

● *Contributed Paper*

## ANALYSIS OF MICROPOROSITY AND SETTING OF REACTIVE POWDER CONCRETE BY PROTON NUCLEAR RELAXATION

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The proton spin-lattice relaxation measured at several frequencies leads to a resolved distribution of four  $T_{1i}$  for reactive powder concrete (RPC). The typical  $T_{1i}$  frequency dependences are quantitatively interpreted by a biphasic fast exchange model and a proton nuclear relaxation of hydrated paramagnetic ions at the surface of the pores. This leads to an estimation of the pore sizes. We present the first application of this nuclear relaxation method to follow *in situ* the kinetics of the hydration and setting of such material. © 1998 Elsevier Science Inc.

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### INTRODUCTION

Reactive powder concretes (RPC) are composed of cement, high silica fume content, and crushed quartz, and they present a very low water-to-cement ratio (15%).<sup>1-2</sup> Though these concretes exhibit very high mechanical and durability properties, a question remains: what is the microstructure of RPC, and how is it related to the macroscopic resistance of these disordered materials?

Here we answer the first part of the question by measuring the proton longitudinal nuclear magnetic relaxation at several frequencies of RPC without adding any solvent. At each frequency, the observed non-exponential recovery is explicitly resolved in terms of a discrete distribution of four spin-lattice relaxation times,  $T_{1i}$ , by the inverse Laplace method.

The observed typical frequency dependence of these four measured proton relaxation times is characteristic of a nuclear paramagnetic relaxation.<sup>3</sup> Electron spin resonance (ESR) at 4 K of RPC quantifies the amount of such paramagnetic impurities (mainly  $\text{Fe}^{3+}$ ).<sup>4</sup> Such a frequency dependence allows validation of our theoretical interpretation in terms of a biphasic fast exchange model and proton nuclear relaxation of hydrated paramagnetic ions at the surface of the pores.<sup>5</sup> This interpretation allows transformation of the discrete distribution of four

spin-lattice relaxation times in terms of a discrete distribution of four hierarchical average pore sizes.

Finally we show that our nuclear relaxation method is useful to follow *in situ* the kinetics of hydration and setting of the RPC.

### PROTON NUCLEAR RELAXATION IN RPC AT SEVERAL FREQUENCIES

The longitudinal proton magnetization decays in RPC have been obtained through the usual inversion recovery method at 20, 40, 100, 300, and 500 MHz. We have also measured these decays in the rotating frame at 17.8 and 38.5 kHz. A representative example of the proton magnetization decay in RPC at 17.8 kHz is displayed in Fig. 1a. For each frequency, we observe a pronounced non-exponential decay. The Laplace inverse method (Contin program<sup>6</sup>) has allowed us clearly to resolve four single exponential components whose individual spin-lattice relaxation times,  $T_{1i}$ , are spread over four orders of magnitude (Fig. 1b). Our observation by differential scanning calorimetry (DSC) of different confined classes of water supports such a multimodal distribution of pores.<sup>5</sup> The typical frequency dependences displayed in Fig. 1c are indicative of the origin of the relaxation process. For instance, the enhancement of the proton

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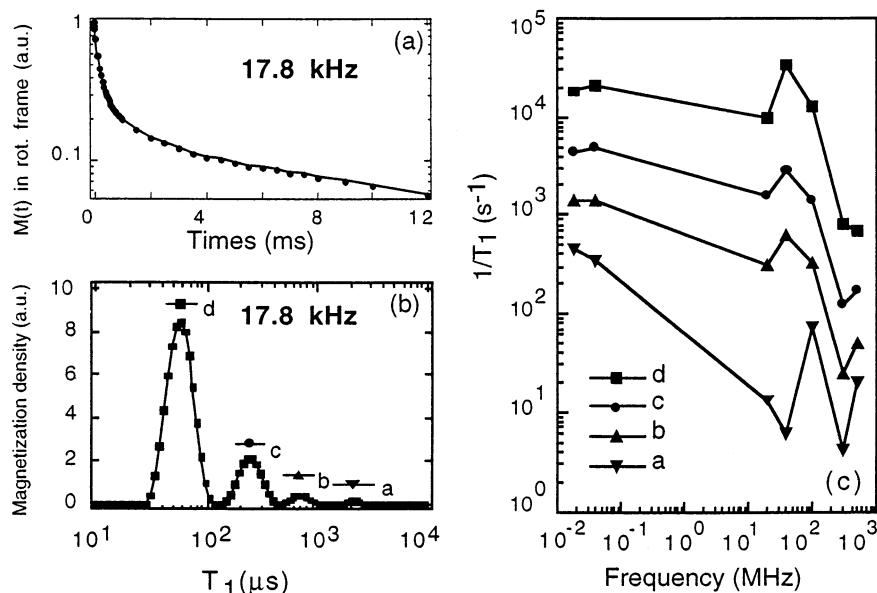


Fig. 1. (a) Recovery of proton longitudinal magnetization at 17.8 kHz. (b) Magnetization density vs.  $T_1$  after Laplace inversion of the curve (1a). (c). Frequency dependences of the four different  $T_{1i}$  values ( $i = \{a - d\}$ ).

relaxivity for these four rates in the 10–300 MHz range reveals a nuclear paramagnetic relaxation process.<sup>3</sup> Here the electron relaxation rate makes a dominant contribution to the effective correlation time for the electron nuclear coupling at the pore surfaces.<sup>5</sup> We confirm the presence of paramagnetic impurities by X-band ESR of the RPC at 4 K.<sup>4</sup> The comparison with the ESR spectrum of a copper reference has allowed quantification of the paramagnetic species at a level of two  $10^{19}$  spins/g of RPC. The analysis of such an ESR spectrum shows that the dominant contribution comes from  $\text{Fe}^{3+}$  ionic species in a high spin state in a distorted octahedral surrounding of oxygen.<sup>4</sup> One notes also a very small amount of  $\text{Mn}^{2+}$  species. We checked that these two paramagnetic species are already present in the cement. The presence of  $\text{Fe}^{3+}$  confirms a Mössbauer study<sup>7</sup> on iron-exchanged calcium silicate hydrate identical to 11 Å-tobermorite, where the authors conclude that there are reasons to suggest that  $\text{Fe}^{3+}$  can enter into the structure of tobermorite and take positions of released  $\text{Ca}^{2+}$  without much loss of the crystallinity.

#### DETERMINATION OF AVERAGE PORE SIZES IN RPC

As discussed above, the main source of the proton surface relaxation comes from the electron-nuclear dipole-dipole relaxation process at the surface of the pores. This process exists through the dipolar fluctuations between the electronic spin-bearing ions, S, and the protons, I, of the close solvation iron-shell (SIS). We have

shown that when diffusion or exchange between the SIS and the “bulk” phase is much faster than the nuclear magnetic resonance (NMR) measurement time, we can apply the biphasic fast exchange model<sup>8</sup> and for each individual decay,  $\exp(-t/T_{1i})$ , the  $i^{\text{th}}$  observed longitudinal relaxation rate is formally given by the relation<sup>5</sup>:

$$\frac{1}{T_{1i}} = \frac{1}{T_{1b}} + 3 \frac{N_s}{\langle R \rangle_i} v_{\text{sol}} \frac{n}{T_{1s}^{H-\text{Ion}}(\omega_1)}. \quad (1)$$

Here  $T_{1b}$  and  $T_{1s}^{H-\text{Ion}}(\omega_1)$  are the “bulk” and SIS relaxation times, respectively. The latter describes the nuclear paramagnetic longitudinal relaxation rate and depends on the proton frequency  $\omega_1$  as described in Refs. 4 and 9. In Eq. (1) we have supposed that the time of residence of the proton species in the SIS is much longer than the corresponding correlation time responsible for the relaxation.  $N_s$  is the surface density of paramagnetic spins,  $S$ .  $N \sim 3$  is the average number of proton species in the volume  $v_{\text{sol}}$  of the “solvation cage” surrounding the  $\text{Fe}^{3+}$  ion. The four average pore radii,  $\langle R \rangle_i$ , are defined through the surface-to-volume ratio,  $S_{\text{pore},i}/V_{\text{pore},i} = 3/\langle R \rangle_i$ , for a spherical pore shape. Because most of the experimental relaxation times are in the millisecond range (Fig. 1c), the overall relaxation is dominated by the SIS contribution, and one can neglect the “bulk” one in Eq. (1).

It is possible to get a value  $N_s \sim 3.2 \cdot 10^{12}$  Fe spins/cm<sup>2</sup> from our ESR measurements,<sup>4</sup> knowing the specific area ( $\sim 50$  m<sup>2</sup>/g) and the porosity ( $\approx 8\%$ ) of the RPC.<sup>1</sup>  $V_{\text{sol}}$

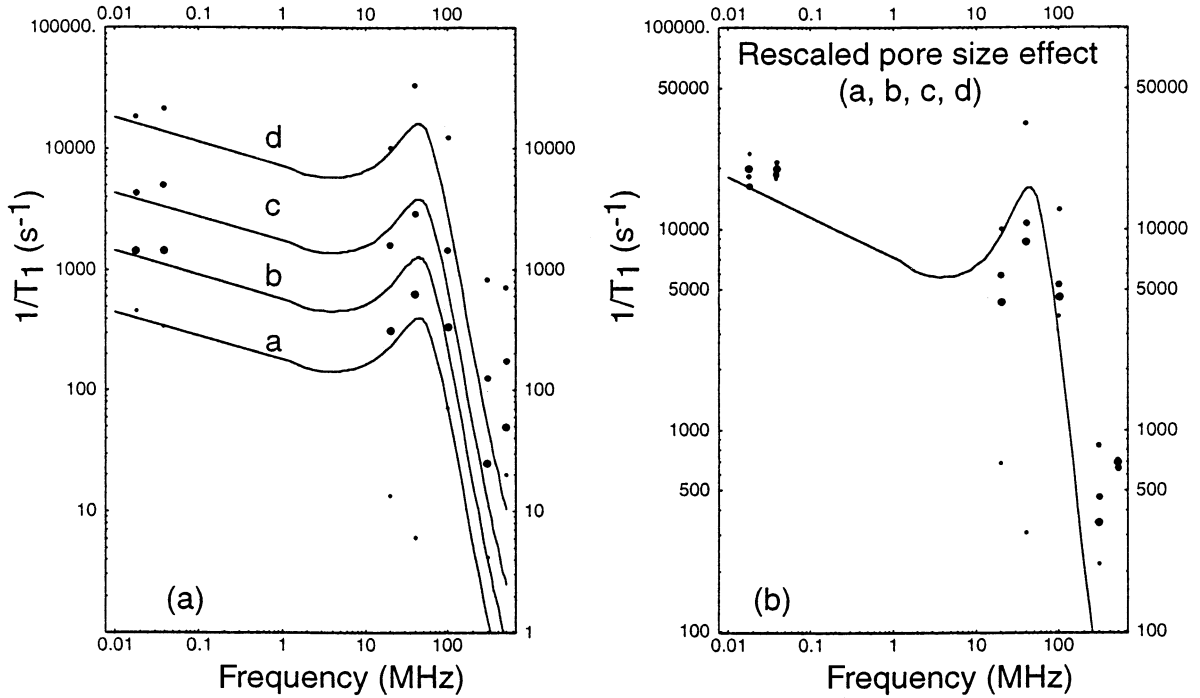


Fig. 2. (a) Best fits obtained (continuous lines) with Eqs. (1 and 2) of the frequency dependences of the four different  $T_{li}$  values ( $i = \{a - d\}$ ) (dots). (b) Frequency dependences of  $1/T_{li}$  rescaled on  $1/T_{ld}$  by the ratio  $\langle R_{i+1} \rangle / \langle R_i \rangle = \alpha \sim 3.7$  ( $i = \{a - d\}$ ).

$\approx 1.2 \cdot 10^{-22} \text{ cm}^3$  is obtained with an interspin distance I-S of 2.2 Å and a proton species shell of 2-Å width.

In order to fit the frequency dependences of Fig. 1c, we substitute in Eq. (1) the Bloembergen-Morgan relation<sup>3</sup> for a nuclear paramagnetic relaxation process. According to this relation, one has, in the very low-frequency range, the constant value  $1/T_{ls}^{H-Ion} \propto 10 H_I^2 T_{le}$ , where  $T_{le}$  is the electronic spin-lattice relaxation time and  $H_I$  is the dipole-dipole coupling between proton ( $I = \frac{1}{2}$ ) and electronic  $\text{Fe}^{3+}$  ( $S = \frac{5}{2}$ ) spins. For an interspin distance I-S of 2.2 Å, one has immediately  $H_I^2 = 6.4 \cdot 10^{13} \text{ s}^{-2}$ . Inversion of Eq. (1) thus leads to a linear relation between the average pore radii,  $\langle R \rangle_i$ , and the measured proton relaxation times,  $T_{li}$ :

$$\langle R \rangle_i = (30 N_s v_{solv} H_I^2 n T_{le}) T_{li} \quad (2)$$

A consequence of such a linear dependence is that the distribution of average pore radii has a similar shape as the one of relaxation times shown in Fig. 1b.

In the discrete distribution of Fig. 1b, one observes a constant value of the ratio,  $\alpha = T_{1+i}/T_{li} \sim 3.7$  ( $i = \{c - a\}$ ), between two consecutive values of  $T_{li}$ . One finds also a similar constant for most of the other frequencies, as shown in the log-log plot of Fig. 1c. Due to

the linear relation in Eq. (2), this means that one has also  $\langle R_{i+1} \rangle / \langle R_i \rangle = \alpha$ . This gives a clear indication of a hierarchical (Apollonian) character of the pores in RPC.

The remaining step is to find an experimental determination of  $T_{le}$ . The electronic relaxation process might be induced either by electron fluctuations in the electrical symmetry at the ion Fe or by dipolar fluctuations, both leading to a square fluctuation coupling about  $10^{19} - 10^{20} \text{ s}^{-2}$ ,<sup>9</sup> thus giving a value of  $T_{le}$  standing in the nanosecond range. To our knowledge there are so far no direct experimental measurements of such a fast electronic relaxation time. The limit of time resolution of pulsed ESR in the high field is about 40 ns and appears not to be sufficiently fast. Here we propose to measure  $T_{le}$  from the unique features of the observed frequency dependences of the four  $T_{li}$ . Our model is able to reproduce quite well the net enhancement of the proton relaxation at 40 MHz of Fig. 1c (see Fig. 2a), leading to a square electronic fluctuation coupling of  $6 \cdot 10^{19} \text{ s}^{-2}$ . Then we deduce a value of  $T_{le} \sim 0.6 \cdot 10^{-9} \text{ s}$  from the best fit displayed in Fig. 2a. One notes that such an enhancement of the proton relaxation is at the origin of the use of contrast agents in whole-body MR imaging.<sup>10</sup> Finally the use of Eq. (2) gives the average pore radii ( $\langle R \rangle_d = 7 \text{ Å}$ ,  $\langle R \rangle_c = 29 \text{ Å}$ ,  $\langle R \rangle_b = 89 \text{ Å}$ , and  $\langle R \rangle_a = 280 \text{ Å}$ ) in RPC from the respective observed  $T_{li}$  ( $i = \{a - d\}$ ).

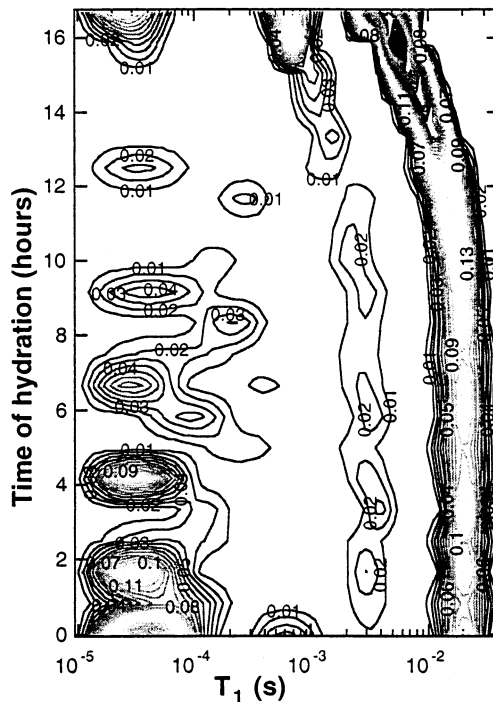


Fig. 3. Contour plot of the local magnetization density versus  $T_1$  and time of hydration, obtained from 20 proton longitudinal nuclear-relaxation experiments measured every 50 min.

In Fig. 2b we show that it is possible to rescale all the frequency dependences observed for the various rates of  $1/T_{1i}$  in a universal one obtained by multiplying the consecutive curves by the scaling ratio  $\alpha$ . This scaling behavior emphasizes the efficiency of our method of characterizing the pore-size distribution in disordered porous media.

#### TIME-RESOLVED PROTON NUCLEAR RELAXATION: MEASUREMENT DURING HYDRATION AND SETTING

Finally our nuclear relaxation method is useful to study in situ (within the NMR tube) the hydration and setting of the RPC. We have measured the proton longitudinal relaxation decays every 50 min during 20 h. For each experiment, we have proceeded to a Laplace inversion, and we get a distribution of magnetization versus  $T_{1i}$  similar to the one presented in Fig. 1b. We present a contour plot (Fig. 3) of the magnetization density varying the time of hydration. The main interest of this two-dimensional representation is to show clearly how the distribution of the magnetization density behaves with the time of setting. For instance, one notes a clear deviation of the two main peaks, in the large  $T_{1i}$  range, to shorter values as the time of hydration increases. This is consistent with a reduction of mobility of water at the

beginning of the setting. Another result is the reduction of the dispersion of the two main peaks (Fig. 3). This might be associated with the net appearance of the largest pore structure after 12 h. We intend to use this technique over a much longer time to explain the inversion of populations of the pore-size distributions between 20 h (Fig. 3) and 6 months (Fig. 1b).

#### CONCLUSION

The proton spin-lattice relaxation rates, measured in a large frequency range and a biphasic fast exchange model of protons close to paramagnetic hydrated ions, have proven the microporosity of RPC. Our method allows a time-resolved analysis of the kinetics of hydration and setting of such a concrete.

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