

● Short Communication

NMR IN POROUS MATERIALS

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Nuclear magnetic resonance (NMR) was used to determine the pore size distribution of hardened Portland cement pastes. The method is based on the well-known freezing point depression of water when confined inside the pore matrix of a material. It is demonstrated how this technique can be applied in cementitious materials to probe the microstructure of the main hydration product: the cement gel. © 1998 Elsevier Science Inc.

Keywords: Nuclear magnetic resonance; Porous media; Freezing point depression.

The microstructure of a porous system is an important characteristic of the material that largely determines not only its mechanical properties but also its transport properties and durability performance. In particular, for cement and concrete the porosity is strongly correlated with strength, and the permeability and the rate at which ions and gases diffuse through the material are of major importance for durability. The traditional methods for measuring pore size distributions, such as sorption isotherms and mercury intrusion porosimetry, suffer from major disadvantages mainly associated with the preliminary drying of the sample.¹

A nuclear magnetic resonance (NMR) technique that probes nondestructively the pore size distribution of porous solids has been recently proposed.² This method is based on the lowering of the freezing point of liquids embedded in capillary pores. Low temperature calorimetry is based on the same property of confined liquids and has been also used as a probe of the pore structure of saturated porous building materials.³ The theoretical basis of this technique is presented here, as well as an application of the method in two hardened ordinary Portland cement (OPC) samples.

Two cement pastes were prepared using commercial OPC. The first sample (OPC reference) contained no additives and was used as a reference sample. The second sample (OPC mixture) contained 6% kiln dust (a mineral additive) and 15% pozzolanic material by weight. NMR experiments were performed on hardened

cement pastes at 200 MHz. The NMR liquid signal following a 90° pulse was recorded as a function of temperature. This signal is recorded after 60 μs from the end of the 90° pulse so that only the liquid part of the decaying signal is detected.

The experimental results are shown in Fig. 1. The NMR signal attributed to the liquid part of the water is recorded as a function of decreasing temperature. As can be seen from Fig. 1, the water inside the pore structure of the sample remains liquid well below the normal freezing point of ordinary bulk water. The lowering of the freezing point of an adsorbed liquid is well known, and many formulas have been proposed in the literature,⁴ most of which are based on the Kelvin equation.

Batchelor and Foster⁵ proposed the following equation:

$$\Delta T = \frac{T_{\text{observed}}}{L} \frac{2M}{r} \left\{ \frac{\gamma_l}{\rho_l} - \frac{\gamma_s}{\rho_s} \right\} T_{\text{normal}},$$

where L is the latent heat of fusion, M is the molecular weight, r is the radius of the capillaries, γ and ρ are the surface energy and density measured at the normal melting point T_0 , and $\Delta T = T_{\text{normal}} - T_{\text{observed}}$ is the depression of the freezing point.

The above form is more convenient than the alternative form

$$\Delta T = \frac{T_{\text{normal}}}{L} \frac{2M}{r} \left\{ \frac{\gamma_l}{\rho_l} - \frac{\gamma_s}{\rho_s} \right\} T_{\text{observed}}$$

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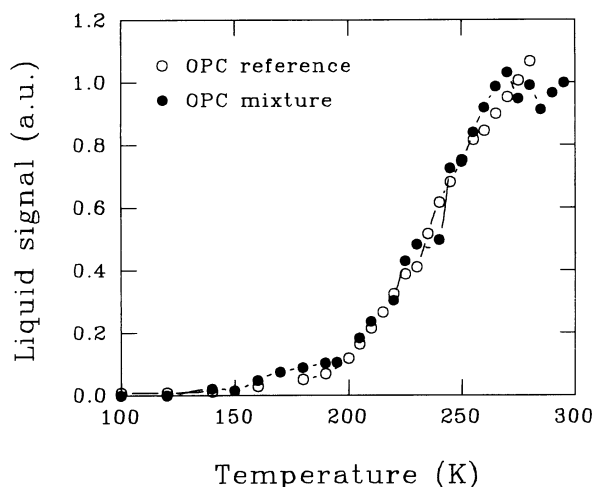


Fig. 1. NMR signal from the pore water as a function of temperature.

which requires γ and ρ to be known for both solid and liquid phases at the lowered melting point T_{observed} .⁵ Based on the above relation, a calibration curve has been constructed for the freezing point depression of pure water confined inside the pores as a function of the pore radius. This is shown in Fig. 2.

Using this calibration curve, the observed temperature has been converted into pore radius, and the derivative of the liquid signal in Fig. 1 has been numerically obtained. This is shown in Fig. 3, where dV/dr has been plotted as a function of the pore radius. This evidently reflects the pore size distribution of the cement pore matrix.

Both cement samples demonstrate a pronounced maximum at around 20 Å. This size corresponds to the

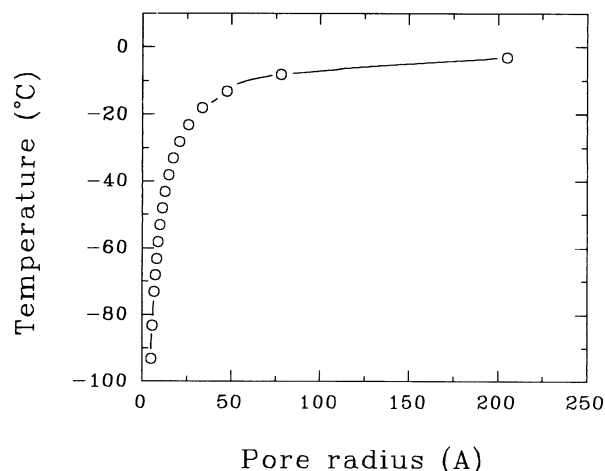


Fig. 2. Freezing point depression of pore water as a function of pore radius.

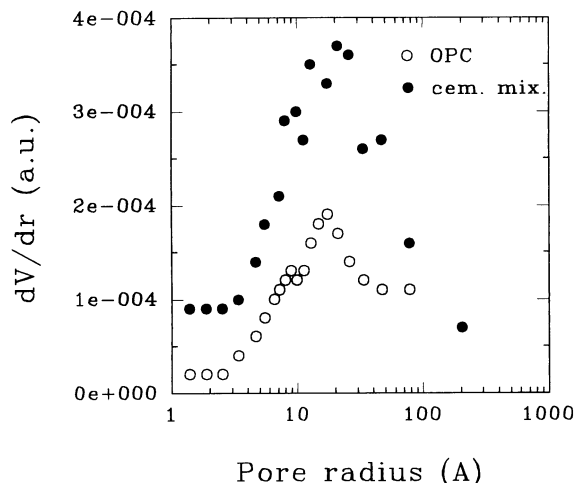


Fig. 3. Pore size distribution for an OPC and a cement mixture.

so-called gel porosity, which is substantially smaller than the capillary porosity measured by other methods. It is clearly seen that this method is sensitive to this type of porosity, which corresponds to the gel cement product. It is also observed that the addition of the additives in the cement mixture does not affect the gel porosity.

The pore size distribution of hardened cement paste as determined from water vapour adsorption experiments⁶ also exhibits a pronounced maximum at 20 Å, thus further verifying the method. Also quite recently Jehng et al.⁷ have employed both NMR relaxation analysis and the freezing depression method in hardened cement pastes and found a pronounced maximum at around 20 Å.

Acknowledgments—This work was sponsored by the North Atlantic Treaty Organization's Scientific Affairs Division in the framework of the Science for Stability Programme.

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