

Stephen F. Austin State University

SFA ScholarWorks

---

Faculty Publications

Chemistry and Biochemistry

---

1992

## Solid-State NMR Characterization of Organics in Cement

Michael A. Janusa  
janusama@sfasu.edu

Follow this and additional works at: [https://scholarworks.sfasu.edu/chemistry\\_facultypubs](https://scholarworks.sfasu.edu/chemistry_facultypubs)

 Part of the [Chemistry Commons](#)

[Tell us](#) how this article helped you.

---

### Repository Citation

Janusa, Michael A., "Solid-State NMR Characterization of Organics in Cement" (1992). *Faculty Publications*. 10.

[https://scholarworks.sfasu.edu/chemistry\\_facultypubs/10](https://scholarworks.sfasu.edu/chemistry_facultypubs/10)

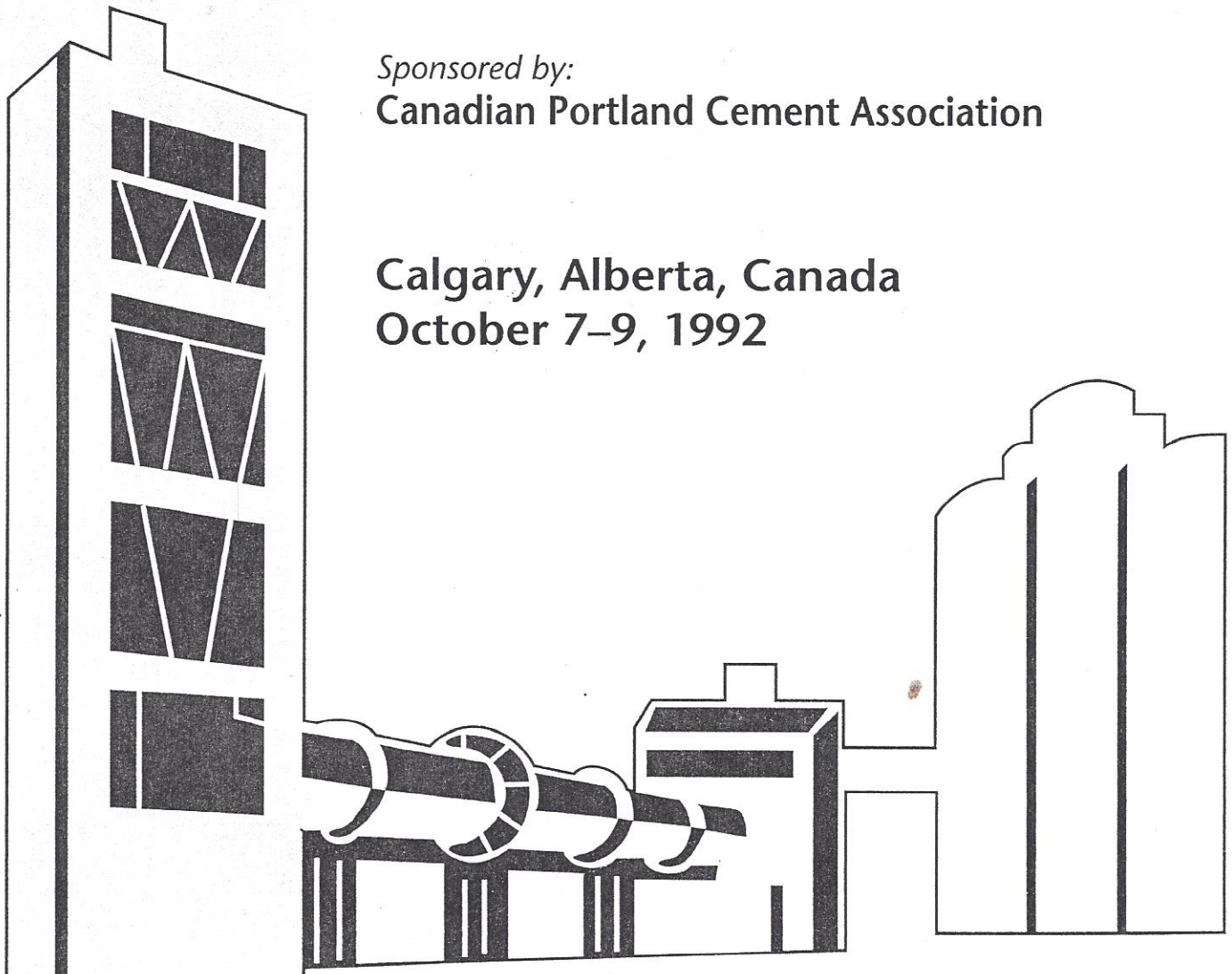
This Conference Proceeding is brought to you for free and open access by the Chemistry and Biochemistry at SFA ScholarWorks. It has been accepted for inclusion in Faculty Publications by an authorized administrator of SFA ScholarWorks. For more information, please contact [cdsscholarworks@sfasu.edu](mailto:cdsscholarworks@sfasu.edu).

# Cement Industry Solutions to Waste Management

*Proceedings of the  
First International Symposium*

*Sponsored by:*  
Canadian Portland Cement Association

Calgary, Alberta, Canada  
October 7-9, 1992



## SOLID-STATE NMR CHARACTERIZATION OF ORGANICS IN CEMENT

Frank K. Cartledge<sup>1</sup>, Leslie G. Butler, Marty E. Tittlebaum, Humayoun Akhter, Devi Chalasani, Michael A. Janusa and Shoulan Yang

### Abstract

Solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) has been applied to cement samples containing water-soluble organics, ethylene glycol, phenol, *p*-bromophenol and *p*-chlorophenol. Cement matrix development has been followed by <sup>29</sup>Si and <sup>27</sup>Al NMR, which shows the organics, particularly ethylene glycol, to be promoters of silicate polymerization despite the fact that they reduce the compressive strength of the pastes. <sup>13</sup>C NMR shows that phenol is completely ionized in cement pastes, but with substituted phenols in the presence of extra added metal salts, ionization is not always complete. <sup>2</sup>H NMR on *d*<sub>5</sub>-phenol shows that even in mature cement pastes, most of the phenol is in a liquid-like environment, presumably dissolved in pore waters. When water is evaporated, the phenol begins to occupy a bound environment with a binding energy of at least 23 kJ/mol (5.5 kcal/mol). Relaxation time measurements on the ethylene glycol system can also be interpreted in terms of a major fraction of the glycol dissolved in pore water and a minor fraction bound to cement surfaces. Clearly, knowledge of the effects of additives on cement matrices and the chemical forms of wastes after cement treatment are prerequisites to understanding and optimizing waste immobilization.

**Key Words:** Portland cement, solidification/stabilization, nuclear magnetic resonance, phenol, ethylene glycol, silicate polymerization, white cement.

---

<sup>1</sup> Author to whom correspondence should be addressed at the Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA.

## Introduction

Portland cement plays a major role in contributing to the solution of various environmental problems, particularly those related to wastes that inevitably must be disposed of in the land. Cement additions improve the physical properties of some major waste streams, such as fly ash and gypsum, to the point that they may be put to practical use in construction projects. In cases of waste streams with a higher content of toxic constituents, particularly heavy metals, the technology referred to as solidification/stabilization (S/S) may be applied to immobilize toxic constituents prior to disposal, and Portland cement is the most common constituent of the binder systems used for this purpose.<sup>1</sup>

The hazardous waste disposal problem is a major national priority. After the best efforts to minimize production of waste and to treat those waste streams (mainly organic-containing) that can be detoxified (through chemical treatment or incineration, for instance), it is still estimated that 16 million metric tons per year are candidates for S/S treatment and landfilling.<sup>2</sup> In addition to these recurring waste streams, there are many cases of land contamination arising through historical malpractice or inadvertent spills for which S/S is also a viable treatment possibility. The best known examples are the so-called Superfund sites, and up to \$20 billion dollars are spent annually on remedial actions at such sites.

There is a strong tendency to use the most economical possible means for treatment of hazardous wastes, and S/S is frequently a strong competitor for that position because of the fact that cement is relatively cheap, and the technology required to mix and place the solidified product is relatively simple. Given this background, it is particularly important to understand the process and to be able to assess its potential for effectiveness when applied to a particular waste stream.

Although there is a significant foundation of work aimed at understanding cements and their hydration reactions, fundamental work devoted to defining the chemistry of the S/S process is all less than 10 years old. For a number of years, we have been conducting research that has as a principal aim the understanding of the detailed chemistry of S/S systems. In practical terms, the two most important questions to address are the extent of immobilization of hazardous constituents and the permanence of the matrix structure and properties under environmental stresses. Clearly, one would ideally like to be able to relate the former (the chemistry of the system) to the latter (practical performance), and that has been a major goal of this research.

The binding agents in common use in S/S are normally cement-like materials (Portland cement, lime/fly ash mixtures, cement and lime kiln dust, etc.), and a variety of additives are also common.<sup>1</sup> Thus, a major complication to detailed study of the process (indeed, a complication to the practical applications as well) is the complexity of the mixtures involved, and in some cases also the variability from batch to batch of major ingredients such as fly ash and kiln dust. In the current work we have restricted ourselves mostly to relatively simple Portland cement systems with a few common additives.

However, even Portland cement alone is already a formidably complex mixture that defies complete characterization. It contains mainly silicate and aluminate minerals, but some are crystalline and some are amorphous, and minor constituents can have important effects on the system. Any specific characterization technique gives only limited

information. Consequently, we have used a variety of microscopic and spectroscopic methods to generate complementary sets of information; however, the present paper will emphasize applications of solid-state nuclear magnetic resonance spectroscopy (NMR).

Solid-state magic angle spinning (MAS) NMR has been used in our studies in several different ways, but principally to characterize the developing cement matrix as hydration occurs. The solid-state  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS NMR spectra contain peaks, often overlapping ones, that correspond to Si in five different environments and Al in two different environments. The  $^{29}\text{Si}$  chemical shifts depend mainly on the degree of condensation of silicon-oxygen tetrahedra.<sup>3,4,5</sup> The symbol, Q, represents a Si atom surrounded by four oxygen atoms. A superscript following the Q shows the number of other Q units attached to the Si atom under study. The principal transformation occurring during cement hydration, as followed by NMR, is the formation of chains containing  $\text{Q}^1$  (chain-terminating) and  $\text{Q}^2$  (chain lengthening) units starting from the orthosilicate ions ( $\text{Q}^0$ ) present in the cement clinker.<sup>6,7,8,9,10</sup> The loss of  $\text{Q}^0$  units as a function of time is a measure of the overall degree of hydration of the cement clinker and agrees well with calorimetric measurements of degree of hydration.<sup>7</sup> Mature cement paste without metal additives contains mainly  $\text{Q}^1$  units, with a smaller proportion of  $\text{Q}^2$  units, and little or no  $\text{Q}^3$  (chain branching) or  $\text{Q}^4$  (crosslinking) units.

Hydration of aluminate phases, which account for roughly 10% of the cement clinker, occurs more rapidly than that of the silicate phases. The chemical shift differences between the 4-coordinate Al atoms present in the clinker and the 6-coordinate Al atoms in the hydrated aluminates can be followed as a function of time in the  $^{27}\text{Al}$  NMR spectra, as was initially shown for hydration of tricalcium aluminate.<sup>11</sup> In all samples of cement clinker that we have examined, both 4- and 6-coordinate Al are present initially, and different lots from different manufacturers show wide variation in the ratio of the two types of Al peaks. Hydration almost always converts the mixture essentially completely to 6-coordinate Al.

A second, qualitatively different, kind of NMR information comes from proton relaxation time measurements, which can define the number of different environments for hydrogen atoms (contained in water molecules or  $\text{OH}^-$  ions) that are present in the cement paste, and the proportions of the total in each environment. These techniques also have been applied to cement hydration previously, usually to white (low iron content) cement in order to avoid paramagnetic effects on relaxation times.<sup>12,13,14</sup>

The present paper will show the range of information that is available from NMR about cement-waste systems by looking in detail at one class of wastes, water soluble organics. Some of our earliest work on S/S concerned phenols and ethylene glycol (EG) in Type I Portland cement, and it involved leaching and extraction studies, SEM with EDAX analysis, x-ray powder diffraction and a variety of physical measurements, including set times and unconfined compressive strength.<sup>15,16,17,18,19,20</sup> The NMR information gathered in that study has never been published, and we have come back to these organic systems recently to apply some more sophisticated experiments. One of our initial goals was to determine the degree of homogeneity of waste distribution in the matrix, so we chose substituent groups on the phenol ring that would make EDAX analysis more simple; consequently, *p*-chloro- and *p*-bromophenol were extensively investigated. We have also shown in separate studies that Cl does not become detached from the aromatic ring during

solidification in OPC,<sup>21</sup> hence detection of Cl means detection of the substituted phenol. The water soluble organics are of real interest in S/S studies, because they are common constituents of waste streams that contain both organics and inorganics. However, since they are water soluble, they are not effectively immobilized toward water leaching unless special measures are taken.

There is a substantial history of studies of interactions of the unsubstituted phenol (PhOH) with cement. It has been assumed in the cement literature that PhOH is converted to calcium phenoxide in contact with cement clinker. Indeed 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".<sup>22</sup> Phenol and mono-substituted phenols typically have pKa's in the range 9 - 11, and the pH of pore waters in hydrated cements is very basic, up to about pH 12.5. 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<sup>2+</sup>, consequently a Ca phenoxide would be expected. It has recently been shown<sup>23</sup> that combination of equimolar quantities of Ca(OH)<sub>2</sub> and PhOH produces PhOCaOH, not (PhO)<sub>2</sub>Ca, and the latter can only be formed under forcing conditions with continuous removal of water. It is possible to distinguish ionized from nonionized phenol by solid-state <sup>13</sup>C NMR, since the *ipso*-carbon of the aromatic ring shifts upfield by about 7 ppm in either PhOCaOH or (PhO)<sub>2</sub>Ca compared to PhOH.<sup>23</sup>

Polyhydroxy organic compounds have also been extensively studied with respect to their retardation of cement hydration, and EG is the simplest example of this class. These species, in contrast to the phenols, have the potential for chelation of metal ions, including Ca<sup>2+</sup>, and this effect has often been cited as the cause of the sometimes dramatic retarding effects of this class of compounds.

## Results and Discussion

Phenol effects on cement We have investigated the organic/cement interactions from the point of view of the effects of organics on the developing cement matrix, as well as the influence of the cement environment on the organic. The former results will be discussed first. Unless specifically stated, all of the results presented refer to 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 (pCP), setting times are approximately doubled, compared to cement alone, and strength is slower to develop.<sup>18</sup> However, the 28-day compressive strength is the same as that of the cement paste without pCP. The effects of *p*-bromophenol (pBP) are similar, but setting is slightly slower and the 28-day compressive strength is about 10% lower. EG has a larger effect, approximately tripling the time to final set and decreasing the 28-day strength by 20%. We have also investigated these samples using SEM and X-ray diffraction (XRD).<sup>24</sup> 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<sup>25</sup> and XRD<sup>24,15,16</sup> still show  $\text{Ca}(\text{OH})_2$  to 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 cement peaks that it is not possible to positively identify the salts in the phenol-cement mixture.<sup>24</sup>

The physical property measurements are a reflection of rate of matrix development, which can also be followed by NMR. Figure 1 shows a plot of the loss of orthosilicate units as a function of time for OPC alone and for OPC containing 10% by weight pCP, pBP, PhOH and EG. At 4 and 8 hours into the hydration process, pCP, pBP and EG actually accelerate formation of silicate dimers and lower molecular weight oligomers, but by 24 hours, the OPC hydration has clearly progressed to a greater extent. At 28 days there is a substantial range of % hydration, with the EG-containing sample exceeding OPC and the PhOH-containing sample lagging farthest behind.

The NMR experiment affords considerable information in addition to simply overall hydration rate. With various additives we have seen very large differences in the proportion of  $\text{Q}^n$  units in the mature paste. For instance, lead additions promote silicate polymerization at long cure times, whereas arsenic additions retard it. The phenols have relatively small effects, but do appear to promote polymerization. Despite the fact that overall % hydration is lower for all the phenol mixtures at 28 days, the proportions of  $\text{Q}^2$  units are essentially the same: OPC alone, 24%; OPC + 10% PhOH, 24%; OPC + 10% pBP, 26%; OPC + pCP, 25%. EG promotes polymerization to a much greater extent; the proportion of  $\text{Q}^2$  units at 28 days being 56%. From many determinations with a wide variety of cement mixtures, we are confident that we can consistently reproduce the proportions of silicate units to  $\pm 4\%$ .

It is clear from this study that there is not a simple relationship between compressive strength and either % hydration or silicate matrix development. In studies of cement pastes without additives, it has been shown that increasing degree of hydration, and particularly increasing proportion of  $\text{Q}^2$  units (both measured by NMR) correlate well with increased compressive strength.<sup>26</sup> By contrast, the EG-containing sample described above has both greater % hydration and proportion of  $\text{Q}^2$  units, but a 20% lower compressive strength.

<sup>27</sup>Al NMR shows very small differences between OPC alone and the organic-containing samples. There is minor retardation in the conversion of tetrahedral Al (Al[4]) to octahedral Al (Al[6]). In OPC pastes, that conversion is almost complete at 1 day, but with the organics there is still 10% or more Al[4] at 1 day. Nevertheless, all the samples (in contrast to some metal salt-containing samples which we have investigated) do progress to almost 100% Al[6] by 7 days.

Cement effects on phenol Some time ago we reported data on extractions of EG from pulverized solids prepared from Portland cement and 10% by weight glycol.<sup>16</sup> That work used pure solvents of varying polarities and also multiple extractions. We concluded that the glycol appeared to occupy more than one environment because polar, aprotic solvents like dimethyl sulfoxide extract much less glycol than water and because multiple extractions even with water did not account for 100% of the glycol. Similar results are obtained for pBP.<sup>27</sup> Water extracts a relatively high proportion of phenols (40% to 60%) from cement-

solidified samples, but the proportion decreases substantially between 90 days and 1 year of cure - down to 9% recovery for pBP at an original loading of 10% by weight.

In recent work, we have applied some additional NMR techniques to look more closely at the environment of the organic components within the cement matrix. We noted above that it is possible to follow the development of several phases of the cement matrix by looking at the time evolution of relaxation times for protons in the curing cement paste. The spin grouping technique allows deconvolution of the observed relaxation time into several components arising from protons in different environments. We have applied this technique to glycol-containing samples, but looking at the protons attached to carbon, not those attached to oxygen. We have followed the spin lattice relaxation time for samples prepared with white (low iron content) cement and  $D_2O$ , and adding 10% of EG- $D_2$ ,  $DO(CH_2)_2OD$ . For the first 24 hours of the hydration process, the proton relaxation can be assigned to two components with relaxation times of 1000 and 200 ms, and magnetization fractions of 88% and 12%, respectively. The minor component, relaxing at the greater rate, is probably glycol adsorbed on the surfaces of cement grains, since at short hydration times iron is likely to be present in the solids, thus promoting relaxation of surface-adsorbed species. The second component is likely to be glycol dissolved in the  $D_2O$  present in the pores. The latter is a reasonable assumption, since we will present evidence shortly that indicates that PhOH, another water-soluble organic, is also mainly present as a solution in pore waters. Unfortunately, in the case of EG- $D_2$ , at longer cure times the relaxation becomes more complex, and it is not possible to use the spin grouping technique successfully. In practice, we have found this to be the case when there are multiple components present which do not differ from one another in relaxation time by a factor of at least 5.

The case of phenols in cement is somewhat more complex, since the phenols are weak acids that can potentially exist under the conditions of cement hydration as either ionized or nonionized species. We have used  $^{13}C$  NMR to investigate samples of solidified cement containing 10% PhOH, pBP and pCP.  $^{13}C$  NMR shows that there is considerable variation in the proportions of ionized and nonionized phenol in the matrix depending on the length of time of cure and the presence of heavy metals along with phenol. Figure 2 shows spectra of PhOH alone,  $PhOCaOH$  alone and a cement sample containing 10% PhOH cured for 2 months. Compared to PhOH, the Ca salt shows coalescence of the *ortho* and *para* carbon peaks, and a substantial difference in chemical shift for the *ipso* carbon. It is the latter shift that is most easily identified in the spectra of the cement samples, such as 2(c), which shows complete ionization to the salt. However, with other additives in addition to a phenol, and at different times of cure, ionization is not complete. We have found cases, as shown in Figure 3, where the phenol is completely nonionized at 7 days of cure, but completely ionized at 2 months. Also, we have seen samples, such as that containing  $Pb(NO_3)_2$ , which show the phenol to be partly ionized. It is not surprising that the relationships are complex, since the nature of the various additives present determine the basicity of the pore waters, which is presumably the major determinant of whether the phenol will be ionized or not.

Thus far, the NMR methods described are ones that have been applied by other workers to cement samples, although not ones containing wastes. Experimental descriptions are available in the cement literature. The next set of experiments uses solid-state deuterium NMR, and since the methods are somewhat less familiar, the experiments will be described



in greater detail. Deuterium NMR is an excellent probe for obtaining the details of molecular motions in solids. Based on a line shape analysis, reorientation modes can be distinguished from one another, and reorientation rates measured in the region of about  $10^3$  to  $10^{11}$  s<sup>-1</sup>. The methods have been applied to the study of motions in a variety of systems, including proteins, lipids, organometallics and polymers. In <sup>2</sup>H NMR, there are four factors that determine the 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<sub>0</sub>.<sup>28</sup> The <sup>2</sup>H line shape is symmetric about the Larmor frequency and is composed to two sets of transitions. The  $|0\rangle \rightarrow |-1\rangle$  transition varies from an offset frequency of -65 kHz to +131 kHz, with the latter corresponding to the z-axis of the electric field gradient aligned with the applied magnetic field and the former corresponding to perpendicular alignment (which 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. 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.

The present work involves phenol which has had all of the ring protons substituted by deuterium. If one assumes that the oxygen atom is anchored, and the phenyl ring is undergoing rapid 180° flips about the C-O bond then the averaged <sup>2</sup>H spectrum will appear as shown in simulation in Figure 4. For slow exchange, the bottom spectrum will be seen, and spectra can be calculated for various stages in between fast and slow exchange. The actual spectra were obtained on samples prepared from white (low iron content) cement, water at a 0.5 w/c ratio and d<sub>5</sub>-phenol at PhOH/c ratios of 0.1, 0.01 and 0.001; 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: 90<sub>x,x</sub>-t<sub>1</sub>-90<sub>y</sub>-t<sub>2</sub>-acquire<sub>x,x</sub>. The 90° pulse length was 3.0 μs, and t<sub>1</sub> was 25 μs; the second delay, t<sub>2</sub>, was adjusted to the echo maximum. Approximately 2000 to 3000 scans were averaged for each experiment. <sup>2</sup>H spin-lattice relaxation times were measured with the inversion recovery technique, using the quadrupole echo pulse sequence with a [180°-τ-] prior to the pulse sequence.

Figure 5 shows spectra obtained for pure d<sub>5</sub>-phenol at 37 °C (a), pure d<sub>5</sub>-phenol at 27 °C (b) and 10% d<sub>5</sub>-phenol in cement cured in an NMR tube at 20 °C (c). Spectrum 5(a) is obtained near the melting point of PhOH and shows a single narrow resonance which indicates that the phenol has liquid-like mobility. Near room temperature, the line shape is broader, but the motion is more complicated than just 180° ring flips and probably includes libration as well. The phenol in cement sample is dominated by the liquid-like spectrum, but the shoulders of the spectra are evidence of 180° ring flips as well.

WFL  
Figure 6 shows spectra for 10% d<sub>5</sub>-phenol in cement, all taken at room temperature: 6(a) sample cured for 2 months in a sealed glass vial, then crushed; 6(b) the previous sample after storage for an additional 10 months; 6(c) sample cured for 2 months, then crushed and dried in an oven for 36 hours at 90°. Clearly, these spectra show more bound phenol than 5(c). In order to determine the percentage of bound phenol, the phenol in cement spectra have been fitted to a model consisting of a simple Gaussian representing the liquid-like phenol and the line shape corresponding to fast two-site jump motion (180° flips). The percentage of deuterons undergoing ring flips is: 5(c), 44 ± 2; 6(a), 55 ± 2; 6(b), 84 ± 2;

6(c),  $95 \pm 3$ .

The spectra in Figure 6 represent samples which have had increasing opportunity for water evaporation. We interpret the result to mean that under ordinary circumstances phenol is present in cement pore waters in ionized form, but mostly dissolved in the water, not as a solid calcium salt. As the capillary pore water is evaporated, an increasing proportion of the phenol shows a bound oxygen and a ring undergoing  $180^\circ$  flips. The latter environment could be a precipitated Ca phenoxide salt or phenoxide bound to surface Ca.

The spectra containing bound phenol correspond to fast exchange, and thus  $T_1$  measurement must be used to determine the ring flip rate. Over a wide range of temperatures (200 - 360 K), a narrow range of  $T_1$ 's (7 - 20 ms) was obtained. We believe that we were constrained to this small range due to the interference of paramagnetic relaxation. Because  $T_1$  data cannot be obtained outside this region, the quality of the data for samples showing  $180^\circ$  ring flips is not sufficient to allow the determination of an activation energy unambiguously. There also appears to be a distribution of activation energies within the solid-like component that cannot be resolved. However, based on constant spectral intensities and line shapes between 260 and 360 K, and the  $T_1$  data, we assign jump rates,  $k \geq 10^9$ . Using a preexponential factor of  $4 \times 10^{13} \text{ s}^{-1}$  and the lowest temperature at which constant intensity and line shape was obtained (260 K), an activation energy for  $180^\circ$  ring flips of 23 kJ/mol (5.5 kcal/mol) is obtained.

If the binding energy of the phenol in the cement matrix is no more than about 23 kJ/mol, then it is not surprising that the phenol is easily leached by water. Solvation energies can provide a driving force that can easily overcome such weak binding. However, the binding may be much stronger if the phenol is adsorbed on a material like an organophilic clay prior to solidification with cement; at least leachability is greatly reduced.<sup>29</sup> The techniques described above should be applicable to determining the proportion of bound phenol (or other labeled organic) and the binding energy in many situations that would be of real interest for S/S technology.

## Conclusions

Water-soluble organics, including ethylene glycol (EG), phenol (PhOH), *p*-bromophenol (pBP) and *p*-chlorophenol (pCP), have been solidified in Type I or white Portland cement and studied by solid-state NMR spectroscopy. All of the following information is available from the NMR experiments, and some of it is uniquely available from that source.

All of the organics initially promote silicate dimerization in the first few hours of hydration, but then become retarders. At long cure times, all are promoters of silicate polymerization, but only EG yields a paste with a higher overall % hydration than OPC alone. The degrees of hydration and degrees of polymerization are not correlated with compressive strength of the pastes, since all of the organics diminish strength. Conversion of aluminates from tetrahedral to octahedral coordination is somewhat retarded by all of the organics.

Relaxation time measurements on  $\text{DO}(\text{CH}_2)_2\text{OD}/\text{D}_2\text{O}$  as a hydrating medium for OPC show that the glycol partitions itself into two environments over the first 24 hours of hydration. The major portion is believed to be dissolved in pore waters, the minor portion adsorbed on cement surfaces. After 24 hours, the relaxation becomes more complex and cannot be further interpreted. Presumably additional environments make contributions to the relaxation.

$^{13}\text{C}$  MAS NMR shows that phenols are normally completely ionized in cement pastes at loadings up to 10% by weight. The ionization is not always complete in the presence of extra added salts, such as  $\text{Cd}(\text{NO}_3)_2$  or  $\text{Pb}(\text{NO}_3)_2$ , but varies with cure time.

Deuterium NMR of  $\text{d}_5$ -phenol in cement shows that the majority of the phenol occupies a liquid-like environment even up to 2 months of cure. That environment is believed to be the phenoxide anion dissolved in pore waters. When water is evaporated from the paste, increasing proportions of the phenol occupy sites in which the oxygen atom is anchored and the aromatic rings under  $180^\circ$  ring flips. The activation energy for the ring flips is approximately 23 kJ/mol, which represents a minimum for the binding energy of the phenol to the cement matrix. Relaxation time measurements indicate that there may be more than one environment for the bound phenol.

The data above provide a good understanding of the reasons that water-soluble organics are not effectively immobilized by Portland cement alone. The NMR techniques are readily applicable to many other cement systems, including ones where the immobilization is much more effective, and are providing very fundamental information about the solidification/stabilization process.

## References

1. Conner, J. R. *Chemical Fixation and Solidification of Hazardous Wastes*, Van Nostrand Reinhold: New York, 1990.
2. Ref. 1, p. 246
3. Lippmaa, E.; Mägi, M.; Samoson, A.; Engelhardt, G.; Grimmer, A.-R. "Structural Studies of Silicates by Solid-State High-Resolution  $^{29}\text{Si}$  NMR", *Journal of the American Chemical Society*, V.102, 1980, pp. 4889-4893.
4. Fyfe, C. A.; Thomas, J. M.; Klinowski, J.; Gobbi, G. C. "Magic-Angle Spinning NMR (MAS-NMR) Spectroscopy and the Structure of Zeolites", *Angewante Chemie International Edition English*, V.22, 1983, pp. 259-275.
5. Lippmaa, E.; Mägi, M.; Tarmak, M.; Wieker, W.; Grimmer, A.-R. "A High Resolution  $^{29}\text{Si}$  NMR Study of the Hydration of Tricalcium Silicate", *Cement and Concrete Research*, V.12, 1982, pp. 597-602.
6. Clayden, N. J.; Dobson, C. M.; Groves, G. W.; Hayes, C. J.; Rodger, S. A. "Solid State NMR Studies of Cement Hydration", *British Ceramic Proceedings*, V.35, 1984,

- pp. 55-64.
7. Barnes, J. R.; Clague, A. D. H.; Clayden, N. J.; Dobson, C. M.; Hayes, C. J. "Hydration of Portland Cement Followed by  $^{29}\text{Si}$  Solid-State NMR Spectroscopy", *Journal of Materials Science Letters*, V.4, 1985, pp. 1293-5.
  8. Rodger, S. A.; Groves, G. W.; Clayden, N. J.; Dobson, C. M. "Hydration of Tricalcium Silicate Followed by  $^{29}\text{Si}$  NMR with Cross-Polarization", *Journal of the American Ceramic Society*, V.71, 1988, pp. 91-6.
  9. Young, J. F. "Investigations of Calcium Silicate Hydrate Structure Using Silicon-29 Nuclear Magnetic Resonance Spectroscopy", *Journal of the American Ceramic Society*, V.71, 1988, pp. C118-C120.
  10. Grutzeck, M.; Benesi, A.; Fanning, B. "Silicon-29 Magic Angle Spinning Nuclear Magnetic Resonance Study of Calcium Silicate Hydrates", *Journal of the American Ceramic Society*, V.72, 1989, pp. 665-8.
  11. Muller, D.; Rettel, A., Gessner, W.; Scheler, G. "An Application of Solid-State Magic-Angle Spinning  $^{27}\text{Al}$  NMR to the Study of Cement Hydration", *Journal of Magnetic Resonance*, V.57, 1984, pp. 152-6.
  12. Lahajnar, G.; Blinc, R.; Rutar, V.; Smolej, V.; Zupancic, I.; Kocuvan, I.; Ursic, J. "On the Use of Pulse NMR Techniques for the Study of Cement Hydration", *Cement and Concrete Research*. V.7, 1977, pp. 385-94.
  13. Schreiner, L. J.; MacTavish, J. C.; Miljkovic, L.; Pintar, M. M.; Blinc, R.; Lahajnar, G.; Lasic, D.; Reeves, L. W. "NMR Line Shape - Spin-Lattice Relaxation Correlation Study of Portland Cement Hydration", *Journal of the American Ceramic Society*, V.68, 1985, pp. 10-16.
  14. MacTavish, J. C.; Miljkovic, L.; Pintar, M. M.; Blinc, R.; Lahajnar, G. "Hydration of White Cement by Spin Grouping NMR", *Cement and Concrete Research*, V.15, 1985, pp. 367-77.
  15. Walsh, M. B.; Eaton, H. C.; Tittlebaum, M. E.; Cartledge, F. K.; Chalasani, D., "The Effect of Two Organic Compounds on a Portland Cement-Based Stabilization Matrix," *Hazardous Waste & Hazardous Materials*, V.3, No. 1, 1986, pp. 111-123.
  16. Chalasani, D.; Cartledge, F. K.; Eaton, H. C.; Tittlebaum, M. E.; Walsh, M. B., "The Effects of Ethylene Glycol on a Cement-Based Solidification Process," *Hazardous Waste & Hazardous Materials*, V.3, No. 2, 1986, pp. 167-173.
  17. Tittlebaum, M. E.; Eaton, H. C.; Cartledge, F. K.; Walsh, M. B.; Roy, A., "Procedures for Characterizing Effects of Organics on Solidification/Stabilization of Hazardous Wastes," *ASTM STP 933, Hazardous and Industrial Solid Waste Testing and Disposal: Sixth Volume*, D. Lorenzen, R. A. Conway, L. P. Jackson, A. Hamza, C. L. Perket and W. J. Lacy, Eds., ASTM, Philadelphia, 1986, pp. 308-318.
  18. Sheffield, A.; Makena, S.; Tittlebaum, M.; Eaton, H.; Cartledge, F., "The Effects of Three Organics on Selected Physical Properties of Type I Portland Cement," *Hazardous Waste & Hazardous Materials*, V.4, No. 3, 1987, pp. 273-286.
  19. Skipper, D. G.; Eaton, H. C.; Cartledge, F. K.; Tittlebaum, M. E., "The Microscopic Fracture Morphology of Hardened Type I Portland Cement Paste Containing para-Chlorophenol," *Hazardous Waste & Hazardous Materials*, V.4, No. 4, 1987, pp. 389-402.

20. Skipper, D. G.; Eaton, H. C.; Cartledge, F. K.; Tittlebaum, M. E., "Scanning Electron Microscopy/Energy Dispersive X-ray Analysis of Type I Portland Cement Pastes Containing paraChlorophenol," *Cement and Concrete Research*, V.17, 1987, pp. 851-863.
21. Cartledge, F. K.; Eaton, H. C.; Tittlebaum, M. E. "The Morphology and Microchemistry of Solidified/Stabilized Hazardous Waste Systems" U.S. EPA Project Report, EPA/600/S2-89/056 (1990); avail. NTIS.
22. Lea, F. M. *The Chemistry of Cement and Concrete*, 3rd Ed. Chemical Publishing Co., Chicago, 1971.
23. Schlosberg, R. H.; Scouten, C. G. "Organic Chemistry of Calcium. Formation and Pyrolysis of Hydroxycalcium Phenoxides", *Energy & Fuels*, V.2, 1988, pp. 582-585.
24. Cartledge, F. K.; Eaton, H. C.; Tittlebaum, M. E., "The Morphology and Microchemistry of Solidified/Stabilized Hazardous Waste Systems," U.S. EPA Project Report, EPA/600/S2-89/056, 1990; avail. NTIS.
25. Chou, A. C.; Eaton, H. C.; Cartledge, F. K.; Tittlebaum, M. E., "A Transmission Electron Microscopic Study of Solidified/Stabilized Organics," *Hazardous Waste & Hazardous Materials*, V.5, No. 2, 1988, pp. 145-153.
26. Parry-Jones, G.; Al-Tayyib, A. J.; Al-Dulaijan, S. U.; Al-Mana, A. I. "<sup>29</sup>Si MAS-NMR Hydration and Compressive Strength Study in Cement Paste," *Cement and Concrete Research*, V.19, 1989, pp. 228-34.
27. Chalasani, D., "Development of Techniques for Studying Interactions of Organic Compounds with Complex Solid Matrices", PhD Dissertation, Louisiana State University, Baton Rouge, LA, 1988.
28. Gerstein, B. C.; Bybowski, C. R., *Transient Techniques in NMR of Solids*, Academic Press, Orlando, FL, 1985.
29. Sheriff, T. S.; Sollars, D. J.; Montgomery, D.; Perry, R., "Modified Clays for Organic Waste Disposal", *Environmental Technology Letters*, V.8, 1987, pp. 501-514.

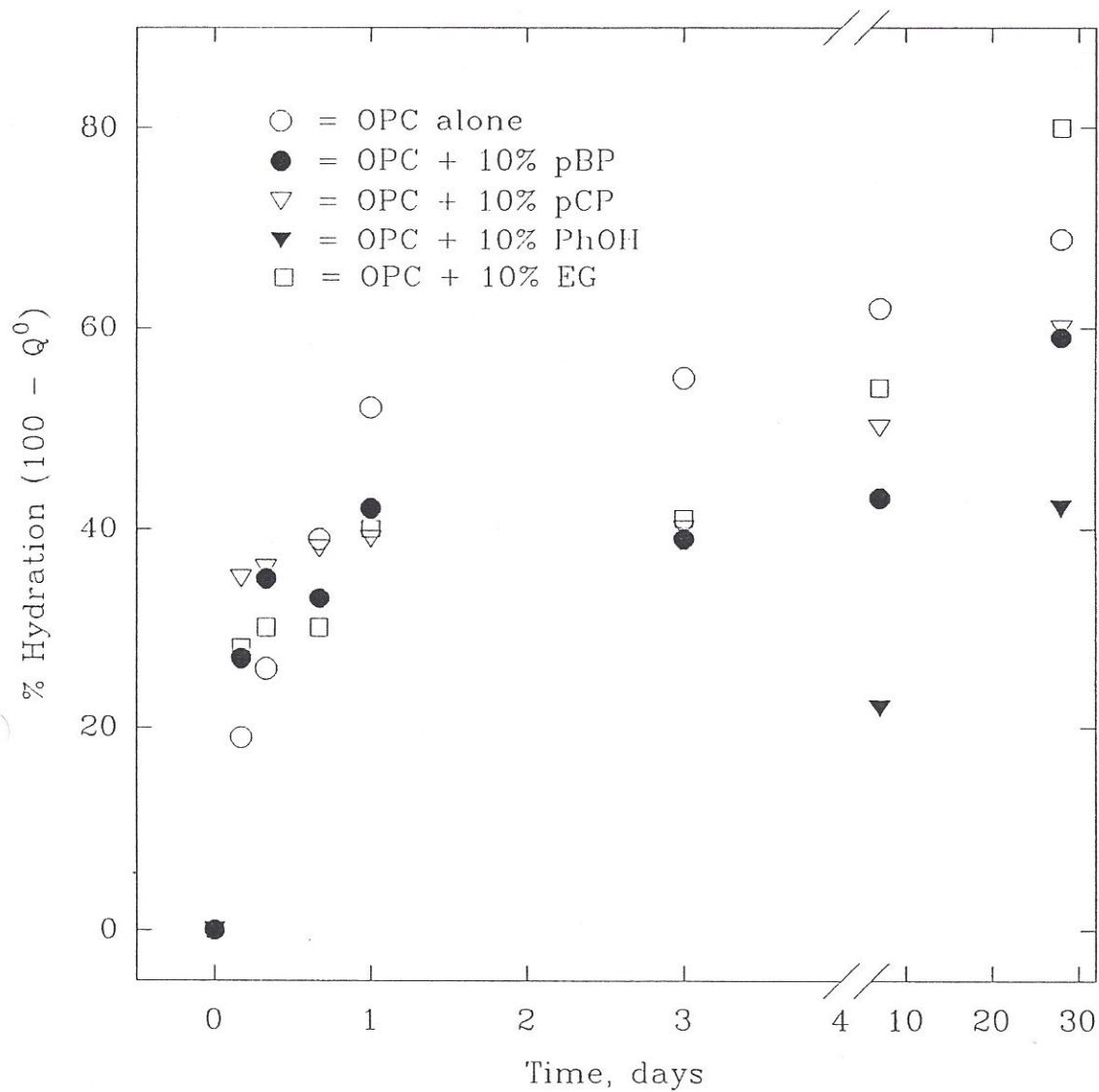
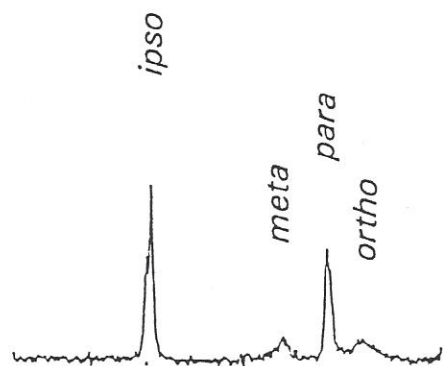
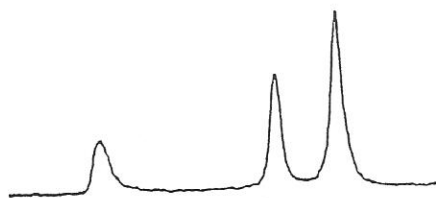


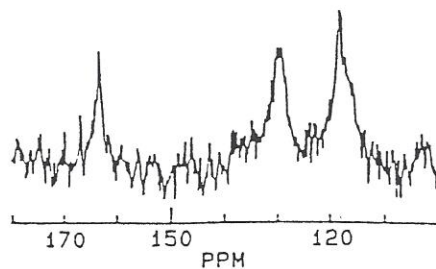
Figure 1. Percent hydration (measured by the loss of orthosilicate units in the  $^{29}\text{Si}$  NMR) as a function of time for pastes prepared from Type I Portland cement with 10% organic and  $w/c = 0.5$ .



Phenol

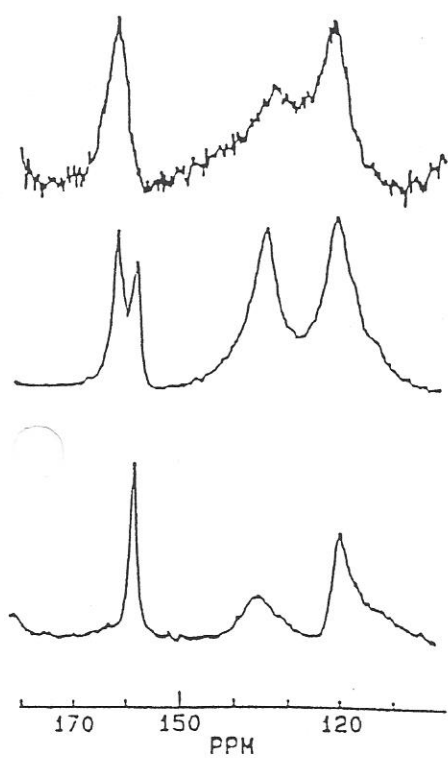


PhOCaOH



10% Phenol in OPC cured 60 days

Figure 2.  $^{13}\text{C}$  MAS NMR spectra of PhOH, PhOCaOH and 10% PhOH in OPC cured for 2 months ( $w/c = 0.5$ ).



OPC +  $\text{Cd}(\text{NO}_3)_2$  + *p*BP, 2 months

OPC +  $\text{Pb}(\text{NO}_3)_2$  + *p*BP, 7 days

OPC +  $\text{Cd}(\text{NO}_3)_2$  + *p*BP, 7 days

Figure 3.  $^{13}\text{C}$  MAS NMR spectra of 10% *p*-bromophenol in Type I Portland cement pastes containing also 10% by weight of Cd or Pb from the nitrate salts, cured for variable lengths of time.



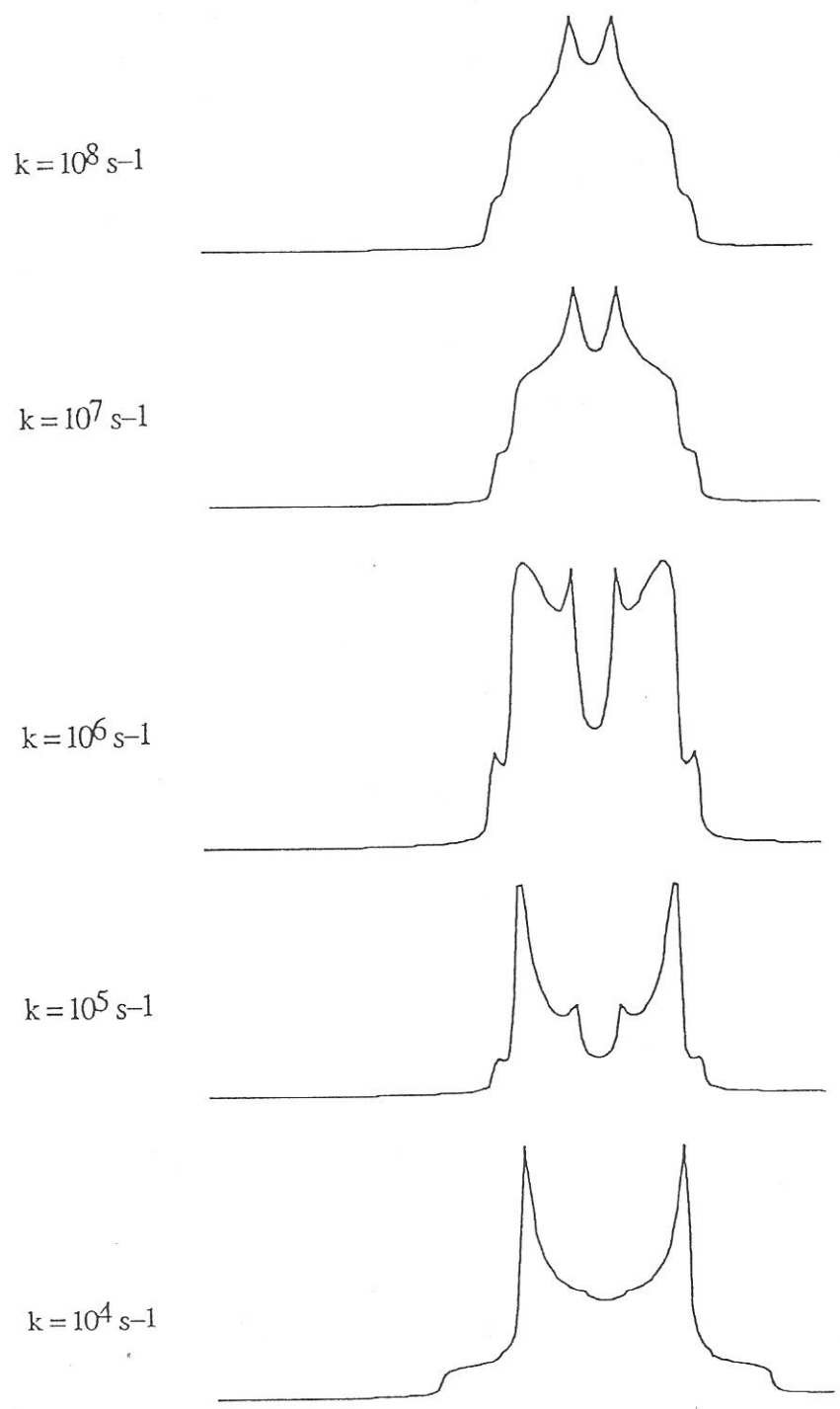


Figure 4. Simulated deuterium NMR line shapes for  $d_5$ -phenol anchored at oxygen and undergoing either fast (above) or slow (below)  $180^\circ$  ring flipping motions.

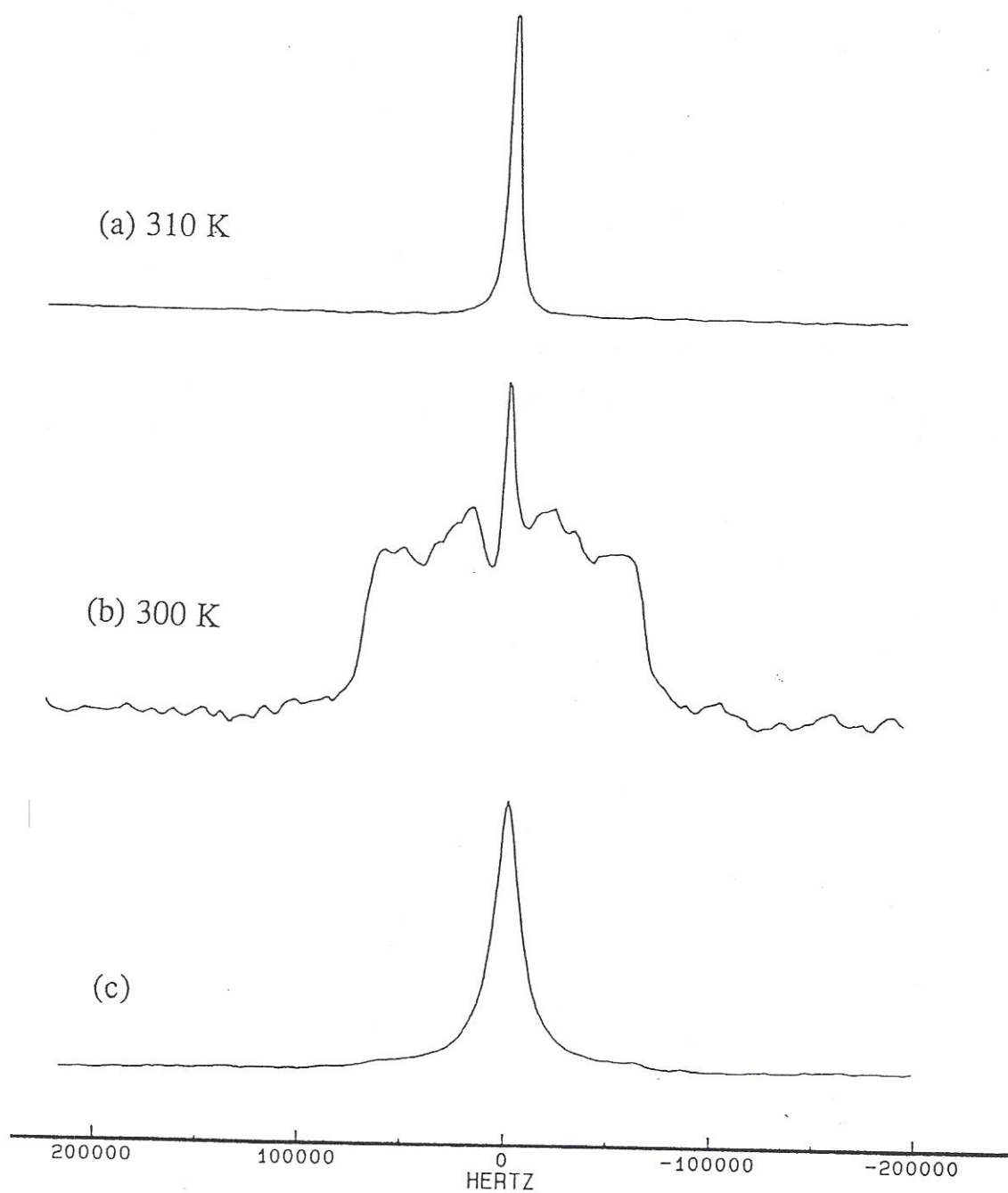


Figure 5. Deuterium NMR spectra of  $d_5$ -phenol (a) as a pure semi-solid at 37 °C; (b) as a pure solid at 27 °C; (c) as a 10% mixture in white cement cured for 28 days in an NMR tube.

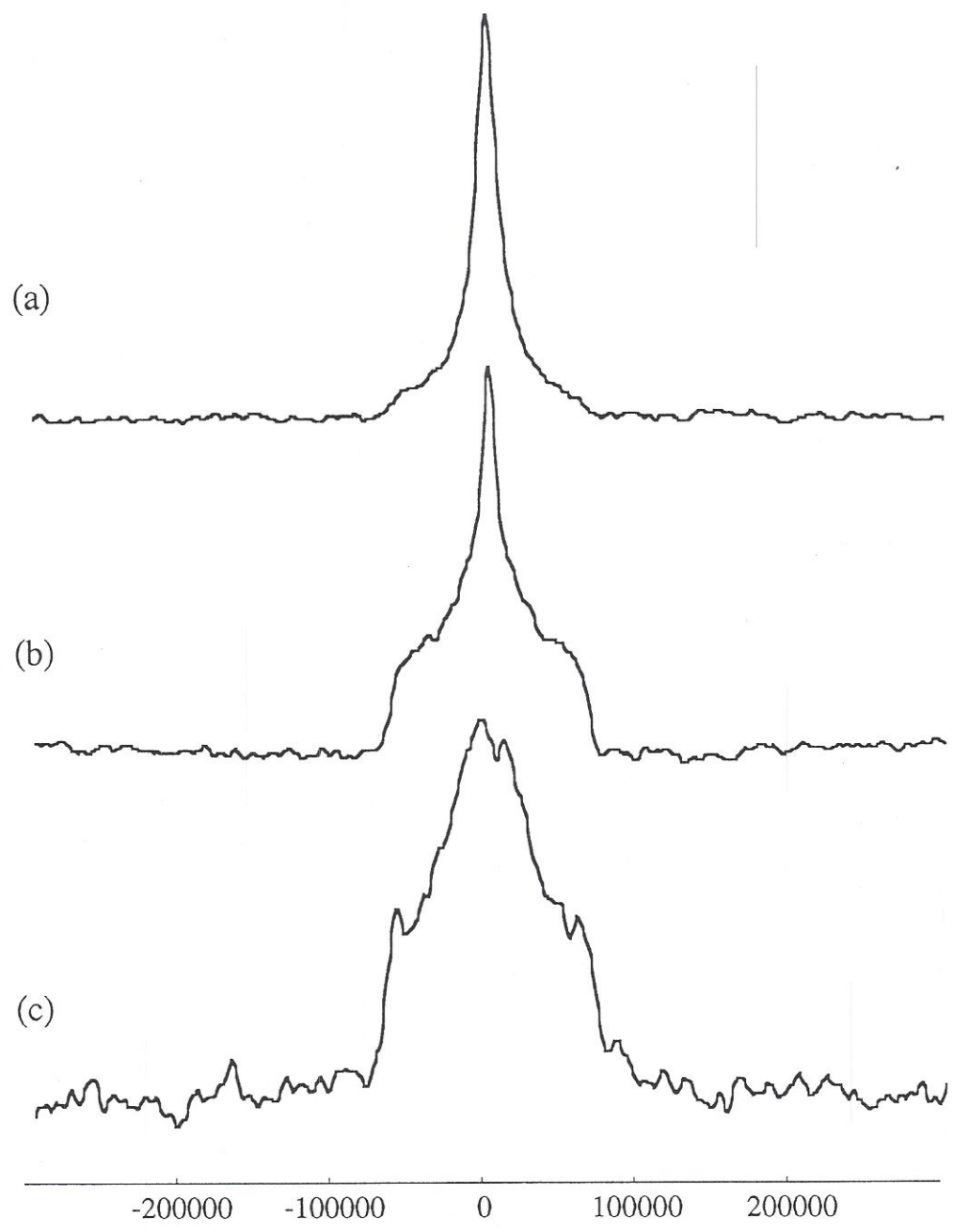


Figure 6. Deuterium wide-line NMR spectra of 10%  $d_5$ -phenol in white cement; (a) sample cured 56 days then crushed; (b) 56-day crushed sample stored for an additional 10 months; (c) 56-day crushed sample heated at 90 °C for 36 hours.



CANADIAN  
PORTLAND CEMENT ASSOCIATION  
ASSOCIATION  
CANADIENNE DU CIMENT PORTLAND

## INFORMATION & REGISTRATION PACKAGE

*International Symposium*

# Cement Industry Solutions to Waste Management

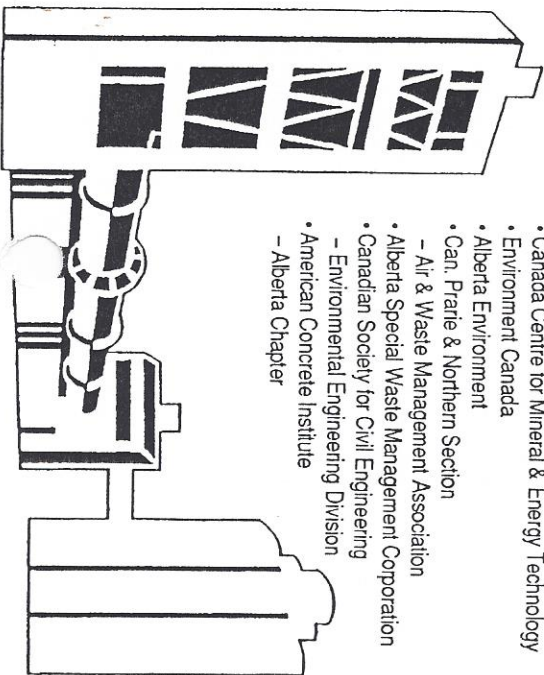
October 7-9, 1992

Calgary Convention Centre  
Calgary, Alberta, Canada

Sponsor: • Canadian Portland Cement Association

Co-Sponsors: • University of Calgary

- Canada Centre for Mineral & Energy Technology
- Environment Canada
- Alberta Environment
- Can. Prairie & Northern Section
- Air & Waste Management Association
- Alberta Special Waste Management Corporation
- Canadian Society for Civil Engineering
- Environmental Engineering Division
- American Concrete Institute
- Alberta Chapter



## REGISTRATION INFORMATION

To register for the symposium, return the attached Registration form. If the form is missing, interested persons can register by sending name, mailing address and telephone number, along with the appropriate fee in Canadian funds to:

CANADIAN PORTLAND CEMENT ASSOCIATION  
201-1155 WEST PENDER STREET  
VANCOUVER, B.C.  
CANADA V6E 2P4  
TELEPHONE (604)685-0582  
FAX (604)685-1574

### REGISTRATION FEE:

Delegates -  
Before Sept. 15, 1992 . . . \$395 (C\$)/\$365.17 + \$25.83 GST)  
After Sept. 15, 1992 . . . \$450 (C\$)/\$420.60 + \$29.40 GST)  
Accompanying Persons . . . . . \$50 (C\$)/\$46.75 + \$ 3.25 GST)

### HOTEL ACCOMMODATIONS

A block of rooms has been set aside for Symposium registrants at the:

Skyline Plaza Hotel	Telephone: (403) 266-7331
110-9th Avenue S.E.	1-800-661-7776
Calgary, Alberta	FAX: (403) 262-8442
T2G 5A6	

The Skyline Hotel is a modern 23-storey hotel situated in the heart of downtown Calgary. The hotel is directly connected to the Calgary Convention Centre, the site of the Symposium.

Room reservations should be made directly with the hotel, prior to September 3, 1992, by calling the toll free number noted above from anywhere in North America. Please refer to the Canadian Portland Cement Association Symposium file.

Delegates to the Symposium are guaranteed a room rate of \$107 per night, plus 7% GST and 5% Hotel Tax, single or double occupancy. A first night deposit is required to confirm your reservation. Reservations received by the hotel after September 3, 1992, will be on "availability" basis at prevailing rates.

### CEMENT PLANT TOUR

Arrangements have been made for a tour of the Lafarge Canada Inc. cement plant at Exshaw, Alta., following the symposium on Friday afternoon, October 9, 1992. Those taking the tour will be back in Calgary by 6:00 PM. Please check the box on the registration form if you plan to attend the cement plant tour.

## SYMPOSIUM PROGRAM

### CONTAINMENT/STABILIZATION/ SOLIDIFICATION SESSION

"Dense High Strength, Low Permeability Materials For Containment" - J.F. Young, Illinois

"Development of Grouting Technology: A P T.M. Gilliam, R.D. Spence, Oak Ridge Nat'l. I

"Cement Stabilized Incinerator Ash For Use Bricks" - T.J. Larsen, Florida Dept. of Transp W.F. Chang, University of Miami

"Chemical Stabilization of Contaminated Soil Using Cement and Cement By-Products" - J.F S. Cotton, P.R. Lear, Chemical Waste Managen

"Solidification of Contaminated Soil Containing Using Cementitious Systems" - V. Yegendran Ltd., D. Stewart, Pol-Con Systems

"Stabilization of Evaporator/Spray Dryer So A.E. Bland, Ash Management Engineering Inc., Ontario Hydro

"Cementation of Toxic Sludges: Italian Experi S. Balzamo, G. De Angelis, F. De Poli, ENEA, I Engineering Division

"Comparison of the Chemical Fixation and Sol Steel Foundry Dust Using Portland Cement an Calcium Sulphate" - A. Andres, I. Ortiz, University del Pais Vasco

"Solid State Nuclear Magnetic Resonance Cha of Organics in Cement" - F.K. Cartledge, L. But M. Tittlebaum, H. Akhter, D. Chalasani, M. Jani Louisiana State University

"Stabilization of Hazardous Inorganic Waste Based Matrices" - E. Zamorani, G. Serrini, Comr European Communities

"Remediation of Oil Refinery Sludge Basin" - Portland Cement Association, W Ten Bruin, Gec