Interpretations and Limitations of Nuclear Magnetic Resonance

PAUL SELIGMANN, Portland Cement Association

● ALTHOUGH the interest of the Applied Research Section of the Portland Cement Association has centered primarily on the possible use of nuclear magnetic resonance for determining the states of binding of the water in hydrated cement paste, the conclu sions drawn as a result of study and the few experiments that have been conducted for the Section are of interest. This belief is based on the fact that most of the hydration products of portland cement are, like the clay fraction of soils, of a colloidal nature (1). In fact, the system concerned is at least as complex as the soil-water system. In addition to the phenomena associated with changes in adsorbed water content, there are the chemical reactions of continued hydration of the cement and the reactions of t hydration products with atmospheric carbon dioxide. No technique has yet been devel oped for determining the precise states of physical and chemical binding of the water in hydrated cement paste.

The Section's interest in nuclear magnetic resonance was first aroused by the appearance of a paper (2) in 1955 dealing with the different proton resonance patterns th appear at various degrees of hydration of cement-water pastes. It appeared from thi work that physically adsorbed and chemically combined water could be distinguished, at least semiquantitatively. A careful study of the potentialities of this method was therefore initiated; this study was completed at about the same time that an earlier speaker, Raymond Blaine, obtained his equipment. The conclusions from this study pertinent to the Section were (a) if the instrument could distinguish no more types of water than were indicated in the 1955 paper, the technique would not be useful either routine work or as a research tool, and (b) in view of this apparent limitation, there would be little or no justification to make the considerable effort required to develop techniques for use of the equipment or to develop detailed theoretical interpretations the patterns obtained.

The first conclusion is based on a variety of results obtained from shrinkage data and X-ray diffraction patterns showing that the portion of the paste water that is eva able at 105 C cannot be a homogeneous adsorbed phase, and further that the precisio of proton resonance measurements was not sufficient for this technique to be used as replacement for the time-consuming, routine adsorption methods now in use. The s ond conclusion was based in part on the scope of the work of the Section and in part o the extreme difficulty of precise interpretation of nuclear magnetic resonance patter

The proton resonance frequency depends on the difference in energy between two proton states representing two possible orientations with respect to the magnetic fie This energy difference, in turn, depends on the field strength as is shown by the foll ing formula:

$$\gamma = \frac{\Delta E}{h} = \frac{\mu H}{h} (\cos \theta_1 - \cos \theta_2)$$

in which

γ = the resonance frequency
ΔE = the energy difference between the two proton orientations
H = the magnetic field strength
μ = the magnetic moment of the proton
θ_1, θ_2 = the angles between the magnetic field and the magnetic moment of the proton in the two orientations
h = Planck's constant

If the magnetic field were completely homogeneous, the resonance pattern would onsist of only one infinitesimally thin line at the resonance frequency given by the rmula. The pattern would therefore be the same for all materials containing hydro-en and would be useful at best only for the quantitative determination of hydrogen con-nt. The real utility of the instrument is based on the fact that the local magnetic field rength at the positions of individual protons is a resultant of the external magnetic eld and the magnetic fields produced by neighboring electrons, nuclei, and other atoms d molecules. The actual pattern obtained, therefore, results from the particular en-ronments in which the protons find themselves, and consequently the patterns them-lves when properly interpreted indicate the states of binding of the protons in the ma-rial under study. Although qualitative conclusions can be readily drawn, as has been own in the two preceding discussions, a more detailed interpretation is exceedingly ficult.

The effect of binding can be illustrated by a description of the difference in patterns tween a liquid and a solid. In a solid, the atoms are rather tightly bound; they are t free to move and as a result the local field may vary considerably from point to int within a lattice. As a result, there is a large range of resonance frequencies be-ise there is a wide variety of local magnetic field strengths. In a liquid, on the other nd, much greater freedom of motion is possible; the application of the external field ises the nuclei and atoms to align themselves in such a way as to cause the local ld to be much more nearly like the external field. The line width is, therefore, con-erably narrower and all portions of the pattern are very close to the frequency that uld be calculated from the external field strength by Eq. 1.

Really precise interpretations of proton magnetic resonance patterns have been made y for single crystals of known structure where all the components of the local mag-ic field could be precisely determined. The cement-water system, like the soil-er system, is far from meeting the prerequisites for such detailed analysis.

It must be recognized, however, that the phenomenon of nuclear magnetic resonance be used in a variety of techniques. The discussions of Blaine and of Pickett were n based on the so-called "wide line" technique, which is very adaptable to the study olid material. There is another technique known as the "spin-echo" technique that ess well known but has been successfully used in determining the states of binding adsorbed" water in various colloidal systems without a precise knowledge of the l magnetic field strengths.

Of great interest in this connection is a paper on the state of water adsorbed on silica (3). At low moisture contents, three distinct classes of water were found in place he single, previously assumed class. Of equal significance is recent work (4) on state of binding of adsorbed water on cellulose. In this system, two distinct types dsorbed water could be distinguished and the frequency of transition between the two s could be determined.

Because of the great promise of this new technique, samples of a particular hydrated ent paste with different evaporable water contents were submitted to the manufac-r of a spin-echo proton magnetic resonance apparatus that has recently become com-cially available. Unfortunately, it was found that the local magnetic fields produced he small quantity of ferric oxide in the cement distorted the patterns sufficiently to roy their value. It is believed, however, that the method still holds great promise he study of colloids containing no iron. Unfortunately, the iron usually present in minerals would cause this technique to be of little value in work with the systems terest to this audience.

lthough the conclusions reached herein appear very discouraging, one further tech-e is being investigated; namely, the study of dielectric constant and dielectric loss r measurements as a function of frequency. In both of the applications of spin-echo nique cited, the results confirmed preliminary indications obtained by studies of the ctric constant of the same materials. Inasmuch as local magnetic fields are not ved to interfere with the ability of a polarized water molecule or hydroxyl group to nate with an external electromagnetic field, this technique appears to hold promise. nticipated difficulty is that the results obtained depend not only on protons but rather l polar or polarizable constituents of the material under study. A recent paper (5)

on measurements of halloysite and kaolinite shows the difficulties in interpretation that may be encountered. It is encouraging, however, that studies on the materials o interest to this audience are being undertaken.

REFERENCES

1. Powers, T.C., and Brownyard, T.L., "Studies of the Physical Properties of Hardened Portland Cement Paste." Jour. Amer. Concrete Inst. (Oct. 1946-April 1947); Proc., 43:101-132, 249-336, 469-504, 549-602, 669-712, 845-88 933-992 (1947), PCA Res. Bull. 22.
2. Kawachi, K., Murakami, M., and Hirahara, E., "Studies on the Hydration and Hardening of Cement (Experimental Studies on Nuclear Magnetic Resonance o Water Molecules in Cement)." Bull. Faculty Engineering, Hiroshima Univ., 4:95-101 (1955).
3. Zimmerman, J.R., Holmes, B.G., and Lasater, J.A., "A Study of Adsorbed Water on Silica Gel by Nuclear Resonance Techniques." Jour. Phys. Chem. 60:1157-1161 (1956).
4. Sasaki, M., Kawaii, T., Hirai, A., Hashi, T., and Odajima, A., "A Study of Sorbed Water on Cellulose by Pulsed NMR Technique." Jour. Phys. Soc. Ja 15:1652-1657 (1960).
5. Goldsmith, B.J., and Muir, J., "Surface Ion Effects in the Dielectric Propertie of Adsorbed Water Films." Trans. Faraday Soc., 56:1656-1661 (1960).