Analysis of microporosity of reactive powder concrete by proton nuclear relaxation

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RÉSUMÉ

La relaxation longitudinale des protons du béton de poudres réactives donne une distribution de quatre $T_{1,i}$. Leurs dépendances en fréquence sont interprétées par un modèle d'échange biphasique rapide et la présence d'ions paramagnétiques hydratés à la surface des pores. On estime ainsi la taille moyenne des pores.

Mots-clés: relaxation paramagnétique nucléaire, confinement, milieux poreux, béton

ABSTRACT

The proton spin-lattice relaxation leads to a resolved distribution of four $T_{1,i}$ for the reactive powder concrete. The $T_{1,i}$ frequency dependences are interpreted by a biphasic fast exchange model of proton and paramagnetic hydrated ions at the surface of the pores. This leads to an estimation of the pore sizes.

Key-words. Nuclear paramagnetic relaxation, confinement, pores, concrete

INTRODUCTION

Reactive Powder Concretes (RPC) are composed of cement, high silica fume content, crushed quartz and present a very low water to cement ratio (15%) [1]. Though these concretes exhibit very high mechanical and durability properties, a question remains: how are these properties related to the microstructure, the texture and the macroscopic resistance of these disordered materials ?

Here, we answer the question by measuring the proton longitudinal nuclear magnetic relaxation of an unprepared RPC without adding any solvent. The observed

non-exponential recovery has been explicitely resolved in term of a discrete distribution of four spin-lattice relaxation times, $T_{1,i}$, by the inverse Laplace method. The observed typical frequency dependence of the measured proton relaxation times is

characteristic of nuclear paramagnetic relaxation. ESR at 4 K of RPC confirms and quantifies the amount of such paramagnetic impurities (mainly Fe). Such a dependence has proved the validity 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 [2]. This has allowed to affect this distribution to four different average pore sizes.

PROTON NUCLEAR RELAXATION AND ESR IN RPC

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. 1(a).
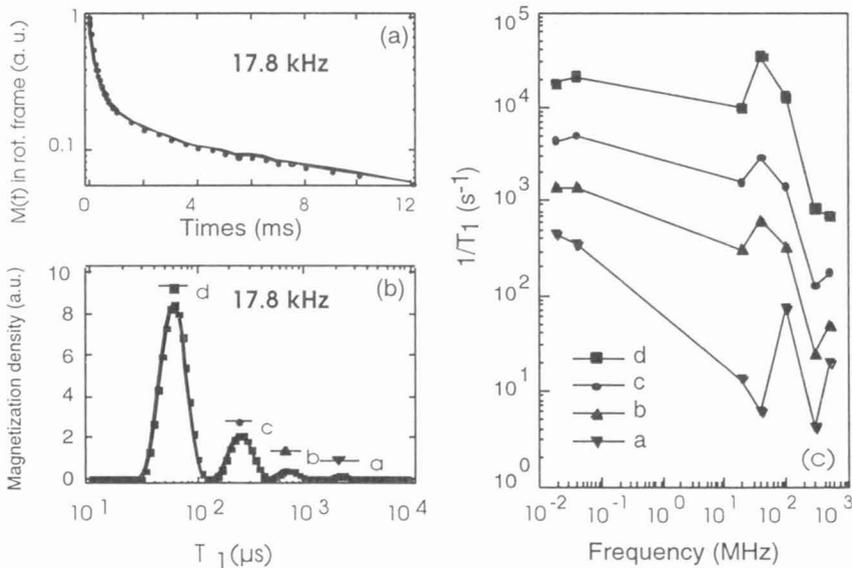

Fig. 1 (a) Recovery of proton longitudinal magnetization at 17.8 kHz. (b) Distribution of magnetization vs $T_{1,i}$ (i = a,..., d) after Laplace inversion of curve (a). (c) Frequency dependencies of the observed four different $T_{1,i}$ (i = a,..., d).

For each frequency, we observe a pronounced non-exponential decay. The Laplace inverse method (Contin program) has allowed to clearly resolve four single-exponential components, whose individual spin-lattice relaxation times, T_{1i}, spread over four orders of magnitude (Fig. 1(b)). Our observation by differential scanning calorimetry of different confined classes of water is in favor of such a multimodal distribution of pores [2]. The typical frequency dependences displayed in Fig. 1(c) are indicative of the origin of the relaxation process. For instance, the enhancement of the proton relaxivity for the first three rates in the 10-300 MHz range reveals a nuclear paramagnetic relaxation process [3]. Here the electron relaxation rate makes a dominant contribution to the effective correlation time for the electron nuclear coupling at the pore surfaces [2]. We confirm the presence of paramagnetic impurities by X-band ESR of the RPC at 4 K (Fig. 2). The comparison with the ESR spectrum of a copper reference has allowed to quantify the paramagnetic species at level of $2 \ 10^{19}$ spins/g of RPC. The analysis of Fig. 2 shows that the dominant contribution comes from iron ionic species in a high spin state in a distorted octahedral surrounding of oxygen. One notes also a very small amount of Mn^{2+} species. We check that these two paramagnetic species are already present in the cement. The presence of Fe^{3+} confirms a Mössbauer study [4] on iron-exchanged calcium silicate hydrate where the authors conclude that there are reasons to suggest that Fe^{3+} can enter into the structure of calcium silicate hydrate and take positions of released Ca^{2+} without much loss of the crystallinity.

DETERMINATION OF AVERAGE PORE SIZES IN RPC

As discussed above, the main source of 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 solvatation iron-shell. We have shown that when diffusion or exchange between the surface and "bulk" phase is much faster than the NMR measurement time, we can apply the biphasic fast exchange model [5] and for each individual decay, $\exp(-t/T_{1,i})$, the ith observed longitudinal relaxation rate is formally given by the relation [2]:

$$\frac{1}{T_{1,i}} = \frac{1}{T_{1b}} + 3 \frac{N_S}{\langle R \rangle_i} v_{solv} \frac{n}{T_{1s}^{H-Ion}(\omega_I)}. \tag{1}$$

Here, T_{1b} and $T_{1s}^{H-Ion}(\omega_I)$ are the "bulk" and surface relaxation times, respectively. The latter depends on the proton frequency ω_I as described in ref. [2]. N_S is the

surface density of paramagnetic spins S. The four average pore sizes $<R>_i$ are defined through the surface to volume ratio $S_{pore,i}/V_{pore,i} = 3/<R>_i$ for a spherical pore shape. Since most of the experimental relaxation times are in the millisecond range (Fig. 1(c)), the overall relaxation is dominated by the surface contribution $1/T_{1s}^{H-Ion}$.

It is possible to get $N_S \sim 3.2 \ 10^{12}$ Fe spins/cm^2 from our ESR measurements (Fig. 2), knowing the specific area (~ 50 m^2/g) and the porosity (Å 8%) of the RPC [1]. The volume of the solvatation cage, v_{solv} Å $1.2 \ 10^{-22}$ cm^3, is obtained with an interspin distance I-S of 2.2 Å and a proton species shell of 2 Å width. In the very low frequency range of Fig. 1(c), the $1/T_{1,i}$ are independent of the proton frequency ω_I and we have shown in ref. [2] that $1/T_{1s}^{H-Ion}(\omega_I) \propto 10 H_I^2 T_{1e}$, where T_{1e} is the

ESR BPR 4K
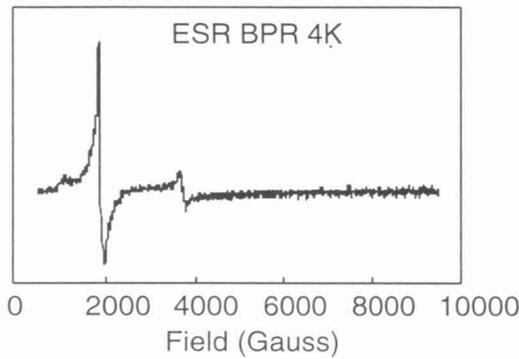
0   2000 4000 6000 8000 10000
Field (Gauss)

Fig. 2 X-band ESR spectrum of RPC at 4 K

electronic spin-lattice relaxation time. T_{1e} might be induced either by electron fluctuations in the electrical symmetry at the ion or by dipolar fluctuations, both leading to a square fluctuation coupling about 10^{19}-10^{20} s^{-2}. We have recently measured $T_{1e}=0.6 \ 10^{-9}$ from the frequency dependence of the proton relaxation times. H_I is the dipole-dipole coupling between spins I and S, giving $H_I^2 = 6.4 \ 10^{13}$ s^{-2} for an interspin distance I-S of 2.2 Å and S=5/2. $n\sim 3$ is the average number of proton species in the volume v_{solv}. Finally, one obtains the following relation between average pore size and proton measured relaxation time:

$$\langle R \rangle_i = \left(30 N_s v_{solv} H_I^2 n T_{1e}\right) T_{1,i}. \tag{2}$$

Substituting all the numerical values given above in (2), one has finally the following estimates of the average pore sizes $\{<R>_d = 7$ Å, $<R>_c = 29$ Å, $<R>_b = 89$ Å and $<R>_a = 280$ Å$\}$ in a reactive powder concrete.

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 probed the microporosity of reactive powder concrete.

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