180° pulse which should have a value near 2 for the more nearly on-resonance 90° orientation.

For the purpose of accurate modeling of NMR line shape, spectra were transferred as binary data files from the Bruker Aspect-3000 computer to a Macintosh II computer via an RS-232 serial connection and the KERMIT file transfer protocol (25, 26). A program (27) written in LabVIEW, a graphical programming language (28), was used to convert the binary files to ASCII data files. The spectra were then fitted to a Gaussian, which represents the liquid-like component, and a 180° ring flip simulation spectrum, which represents the solid calcium phenoxide. The Levenberg-Marquardt nonlinear least-squares algorithm (29, 30) was used to obtain the best fit. This program was written in Matlab v3.5f, a vector-oriented programming language (31, 32).

Theory

In most solid-state deuterium NMR spectroscopy of static systems, i.e., a reorientation rate slower than about 10^3 s⁻¹, there are four factors that determine the deuterium NMR transition frequencies: the Larmor frequency, the

quadrupolar coupling constant, the asymmetry parameter, and the angle between the z -axis of the electric field gradient and the applied magnetic field, H_0 (33). The deuterium line shape is symmetric about the Larmor frequency and is composed of two sets of spin-state transitions, $|+1\rangle \rightarrow |0\rangle$ and $|0\rangle \rightarrow |-1\rangle$. As shown in Figure 1, the $|0\rangle \rightarrow |-1\rangle$ transition varies from an offset frequency of -65 to $+131$ kHz (positive quadrupolar coupling constant). The transition at $+131$ kHz corresponds to the z -axis of the electric field gradient aligned with the applied magnetic field ($\theta = 0^\circ$); -65 kHz corresponds to the perpendicular orientation, $\theta = 90^\circ$, and is more intense due to a $\sin \theta$ weighting factor. For a C-D bond, the electric field gradient z -axis is roughly aligned with the C-D bond vector, hence the labeling in Figure 1.

The quadrupole coupling constant determines the width of the line shape and can be obtained from the frequency separation between two sets of transitions at the same angle, θ

$$\Delta\nu = \frac{3}{4} \left(\frac{e^2 q_{zz} Q}{h} \right) (3 \cos^2 \theta - 1) \quad (2)$$

where $e^2 q_{zz} Q/h$ is the quadrupole coupling constant, typically about 175 kHz (we assume that the asymmetry parameter is near zero) (34). Hence, for a static, C-D site, one expects a frequency separation between the peaks of the line shape ($\theta = 90^\circ$) of $\Delta\nu = (3/4) 175 \text{ kHz} = 131 \text{ kHz}$, as shown in Figure 1.

If there is motion on a time scale faster than that defined by the separation between the rf pulse of the quadrupolar echo sequence, then one obtains an average of transition frequencies. However, the mode of motion affects the averaging process. Shown in Figure 1 is a single deuteron in phenol at two different orientations. When the C-D bond is aligned with H_0 , the $|0\rangle \rightarrow |-1\rangle$ transition frequency is $+131$ kHz. When the phenyl ring executes a 180° flip about the axis shown, the orientation of the C-D bond with respect to the magnetic field changes. Now, $\theta = 120^\circ$ and a different $|0\rangle \rightarrow |-1\rangle$ transition frequency is expected, about -16 kHz, as shown in Figure 1. Since the reorientation rate is rapid, the observed transition becomes the average of the two. The calculation of the line shape now requires averaging over all possible orientations of the flipping axis as well as over initial orientations of the C-D bond vector.

Other factors which can affect the line shape include the relative population of sites (35) and reorientation rates that are comparable to the time scale defined by t_1 in the pulse sequence (36). In this work, the mirror symmetry of the phenol molecules will assure an even population of orientations. However, reorientation rates in the intermediate regime can occur. Thus, shown in Figure 2 are simulated line shapes (37) for a wide range of rates. It is important to note that there is a loss of spectral intensity in the intermediate exchange regime. The reason for this loss is the fact that the last pulse in the quadrupole echo pulse sequence does not completely refocus the magnetization evolution due to the irreversible jump dynamics (38). For exchange rates in either the fast or slow limits, the integrated area of the resonance is proportional to the number of deuterons. By comparing the line shapes of the simulated spectra to the fully relaxed experimental spectra, the mode and rate of motion can be determined for the motions in the intermediate exchange regime. Lastly, in the two regimes where the line shape is

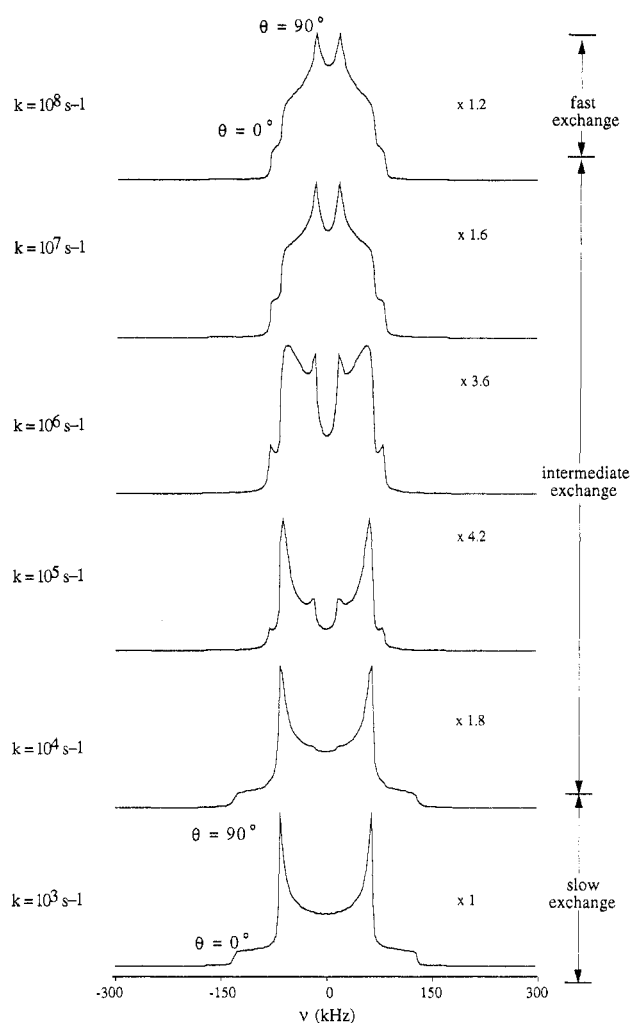


Figure 2. Simulated spectra for a quadrupole echo pulse sequence showing the effect of flip rate on the deuterium NMR line shape for d_5 -phenol rings executing 180° flips. Important parameters are as follows: $\nu_L = 30.7$ MHz, 90° pulse length = $3 \mu\text{s}$, delay between rf pulses = $25 \mu\text{s}$, $e^2 q Q/h = +175$ kHz, and $\eta = 0$. Spectra for the intermediate exchange rates are vertically expanded by the factors shown in the figure.

independent of rate, anisotropic spin-lattice relaxation times, $T_1(\theta = 0^\circ)$ and $T_1(\theta = 90^\circ)$, can be used to determine the reorientation rate, provided that the mode of motion is known (18, 39).

Results

Spectra were acquired on pure d_5 -phenol using the quadrupole solid echo pulse sequence at various temperatures and are shown in Figure 3. Figure 3a is the spectrum near the melting point of phenol at 41°C and shows a single narrow resonance which indicates that d_5 -phenol has liquid-like mobility. Near room temperature the line shape is broader, but the motion is more complicated than just 180° ring flips. Probably there is a combination of 180° ring flips and libration; similar spectra can be found for phenyl rings in polymers (40). At 250 K, a broad resonance is obtained which is nearly that of static phenyl rings or flip rates less than 10^4 s^{-1} .

At this point, we wish for the reader to note and remember three ^2H NMR line shapes: (a) the narrow, simple peak for liquid phenol (Figure 3a); (b) the broad resonance for solid phenol (Figure 3d); and (c) the broad

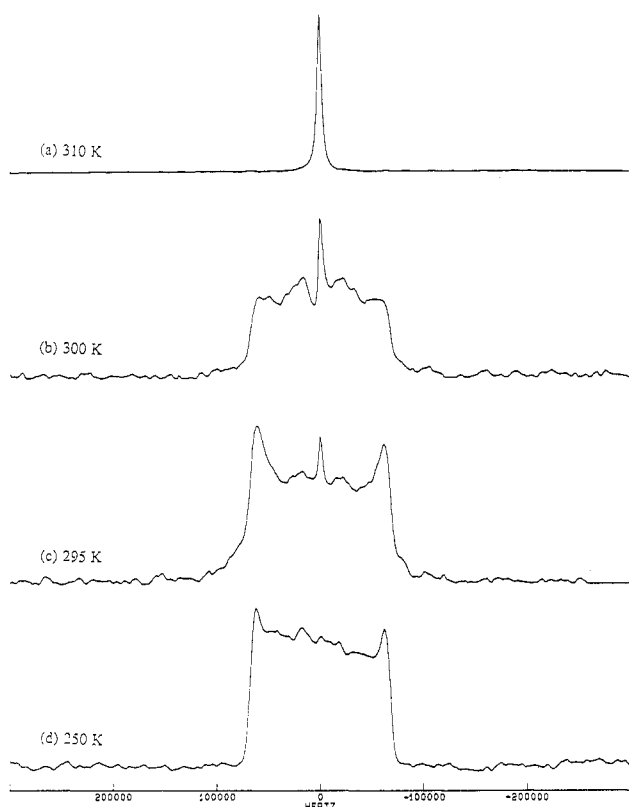


Figure 3. Deuterium NMR spectra for pure d_5 -phenol. The line shape at 310 K indicates liquid-like mobility whereas the more complex line shape at the lower temperature shows restricted mobility. However, some motion is still present at 250 K.

but well-defined resonance of a phenyl ring constrained to move only by 180° flips about a C_2 axis (Figure 2, $k = 10^8 \text{ s}^{-1}$). The last spectrum is the one that implies binding between the phenol waste and the cement matrix and, therefore, perhaps successful S/S. Observation of liquid phenol will certainly indicate that the phenol is able to move within the matrix on a microscopic scale (and probably also on a macroscopic scale).

Samples at 0.1, 1, and 10% d_5 -phenol by weight in cement were studied at various temperatures. These samples were placed in NMR tubes upon mixing and allowed to cure for 1 month (cement matrix undisturbed). Representative spectra are shown in Figure 4. The dominant feature for all samples studied between 260 and 360 K is a liquid-like spectrum. The shoulders of the spectra (Figure 4b,c) at $\pm 65 \text{ kHz}$ are evidence of deuterons executing 180° ring flips while the large spike in the middle indicates deuterons that have liquid-like mobility. At lower temperatures, say 230 K, a static line shape (Figure 4e) is observed and is similar to that obtained for pure d_5 -phenol at 250 K. Even the 0.1% sample shows liquid-like and static line shapes similar to that for the 10% sample at the corresponding temperature. The same samples were examined after 1 year of cure, and the spectra are very similar to those obtained at 1 month.

These results suggest that there are two different environments for phenol in cement and that these environments persist for a long time. One environment consists of the phenol in cement that has a mobility-like liquid phenol and appears not to be bound to the cement matrix; we will refer to this component as the liquid-like component. This component probably consists of phenol present in cement pore water in ionized form. A second

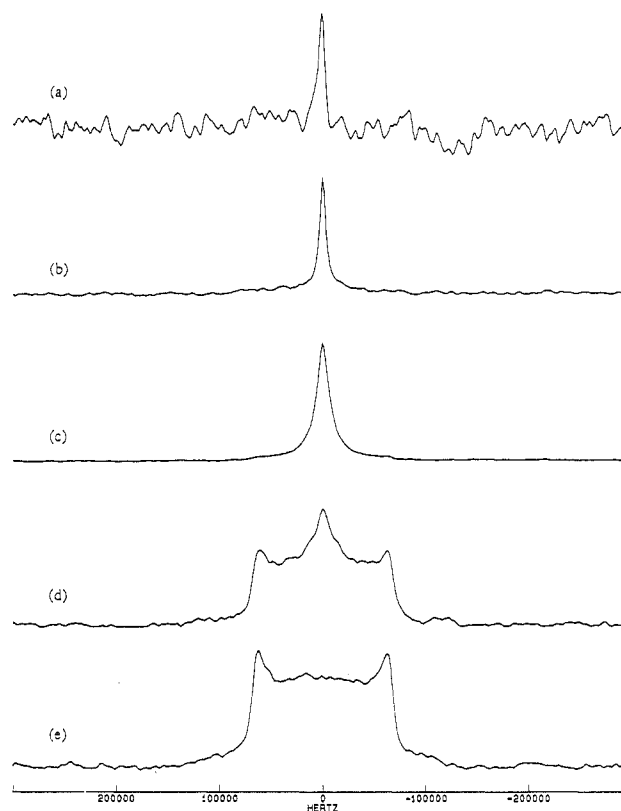


Figure 4. Deuterium NMR spectra for d_5 -phenol in white portland cement cured in NMR tubes for 1 month: (a) 0.1% phenol by wt, 293 K; (b) 1% phenol by wt, 293 K; (c) 10% phenol by wt, 293 K; (d) 10% phenol by wt, 240 K; (e) 10% phenol by wt, 230 K. Even at low loading, there is still liquid-like mobility for most of the phenol.

environment consists of the phenol in cement that is executing 180° ring flips; the constrained motion implies binding of the phenol through the hydroxy group. This more rigid form is presumably a calcium phenoxide salt and may or may not be bound to the cement matrix (precipitated Ca phenoxide salt or phenoxide bound to surface Ca). For simplicity, we will refer to this rigid form as solid calcium phenoxide. The most important result is the observation of liquid-like phenol, even after 1 year of cure. Clearly, S/S with portland cement has failed to immobilize phenol on a microscopic scale.

The NMR spectra were fitted to a simple model to determine what percentage of the phenol exists as liquid-like phenol and, therefore, is not bound to the cement matrix. The model consists of a simple Gaussian representing the liquid-like phenol and the line shape corresponding to fast two-site jump motion (180° ring flips). The equation used for the fit is as follows:

$$g(\nu) = A^{\text{liq}} \exp[-\ln(2)(\nu/\Delta\nu)^2] + A^{2\text{-site}} g(2\text{-site}) + \text{offset} \quad (3)$$

where A^{liq} and $A^{2\text{-site}}$ are the coefficients for the contribution for the liquid-like and two-site jump motion (Figure 2, $k = 10^8 \text{ s}^{-1}$). The parameter $\Delta\nu$ is the half-width at half-maximum, and the vertical offset are variables. The choice of the two-site line shape for $k = 10^8 \text{ s}^{-1}$ is made on the basis of temperature-independent line shapes and constant intensities, down to 260 K, implying that the jump rate for the two-site phenols is faster than $k = 10^8 \text{ s}^{-1}$ at 300 K. The fit, eq 3, includes only the line shape for the ortho and meta deuterons of the d_5 -phenol. The deuteron bound

Table I. Fraction of d_5 -Phenol Bound to or Precipitated in Cement Matrix

wt % phenol in white portland cement	cure time	χ^2_v	solid calcium phenoxide (% phenol executing 180° ring flips)
1% in NMR tube ^a	1 month	0.82	45 (2)% ^c
	1 year	0.95	48 (2)%
	14 month	1.2	52 (2)%
10% in NMR tube ^a	1 month	0.55	44 (2)%
	1 year	0.62	55 (2)%
	15 month	1.1	80 (2)%
10% crushed at 2 month, ^b no oven treatment	2 month	0.85	55 (2)%
10% crushed at 2 month, ^b oven treated at 2 month, 36 h, 90 °C	2 month	0.28	95 (3)%

^a Sample prepared, then forced into 5-mm NMR tube and allowed to cure. ^b Sample removed from vial and then crushed to fine powder, ~ 100 mesh. ^c The numbers in parentheses represent 1 standard deviation.

to the para carbon is aligned with the C_2 axis; therefore, this deuteron is not affected by the 180° flips. Even with rapid flipping, this deuteron should still show a static powder pattern (41). The line shape for the para deuterons, given by Figure 2 ($k = 10^3 \text{ s}^{-1}$), was excluded based upon the conclusion that the $^2\text{H } T_1$ is longer for this site compared to the other deuterium sites. Two observations lead to this conclusion: (1) The $k = 10^3 \text{ s}^{-1}$ line shape was not observed in any tube samples. (2) An inversion-recovery experiment yielded two components in the resonance at $\pm 65 \text{ kHz}$; the larger component has a short T_1 (0.016 s) while the less abundant component has a T_1 of 0.32 s (42). Based on the longer T_1 and the smaller abundance, the smaller component is believed to be due to the para deuteron. Since all experiments done to measure the ratio of liquid-like to solid calcium phenoxide were done with a relaxation delay of 0.2 s, the interference of the para deuteron is partially eliminated. Table I contains a summary of all the results obtained by this fitting procedure and one example is shown in Figure 5. For the 10% phenol in cement sample, the percent solid calcium phenoxide increased from 44 (2)% at 1 month solidified to 55 (2)% at 1 year. The fraction of solid calcium phenoxide continued to increase with additional cure time, Table I. The 1% phenol in the cement sample remains basically the same from 1 month to 1 year with approximately 46 (2)% being solid calcium phenoxide. These results suggest that for cure times up to 1 year approximately 50% of the phenol in cement has a mobility like a liquid and appears not to be bound to the cement matrix.

Because of the extremely basic aqueous solution in portland cement, $\text{pH} \approx 12$, and the weak acidity of phenol, $\text{p}K_a \approx 10$, most of the liquid-like phenol is probably dissolved as the phenoxide ion in the pore water of the cement matrix. We have independent ^{13}C NMR spectral data confirming that ionization has taken place (43). An operative assumption here is that much of the pore water in the cement matrix can be removed by crushing the sample, followed by overnight oven treatment, for example, 24 h at 95 °C. After oven treatment, one sample had a 13.5% loss in weight due to the evaporation of pore water. As a result the precipitation of the phenoxide, mainly as Ca salts, will occur. Figure 6 shows spectra of 10% d_5 -phenol in cement sample that was crushed after 2 months of cure. Figure 6a, taken at 295 K immediately after

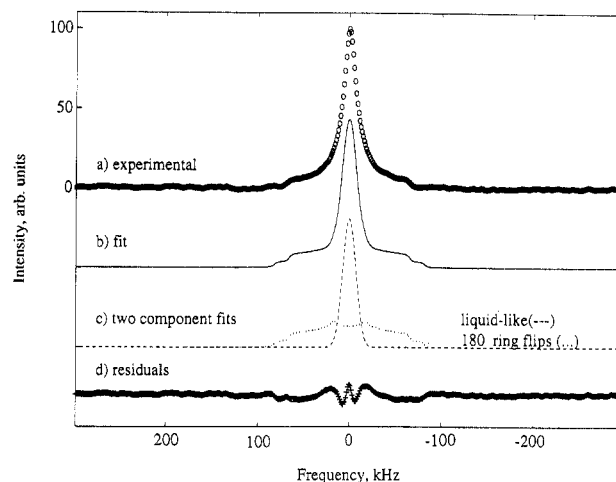


Figure 5. Results from a nonlinear least-squares analysis of the ^2H NMR spectrum for 10% d_5 -phenol by wt in white portland cement solidified in an NMR tube for 1 year: (a) experimental ^2H NMR spectrum; (b) best calculated fit with eq 3; (c) the fit is composed of two deuterium components, liquid-like (---) and 180° ring flips (···); (d) residuals. $\chi^2_v = 0.62$. The amount of solid calcium phenoxide (phenol executing 180° ring flips) = 55 (2)%; the remaining phenol exists in a freely mobile, liquid-like phase and is not bound to the cement matrix.

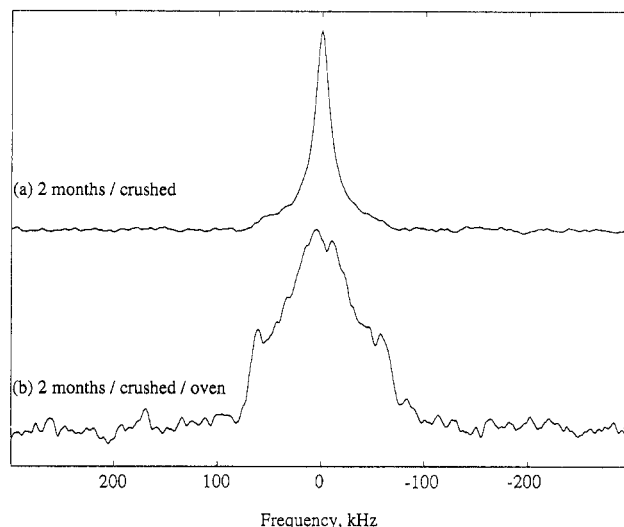


Figure 6. Deuterium NMR spectra for 10% d_5 -phenol by wt in white portland cement sample that has been crushed after a 2-month cure: (a) immediately after crushing, 298 K, spectrum shows large liquid-like phenol resonance, 45 (2)%; (b) a similar sample as in (a), but after forced drying of pore water (oven treatment for 36 h at 90 °C). Spectrum acquired at 298 K and shows very little liquid-like phenol, about 5 (3)%.

crushing, shows a liquid-like spectrum; the best fit indicates 45 (2)% of phenol in the sample has liquid-like mobility. In contrast, after oven treatment, Figure 6b, the spectrum shows a line shape corresponding to 180° ring flips and has little evidence of a liquid-like phase; only 5 (3)% of the phenol retains liquid-like mobility. The samples corresponding to Figure 6a,b were studied again at 1 year. An increase in the liquid-like component for the sample in Figure 6b indicated readsorption of water from the atmosphere. Additional experiments on the other samples, including monitoring of sample mass (water gain/loss), show effective reversibility for the oven treatment process. That is, dried samples were rehydrated and the ^2H NMR line shape was transformed from restricted motion (Figure 6b) to mostly liquid-like mobility (Figure 4c).

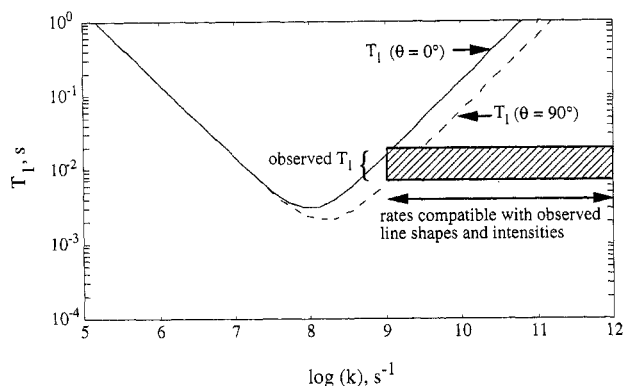


Figure 7. Theoretical deuterium T_1 curves at 30.7 MHz as a function of 180° flip rate and tentative minimum jump rate at low temperature, 260 K, based on experimental T_1 data and line shape.

Since the spectrum in Figure 6b, showing 180° ring flips, is in the fast-exchange regime (Figure 2), the ring flip rate must be 10^8 s^{-1} or faster. In principle, the ^2H spin-lattice relaxation time, T_1 , can be used to measure the rate in the fast-exchange regime. The theoretical T_1 ($\theta = 0^\circ$) and T_1 ($\theta = 90^\circ$) curves as a function of the 180° flip rate for phenol at a Larmor frequency of 30.7 MHz are shown in Figure 7. Unfortunately, over a range of temperatures, 200–360 K, a rather narrow range of T_1 's (7–20 ms) was obtained. This small range in ^2H T_1 is probably due to the interference of paramagnetic relaxation from Fe^{3+} sites, otherwise longer T_1 's would have been observed at the higher temperatures. Therefore, the quality of the T_1 data for samples showing 180° ring flips is not sufficient to allow us to determine the activation energy, E_a , unambiguously. Also, there seems to be a distribution of activation energies within the solid-like component that cannot be resolved from the T_1 data. However, based on constant spectral intensities and unvarying line shapes between 260 and 360 K and combined with the T_1 data, the bulk of the sites have jump rates $\geq 10^9 \text{ s}^{-1}$. By using an estimated value for the preexponential factor of $4 \times 10^{13} \text{ s}^{-1}$ and the lowest temperature (260 K) for which constant intensity and line shape were obtained, we estimate that the largest possible activation energy for 180° ring flips is approximately 5.5 kcal/mol.

For comparison, in amorphous poly(*p*-phenylene) at room temperature, 180° ring flips are rapid and have a correlation time of about 10^{-7} s^{-1} (44). This corresponds to an activation energy close to 9 kcal/mol. The crystalline component of poly(*p*-phenylene) has a higher but undetermined activation energy. In fact, the spectra for poly(*p*-phenylene) at different temperatures are quite similar to those found herein for phenol-cement (after oven treatment or evaporation), with the single difference of a somewhat lower activation barrier for phenol-cement.

Discussion

Solid-state ^2H NMR spectroscopy has several highly useful advantages for the study of solidification/stabilization (S/S) processes: (1) Since the isotope is not abundant, the molecules to be studied must be isotopically enriched. Thus, only a selected component of a rather complex material is visible; the rest of the material is a noninterfering matrix. (2) Solid-state ^2H NMR is particularly useful for detecting microscopic motion of molecular species, both the rate and the mode of motion.

Because of the goal of S/S, the study of molecular motions is crucial in identifying successful strategies. (3) Solid-state ^2H NMR is a noninvasive, nondestructive technique. The same sample can be studied repeatedly. (4) Solid-state ^2H NMR spectra will always consist of overlapping resonances, i.e., a narrow liquid-like resonance and a broad resonance from a constricted site. Within some modest limits, multiple components (usually two) can be monitored. Limitations here are similar to those affecting any technique used to study a system having broad distributions of sites within each component. (5) Temperature-dependent solid-state ^2H NMR spectra are relatively easy to acquire. Therefore, the rate of motion can be studied as a function of temperature, and activation energies can be extracted. Under favorable circumstances, the measured activation energy may correspond to a feature important in the S/S process.

There is a wide variation in the deuterium line shape, corresponding to changes in the mode and rate of d_5 -phenol reorientation in portland cement. At room temperature, most phenol in cement is very mobile, even to relatively low loadings, 0.1% by weight, of phenol in cement. These results can be compared with other research on phenol and related wastes in cement, which shows that phenol is poorly immobilized by portland cement. Even though the samples are nominally dry and solid in appearance, we believe voids containing liquid-like phenol are present because of the liquid-like ^2H NMR resonance for a significant fraction of the phenol. Furthermore, the liquid-like spectrum was observed for loadings ranging from 0.1% to 10%. The content of the voids is not given by deuterium NMR nor by SEM, which has shown evidence of voids in the phenol-cement matrix (45). Possibilities are an aqueous solution of an alkali or alkaline earth salt of phenol. The calcium salt of phenol has been characterized by FTIR and ^{13}C CP/MAS NMR techniques which indicate that the ipso carbon shifts downfield by about 7–10 ppm upon formation of the salt (11). The ^{13}C CP/MAS NMR spectroscopy of phenol-cement (4, 43) and the ^{13}C NMR spectra of $[1-^{13}\text{C}_1]$ phenol versus $[1-^{13}\text{C}_1]$ phenol-cement (46) show that there is approximately a 8 ppm shift of the ipso carbon. This indicates the formation of a phenoxide, and the ^{13}C NMR spectra also show no presence of phenol in the nonionic form.

This research has shown that the majority of the phenol in a cement matrix, even at 0.1% loading, is in a liquid-like form, but there is at least one environment that exists in which the phenolic oxygen is immobilized within the matrix. It is certainly understandable that the chemistry of phenol could be quite complex under the conditions of a hydrating cement paste. The basic chemical forms could be PhOH , PhOCaOH , or $(\text{PhO})_2\text{Ca}$ or even ones in which the PhO replaces HO bound to Si or Al , i.e., PhOSiO_3^{3-} or $\text{PhOAl}(\text{OH})_3^-$, for instance. The solubilities of these chemical forms are not known, certainly not in the high ionic strength cement pore water. In addition, there are many possibilities for binding to surfaces by ionic interaction of PhO^- or hydrogen bonding by PhOH .

Our current physical interpretation of these results is that most of the phenol is dissolved as the phenoxide ion in the pore water of the cement matrix. Calcium phenoxide is formed, which in a highly basic condition such as the cement hydration process is believed to be slightly soluble in water. It has been previously determined by a study of proton relaxation times of white cement and deionized

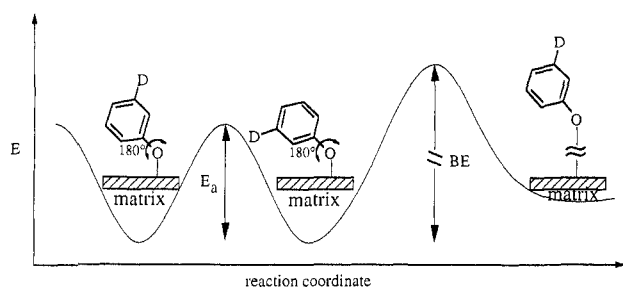


Figure 8. Scheme for molecular motion and ultimate dissociation of phenoxide from a matrix illustrating the connection between E_a for 180° ring flips and the phenoxide-matrix binding energy. Based on the ^2H NMR line shape and T_1 results for an oven-dried sample, the maximum barrier for 180° ring flips is 5.5 kcal/mol at most sites, though, some sites may have a smaller value for E_a . Since the ^2H fast-exchange line shape is observed, the activation energy for 180° ring flips must be less than the bond dissociation energy, BE. If $\text{BE} < E_a$, then only the static and liquid-like line shapes would have been observed, not the $k = 10^9 \text{ s}^{-1}$ line shape as found here. Since the maximum E_a is 5.5 kcal/mol, the BE at most sites must be greater than 5.5 kcal/mol.

water that there is 50% pore water available after 1 month (47) and some pore water after 1 year (48). Since calcium phenoxide is slightly soluble, the excess pore water in cured portland cement is a major problem for S/S of phenol in cement. We assume that our crushed samples allow the evaporation of pore water and eventual precipitation of the phenoxide as mainly Ca salts. The activation energy of phenol undergoing 180° flips is approximately 5.5 kcal/mol, which is approximately 10 times greater than RT . The activation energy for this process is important as it sets a lower limit for the phenol-cement bond strength (Figure 8). Since the activation energy for ring flipping must be less than the phenol-matrix dissociation energy, the phenol-matrix dissociation energy must be greater than 5.5 kcal/mol; that is, 23 kJ/mol of energy can be added to the system, and the phenol stays in a bound state. It is not surprising that the phenol is easily leached by water even if the binding energy of phenol in the cement matrix is much more than about 23 kJ/mol. Solvation energies can provide a driving force that can overcome such binding. In fact, the studies of dried and rehydrated sample, which then show liquid-like mobility, are consistent with the macroscopic observation of leaching.

Conclusion

Solid-state deuterium NMR provides information about the dynamics of a specifically labeled (deuterated) waste in the cement matrix. Both mode and rate of the molecular reorientation affect the spectrum. A distribution of modes and activation energies can exist in a heterogeneous environment such as a cement, and these can be monitored nondestructively by solid-state ^2H NMR spectroscopy.

Important results can be obtained by this technique that are not otherwise obtainable. Over a wide range of loading levels, approximately 50% of the phenol in cement remains quite mobile. The fraction of phenol that is bound to the cement matrix and is executing 180° ring flips has a dissociation energy greater than approximately 5.5 kcal/mol. This is a very important number because it is the lower limit of the phenol-matrix dissociation energy. Phenol is not successfully immobilized in cement on a microscopic scale because the phenoxides are slightly soluble in a highly basic medium such as the pore water in portland cement, and this microscopic behavior is

presumably the reason for macroscopic observations of high leaching potential for cement-solidified phenols.

The ^2H NMR-based procedure introduced herein gives a rapid answer to the question of determining whether waste molecules are tightly or loosely bound to a cement matrix. A main advantage is that the liquid-like waste component can be easily monitored. Also, if the waste is found to be tightly bound to the matrix, the strength of that bond can, under some circumstances, be determined by this method. The bond strength is clearly relevant to an evaluation of the reliability of the S/S process for a particular waste.

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