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On the interpretation of ^{1}H 2-dimensional NMR relaxation exchange spectra in cements: Is there exchange between pores with two characteristic sizes or Fe^{3+} concentrations?

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ABSTRACT

We discuss the effect of paramagnetic impurity content (thought to be predominantly Fe^{3+}) in cement pastes on the interpretation of ^{1}H NMR T_2–T_2 exchange spectra. Through measurements on synthesised C–S–H with greatly reduced paramagnetic impurity concentration, we show that the spectra cannot be explained by exchange between regions of different Fe^{3+} concentration but rather are explained by exchange between regions of different pore size.

It is widely accepted that the observed spin-lattice and spin-spin NMR relaxation rates, $1/T_1^{obs}$ and $1/T_2^{obs}$ respectively, of water ^{1}H confined within porous media such as cements are related, in the fast diffusion limit, to the corresponding bulk rates by

$$\frac{1}{T_{1,2}^{obs}} = \lambda_{1,2}\frac{S}{V} + \frac{1}{T_{1,2}^{bulk}} \approx \lambda_{1,2}\frac{S}{V} \qquad (1)$$

where $\lambda_{1,2}$ are the corresponding surface relaxivities and S and V are the pore surface area and volume respectively [1]. Hence, a measure of either relaxation time affords a measure of a characteristic pore size, $r \approx V/S$. Observation of a distribution of relaxation times is evidence for a distribution of pore sizes. Eq. (1) reflects the fact that relaxation primarily occurs by water ^{1}H diffusing to, and interacting with, the pore surface. In cements, the dominant interaction is magnetic dipolar with surface paramagnetic impurities, principally Fe^{3+}. The fast diffusion limit corresponds to the fact that water must diffuse a distance which is large compared to the pore size during the relaxation in order that molecules repeatedly encounter the surface.

In a series of recent papers, [2,3], we have presented 2-dimensional ^{1}H NMR relaxation data as evidence not only of a distribution of pore types in cements, but additionally of water exchange between pores with two distinctive sizes. Two diagonal peaks suggested two pore sizes. Off-diagonal peaks implied exchange. Analysis suggested that water exchanges between pores with characteristic sizes ranging from 0.7 to 1.3 nm and 13 to 25 nm, and that the exchange rate is of the order of 5 ms^{-1}. Observation of this exchange is important to an understanding of water dynamics within the C–S–H gel phase of cement.

The original analysis was based on an assumption of uniform surface relaxivity. In subsequent discussion [4], the question was raised as to the validity of an alternate explanation whereby water is seen to exchange between two pore environments with pores of comparable size ($r \approx V/S$) but different surface relaxivity (λ). The apparently larger pore type could, instead, have a lower concentration of surface Fe^{3+} impurities than the apparently smaller pores. The observed 2D relaxation spectra would be unchanged. The different scenarios are presented in Fig. 1(a) and (b). Plausible explanations of how this might come about due to inhomogeneous Fe distribution in cement particles and/or due to inhomogeneous Fe dissolution/precipitation during hydration and curing reactions were informally suggested but not confirmed.

It is the purpose of this short note to confirm that the alternate explanation is almost certainly incorrect. This confirmation comes from the observation, Fig. 2, that the characteristic relaxation pattern of two dominant reservoirs linked by two exchange peaks observed in white cement, reproduced here, and grey cement shown elsewhere [5], is seen shifted by one order of magnitude to slower rates in synthesised C–S–H. The synthesised C–S–H has been shown to be substantially free of paramagnetic impurities, using electron spin resonance, (ESR) Fig. 3. The ESR spectra are presented, as is normal, in derivative format. Thus the total paramagnetic concentration of a sample is proportional to the total area under the integrated spectrum. The pore surface concentration of Fe^{3+} in similar white cement has previously been estimated as $2.5 \times 10^{11} \pm 20\%$ Fe^{3+} cm^{-2} [3]. It is clear that the concentration for synthesised C–S–H is

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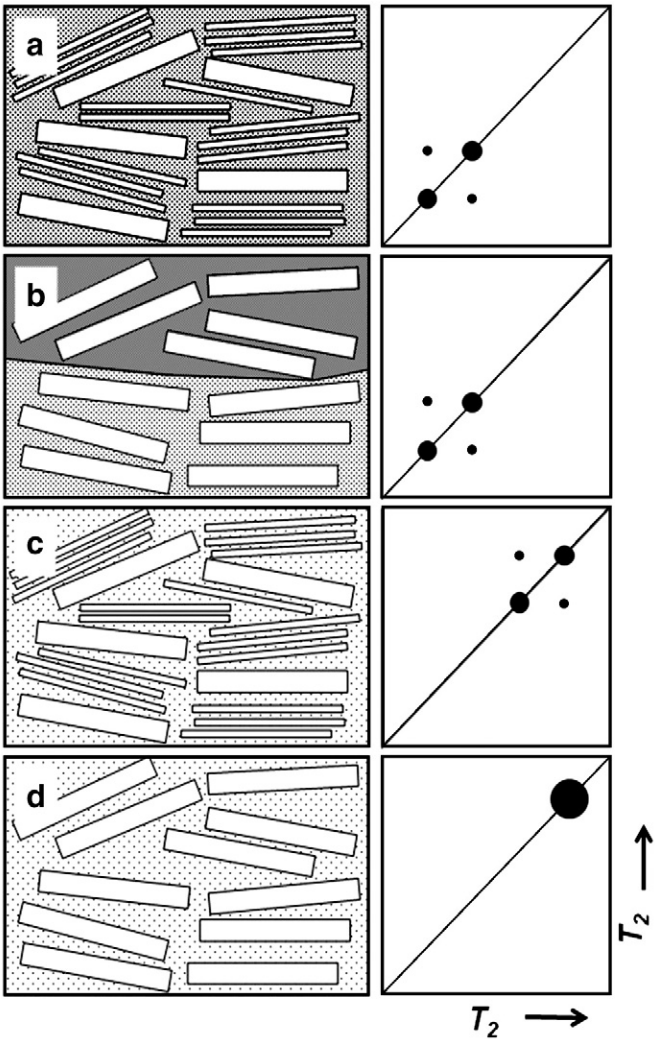

Fig. 1. A highly stylised schematic of inferred C–S–H pore structure (left column) and the expected T_2–T_2 map (right column) for each of the alternate structures. (a) Planar pores of two characteristic sizes (widths, $r \approx V/S$) are embedded in a matrix of uniform paramagnetic impurity concentration (suggested by the patterned background). (b) Pores of a single size are embedded in regions of different paramagnetic impurity concentrations. The T_2–T_2 map is unchanged. (c) The two pore sizes are embedded in a matrix of very low paramagnetic impurity concentration as in synthesised C–S–H. The T_2–T_2 map shifts up the diagonal. (d) Pores of a single size are embedded in a matrix of very low paramagnetic impurity concentration. The T_2–T_2 map collapses to a single diagonal peak high on the diagonal.

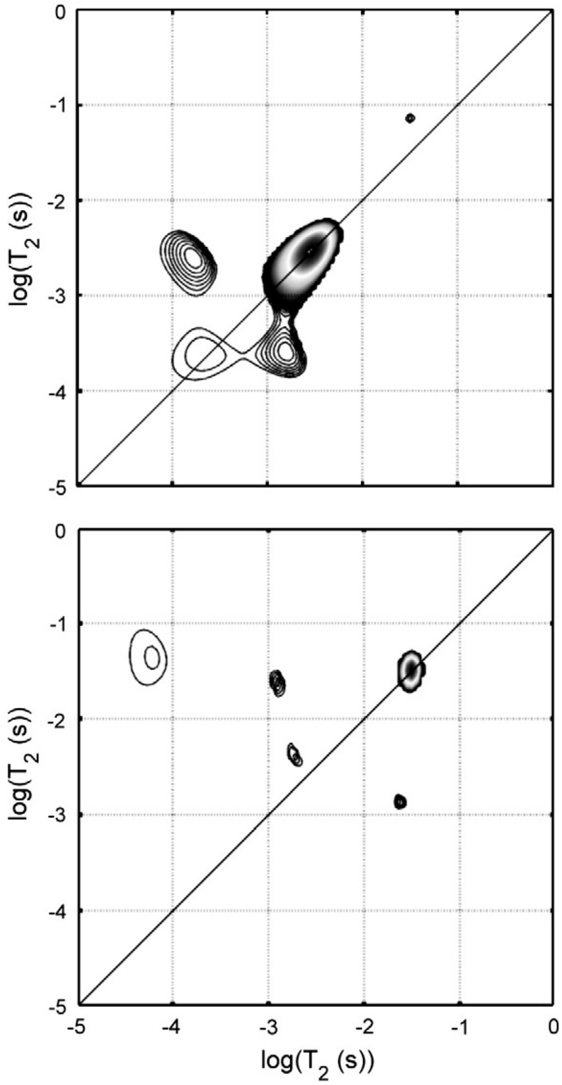

Fig. 2. Top, a T_2–T_2 spectrum recorded from a 1 day old white Portland cement sample cured at 20 °C. Bottom, the same experiment performed on synthesised C–S–H.

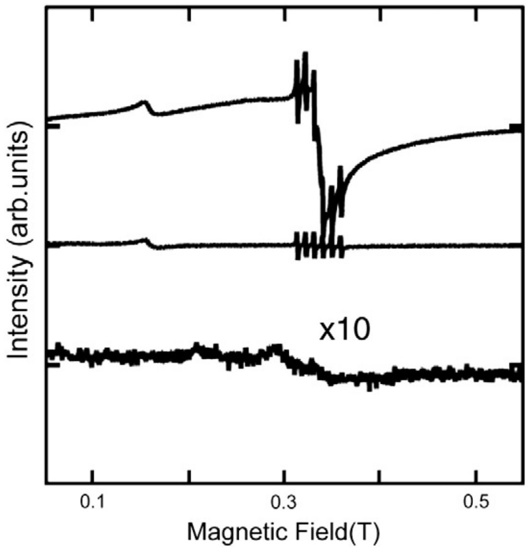

Fig. 3. ESR derivative spectra of (top to bottom): a commercial grey Portland cement, a white Portland cement and synthesised C–S–H (shown times 10).

negligible compared to white cement which is in turn much lower than grey cement.

Movement of the ^{1}H NMR relaxation spectrum up the diagonal as observed is indicative of the surface relaxivity decreasing by a constant factor, Fig. 1(c), due to a decrease in paramagnetic concentration. If, alternatively, in synthesised C–S–H there was only one pore size then the pattern would collapse to a single peak, Fig. 1 (d). This has not been seen. Clearly, the only plausible interpretation of the synthesised C–S–H spectrum is that there remains exchange between pore types of different size with relaxation by low-level, residual surface interactions.

The data shown in Fig. 2 are 2D ^{1}H NMR relaxation exchange spectra recorded from white cement and from synthesised C–S–H. The data is recorded with an exchange time of 3 ms, but is otherwise in every respect acquired and analysed in similar fashion to that previously presented [3]. The reader is therefore referred to that earlier work for a full discussion of the data acquisition method and interpretation. The white cement was prepared as previously reported.

The synthesised C–S–H was made from analytical grade materials at the University of Bourgogne (Dijon) following the same procedure as in [6]. The C/S ratio is 0.75. The spectral peaks in synthesised C–S–H are notably sharper than in white cement, possibly arising from a more uniform microstructure. The small peak at $(\log(T_2\,(\mathrm{s})), \log(T_2\,(\mathrm{s}))) = (-4.5, -1.5)$ is almost certainly noise and artefact.

There has been considerable speculation as to the nature of the pores in cement as revealed by NMR relaxometry. The signal attributed to water in the smallest pores could arise from the interlayer water within the C–S–H nano-particles. The next reservoir could be the water in the inter-particle spaces. Another explanation is that both reservoirs are inter-particle water and that the two sizes arise from inhomogeneity of the inter-particle packing density. The current data throw no further light on this discussion. However, analyses of NMR solid echo data and of double quantum filtered NMR spectra to be reported elsewhere [5,7] suggest that the former assignment prevails.

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References

[1] F. D'Orazio, J.C. Tarczon, W.P. Halperin, K. Eguchi, T. Mizusaki, Molecular diffusion and nuclear-magnetic-resonance relaxation of water in unsaturated porous silica glass, Phys. Rev. B 42 (1990) 9810–9818.
[2] P.J. McDonald, J.-P. Korb, J. Mitchell, L. Monteilhet, Surface relaxation and chemical exchange in hydrating cement pastes: a two-dimensional NMR relaxation study, Phys. Rev., E 72 (2005) 011409.
[3] L. Monteilhet, J.-P. Korb, J. Mitchell, P.J. McDonald, A NMR T_2-store-T_2 2-dimensional correlation relaxation study of cement pastes, Phys. Rev. E 74 (2006) 061404.
[4] Informal discussion, NANOCEM open meeting 2006.
[5] A. Valori, Characterisation of cementitious materials by ^{1}H NMR, PhD Thesis, University of Surrey, available at: http://www.nanocem.org/fileadmin/nanocem_files/documents/MC-RTN/Projects/Project_4/thesis_valori_final.pdf.
[6] S.-Y. Hong, F.P. Glasser, Alkali binding in cement pastes: Part I. The C–S–H phase, Cement and Concrete Research, 29, 1999, pp. 1893–1903.
[7] P.J. McDonald, V. Rodin, A. Valori, Characterisation of intra- and inter-particle C–S–H gel pore water in white cement based on an analysis of NMR signal amplitudes as a function of water content. Submitted to Cement and Concrete Research.