Probing the Surface Area of a Cement-Based Material by Nuclear Magnetic Relaxation Dispersion

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We show how nuclear magnetic spin-lattice relaxation dispersion of ^{1}H water can provide a direct reliable value of the specific surface area of a cement-based material. The remarkable features of the relaxation dispersion support an interpretation in terms of coupled solid-liquid relaxation at pore interfaces, surface diffusion, and nuclear paramagnetic relaxation. The measurement is sufficiently fast to be applied continuously during the progressive hydration and setting of the material. This method is relevant to other chemically reactive porous media in chemical engineering and oil recovery.

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What is the specific surface area S_p of a hydrated cement-based material and how it behaves with the duration of hydration? This question is also relevant to other chemically reactive nanoporous materials occurring in heterogeneous catalysis, membrane separation, chemical engineering, oil recovery, and even in food science. Interest of such a surface area is to give insight into the microstructure and about its impact on macroscopic properties. Probing a direct reliable value of S_p, is fundamental for characterizing the highly disordered internal porous microstructure encountered in these materials. This is all the more important for hardened cement paste known as the main ingredient of concrete, the world's most widely used manufactured material. Here the value of S_p is directly related to the mechanical performance. However, most of the existing techniques have been shown to be inadequate. For instance, widely dispersed values of S_p, ranging between 80 and 300 m^2/g have been already obtained [1], including: nitrogen gas sorption [2], mercury intrusion [3], small-angle x-ray (SAXS [4]) and neutron (SANS [5]) scattering, and nuclear magnetic relaxation (NMR [6–8]). The SAXS data fall above this range and differ from the SANS data performed on similar materials. The gas sorption requires a preliminary drying and is limited in pore sizes. The mercury invasion requires high pressures that perturb the porosity. NMR measurements for proton [6] and deuteron [7] have spotted only a single high frequency that makes difficult the separation of the surface and bulk contributions from the overall measured relaxation rate. Moreover, some of these NMR measurements require successive liquid saturation and drying [6] or use of cryoporometry [9,10] that might perturb the microstructure.

In this Letter, we propose a new NMR approach to probe directly the surface area of a hydrated cement-based material that does not require any drying or temperature modification. Although this nondestructive method concerns here an application to cement materials, it could become relevant to characterize the microstructure of any other water-saturated reactive porous media. Our method is based on a clear separation of surface ($R_{1\text{-surf}}$) and bulk ($R_{1\text{-bulk}}$) contributions of the overall ^{1}H nuclear spin-lattice relaxation rate (R_1) of water confined within the hydrated cement. For that purpose, we use nuclear magnetic relaxation dispersion (NMRD), the measurement of R_1 as a function of magnetic field strength or nuclear Larmor frequency [11]. The benefit of exploring the range of low frequency is to isolate the typical NMRD dispersion features of $R_{1\text{-surf}}$ associated with the different processes of molecular surface dynamics. An original model based on solid/liquid cross relaxation, proton surface diffusion, and nuclear paramagnetic relaxation, in the presence of progressive hydration, is proposed to interpret the remarkable features of the proton NMRD. This allows us to probe directly the surface area of a very reactive and disordered material. This method is sufficiently rapid to be applied continuously during the progressive hydration and setting of cement.

A mortar sample is prepared by mixing cement, sand, silica fume, water, and superplasticizer with a water to cement ratio $w/c = 0.38$. Before the addition of water, the specific surface area of the various grains is very low whereas after the dissolution-precipitation process, calcium silicate hydrate structures (CSH) appear at the surface of the grains leading to a very high surface area that increases continuously with time. We present in Fig. 1 the proton NMRD data obtained for increasing duration of hydration for such a mortar. Measurements are performed, at a temperature stabilized at 25 °C, on a fast-field cycling spectrometer from Stelar Company. The NMRD dispersion curves, shown in Fig. 1, have been obtained for 50 different measured field values between 0.01 and 10 MHz. An individual NMRD curve is obtained in 20 min or so. This is sufficiently rapid to follow the hydration of the mortar every 30 minutes during the first 12 h. Complementary relaxation and line shape measurements have been made on a Bruker 360 MHz spectrometer. We evidence by electron spin resonance a

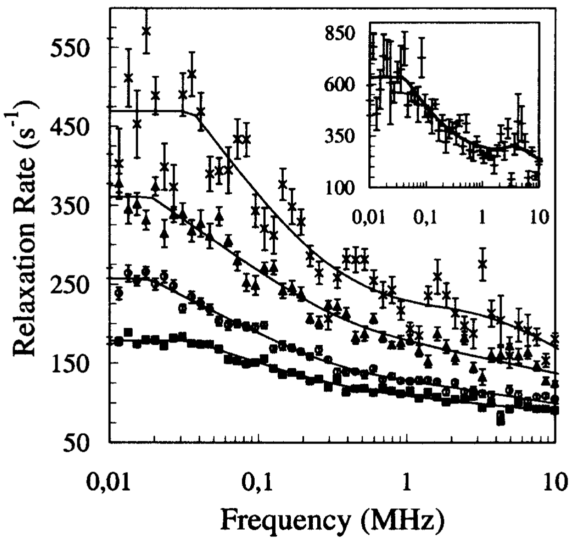

FIG. 1. Measured water ^{1}H spin-lattice relaxation rates of a hydrated mortar at $w/c = 0.38$ as a function of the proton Larmor frequency, for different duration of hydration: 0 h 34 min (■), 7 h 34 min (○), 8 h 45 min (▲), and 9 h 40 min (×). The inset represents the NMRD data obtained after 10 h 32 min (+). The continuous lines correspond to the best fits obtained with Eqs. (2) and (6).

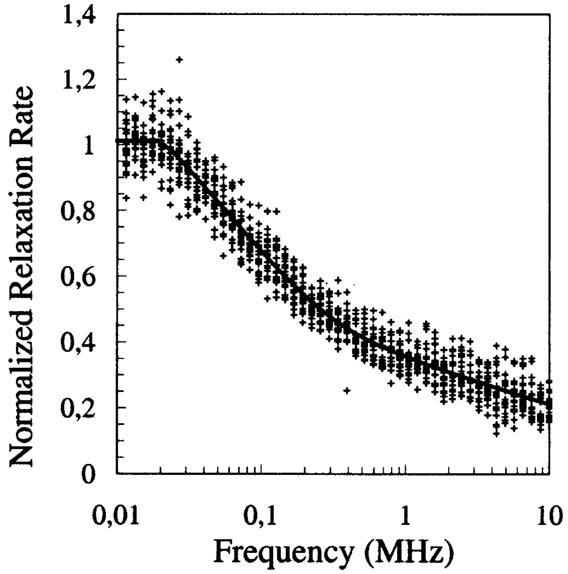

FIG. 2. Renormalization of the data obtained in Fig. 1 for all hydration times.

quantity of $\eta_S = 1.17 \times 10^{19}$ paramagnetic ions Fe^{3+} per gram of dry material. Assuming a uniform distribution, we deduce a proportion of surface Fe^{3+} impurities, $S_p\, \rho_d\, \xi$, to which relaxation of liquid protons of the saturated porous media is sensitive. Here $\rho_d = 2.5$ g/cm^3 is the density of the material and $\xi = 6$ Å is the average interlayer distance between two Fe^{3+} ions [12]. The surface density of Fe^{3+} impurities thus becomes $\sigma_S = \eta_S \rho_d \xi = 1.8 \times 10^{12}$Fe^{3+}/cm^2, and is independent of S_p.

We note three remarkable features in the ^{1}H NMRD of water in hydrated mortars (Fig. 1). (i) There is a plateau below a crossover frequency at $\omega_c \sim 22$ kHz. (ii) Above ω_c, one observes a bilogarithmic dispersion behavior, characterized by a 10/3 slope ratio, for every duration of hydration. This frequency behavior is unambiguously consistent with a two-dimensional proton-water diffusion at proximity of the paramagnetic relaxation centers [13]. (iii) Between 3 and 5 MHz, one notes an enhancement of the relaxation after 10 h of hydration. A renormalization of the ^{1}H NMRD data collected for all durations of hydration has been achieved by subtracting the limiting constant bulk relaxation rate at high frequency and dividing the resulting data by the value of the respective low frequency plateau (Fig. 2). This renormalization proves that the same nuclear magnetic relaxation process occurs for every duration of hydration. The unique crossover frequency ω_c is indicative of a fundamental modification in the relaxation when the correlation time reaches the value $\tau_c \sim 1/\omega_c = 7.2$ μs.

We now propose a theoretical model that reproduces all these relaxation features. Basically, when considering the nuclear relaxation of water embedded in solid cement, there are a liquid and a solid spin density of longitudinal magnetizations m_w and m_{sol}, respectively. Introducing the dimensionless variable for the departure to equilibrium $M(t) = [m(t) - m^{\mathrm{eq}}]/m^{\mathrm{eq}}$, these two spin populations are coupled through the cross relaxation at the solid-liquid interface [14,15]

$$\frac{d}{dt}\begin{bmatrix} M_{\mathrm{sol}}(t) \\ M_w(t) \end{bmatrix} = \begin{bmatrix} R_{1,\mathrm{sol}} + k/F & -k/F \\ -k & R_{1,w} + k \end{bmatrix} \begin{bmatrix} M_{\mathrm{sol}}(t) \\ M_w(t) \end{bmatrix}. \tag{1}$$

Here $R_{1,w}$ and $R_{1,\mathrm{sol}}$ are the spin-lattice relaxation rates for the confined liquid-proton water and solid protons in the solid hydrates, k is the dipolar cross-relaxation rate from the water protons to the solid-proton species, and F is the ratio of the solid-proton population to the liquid-proton population at equilibrium $F = m_{\mathrm{sol}}^{\mathrm{eq}}/m_w^{\mathrm{eq}}$ [15]. To support this model, we used a Bruker NMR spectrometer operating at 360 MHz with a very short dead time (3 μs) and observed, in the inducing period of a hydrated mortar, a superposition of broad and narrow line shapes associated with solid $M_{\mathrm{sol}}(t)$ and liquid $M_w(t)$ components, respectively. The biexponential spin-lattice relaxation observed, during the same period, confirms also the proposed model. However, with the fast-field cycling spectrometer, one observes only the signal $M_w(t)$ of the liquid. It is a linear combination of fast R_{fast} and slow R_{slow} exponential recovery terms whose amplitudes depend on the eigenvectors of the matrix in Eq. (1). We show that R_{slow} dominates the relaxation and depends on the strength of the frequency dependent coupling rate k. Below ω_c the system reaches long correlation times typical of the rigid-lattice limit τ_c. k is limited by the transfer of dipolar energy (spin diffusion) within the bound solid proton. It thus becomes proportional to the value of the spin-spin relaxation rate, $1/T_2$, of a solid spin system, which is very high and known to be independent of the Larmor frequency. In consequence, k reaches the strong coupling limit where $k \gg R_{1,\mathrm{sol}}$ and $R_{1,w}$. The time decay of $M_w(t)$ is controlled by $R_{\mathrm{slow}} = (R_{1,w} + FR_{1,\mathrm{sol}})/(1+F) \sim FR_{1,\mathrm{sol}}/(1+F)$ in this low frequency range. The observed plateau below ω_c is thus characteristic of the rigid-lattice limit of the solid-proton hydrates. Above ω_c, the system experiences correlation times much shorter than τ_c. This favors the condition of weak coupling where $k \ll R_{1,\mathrm{sol}}$ and $R_{1,w}$. The time decay of $M_w(t)$ is now only controlled by $R_{\mathrm{slow}} = R_{1,w}$, where $R_{1,w}$ is associated to the water-proton dynamics as shown by the typical bilogarithmic dispersion curves displayed in Fig. 1. One thus summarizes the frequency dependence of R_1 as follows:

$$R_1(\omega) = \begin{cases} FR_{1,\mathrm{sol}}/(1+F) = Cte & \text{for } \omega \le \omega_c, \\ R_{1,w}(\omega) & \text{for } \omega \ge \omega_c. \end{cases} \tag{2}$$

We show below that these different frequency dependencies allow a direct separation of the solid and liquid surface proton-water relaxations that helps us to obtain S_p.

We have recently addressed the frequency dependence of $R_{1,w}$ when a large number of protons (I) water molecules diffuse in pores with a surface density σ_S of fixed paramagnetic impurities of spins (S) [13]. The gyromagnetic ratio of the electron, γ_S, being much larger than that of the proton, γ_I, ($\gamma_S = 658.21\ \gamma_I$), the proton spin relaxation is due to the modulation of the I-S dipole-dipole interactions by translational diffusion. Basically, we consider two distinct phases: a surface-affected liquid phase of spin-lattice relaxation rate, $R_{1\text{-surf}}$, and a bulk liquid phase of spin-lattice relaxation rate, $R_{1\text{-bulk}}$, and suppose a biphasic exchange sufficiently fast to justify that

$$R_{1,w}(\omega_I, \omega_S) = R_{1\text{-bulk}} + \frac{N_S}{N} R_{1\text{-surf}}(\omega_I, \omega_S), \tag{3}$$

where ω_I and ω_S are the Larmor frequencies of proton and electron, respectively. N_S/N is the ratio of the number of water molecules at the pore surface to the total one exchangeable in the sample. One introduces the density of the water ρ_w and an interfacial water layer of size $x\varepsilon$, where $\varepsilon = 3.8$ Å is the water molecule size. $x\varepsilon \sim 10$ Å according to previous calorimetry and NMR studies [16]. One thus has $N_S/N = x\varepsilon\rho_w S_{p,NMR}$ where $S_{p,NMR} = S_p F$ is the NMR-based value of the specific surface area. The relaxation rate in the bulk phase, $R_{1\text{-bulk}}$, is caused by the fast molecular reorientations and translations and is independent of frequency in the low field range studied. A formal expression of $R_{1\text{-surf}}$ is obtained by mixing the relaxation rate, $R_{1\text{-Fe}}$, of the water protons linked to the first coordination sphere of paramagnetic centers Fe^{3+} with the relaxation rate, R_{1S}, of proton species diffusing at the pore surface around such centers:

$$R_{1\text{-surf}}(\omega_I, \omega_S) = R_{1S} + \frac{N_{\mathrm{Fe}}}{N_S} R_{1\text{-Fe}}. \tag{4}$$

$N_{\mathrm{Fe}}/\mathrm{N}_S \ll 1$ is the ratio of the number of water molecules at the surface relaxing sites to that at the pore surface. This ratio becomes $N_{\mathrm{Fe}}/N_S = n\varepsilon^2\sigma_S = n\varepsilon^2\eta_S\rho_d\xi$, where n is the average number of water molecules on Fe^{3+} ions. Substitution of Eq. (4) into Eq. (3) thus gives

$$R_{1,w}(\omega_I, \omega_S) = R_{1\text{-bulk}} + \frac{N_S}{N} R_{1S} + \frac{N_{\mathrm{Fe}}}{N} R_{1\text{-Fe}}, \tag{5}$$

where $N_{\mathrm{Fe}}/N = n\varepsilon^3\eta_S\rho_d x\rho_w\xi S_{p,NMR}$. We showed the remarkable sensitivity of NMRD to the local dimensionality experienced by the diffusing proton molecule on channel pores [13]. In spatial confinement, the reduced dimensionality forces more frequent I-S molecular reencounters that modify the long time decay of the dipolar correlation functions. This gives either a logarithmic or a $1/\sqrt{\omega_I}$ frequency behavior when the proton dynamics appears to be two- or one-dimensional, respectively [13]. In particular, we proposed an analytical bilogarithmic frequency expression for R_{1S}, in the presence of two-dimensional I-S molecular reencounters [13]. On the other hand, the theory of nuclear paramagnetic relaxation is well established and leads to a sum of two Lorentzian frequency dependences for $R_{1\text{-Fe}}$ [14,17]. Substituting these two very different analytical expressions into Eq. (5) gives finally

$$\begin{aligned} R_{1,w}(\omega_I, \omega_S) = R_{1\text{-bulk}} &+ \frac{x\varepsilon}{60}\rho_d\rho_w\eta_S\xi S_{p,NMR}(\gamma_I\gamma_S\hbar)^2 S(S+1) \\ &\times \left\{\frac{\pi}{\varepsilon^4}\tau_m\left[7\ln\left(1+\frac{1}{\omega_S^2\tau_m^2}\right)+3\ln\left(1+\frac{1}{\omega_I^2\tau_m^2}\right)\right]+\frac{8n\varepsilon^2}{r_{IS}^6}\tau_c\left[\frac{7}{1+\omega_S^2\tau_c^2}+\frac{3}{1+\omega_I^2\tau_c^2}\right]\right\}. \end{aligned} \tag{6}$$

Here τ_m is the correlation time characterizing the two-dimensional diffusion of the proton species at the surface of the pores, $r_{IS} = 2.7$ Å is the distance of minimal approach between I and S spins, $S = 5/2$ for Fe^{3+}. The correlation time τ_c of the nuclear paramagnetic relaxation is given by $1/\tau_c = 1/\tau_{ex} + 1/T_{1\mathrm{Fe}}$ where τ_{ex} ($\tau_{ex} \gg T_{1\mathrm{Fe}}$) is the lifetime of water in the ligand field of the ferric ions. The electronic spin-lattice relaxation time of the paramagnetic impurity $T_{1\mathrm{Fe}}$ (of the order of 10^{-11} s) is defined as $T_{1\mathrm{Fe}}^{-1}(\omega_S) = H_S^2\tau_\nu[(1+\omega_S^2\tau_\nu^2)^{-1} + 4(1+4\omega_S^2\tau_\nu^2)^{-1}]$ [17], where τ_ν is the correlation time for the electron-lattice relaxation interaction and H_S^2 is the intensity of the electronic spin fluctuations. One sees from

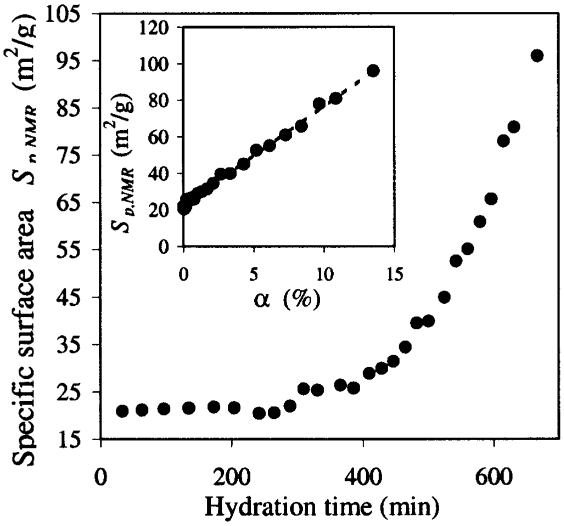

FIG. 3. Variation of the NMR-based specific area of hydrated material as a function of the hydration time (main figure) and the degree, α (%), of chemical reactions (inset).

Eq. (6) that the effect of the nuclear paramagnetic relaxation is limited to a narrow band in the highest range of frequency of our measurements. Its contribution appears when a certain population of bounded water molecules (typical value of $n \sim 2$) exists in the ligand field of Fe^{3+}. The typical enhancement of the overall proton frequency dependence seen in the inset of Fig. 1, after about 10 h of hydration, thus gives a NMR evidence of such bounded water.

Substituting Eq. (6) into Eq. (2) allows us to reproduce all the frequency features of Fig. 1. Almost all parameters present in Eq. (6) are either known or measured independently. For instance, we measured the bulk contribution $R_{1b} \sim 55$ s^{-1} at higher field and check that it is constant over the first 12 h of hydration. We associate the low frequency plateau value of Fig. 1 to $FR_{1,\mathrm{sol}}/(1 + F)$. The only adjustable parameters are $S_{p,NMR}$ and τ_m. This latter is found as $\tau_m = 0.7$ ns during the first 7 h and progressively increases to $\tau \approx 1.3$ ns after 12 h.

We have displayed in Fig. 3, the variation of the obtained $S_{p,NMR}$ with the duration of hydration. It is almost constant in the inducing period and increases rapidly after the time of setting (~ 6 h). The linear relation found (inset of Fig. 3) between $S_{p,NMR}$ and the degree α (%) of advancement of chemical reaction measured by thermal heating makes sense and proves the significance of this figure. Though $S_{p,NMR}$ ranges within the results of most other techniques, there are several advantages in favor of our measurements. (i) Proton NMRD is neither invasive nor destructive because one measures the response of the mixing water itself in the normal saturated state of cement. No liquid or gas intrusions, no drying or other temperature and pressure modifications are required that risk to perturb the microstructure. This is important because the CSH gel structure formed at early times is delicate and easily damaged by drying. (ii) The measurement is sufficiently fast to be applied continuously during the progressive hydration and setting of this material. (iii) The remarkable features of the proton NMRD at low frequency allows us to probe directly the proton surface dynamics that contributes really to $S_{p,NMR}$. (iv) A significant new insight of our results is the clear separation, in Fig. 1, of the NMRD of mobile water at the surface of the pores from the one of bounded water. The nonidentification of these two kinds of water has been, in previous NMR experiments, the source of systematic errors in $S_{p,NMR}$. (v) Another insight is that we follow closely the rapid setting of the very high intrinsic surface area of the low density CSH formed in the early ages of hydration. We used recently this method to follow the evolution of a white cement paste for several months and showed that the method gives the evolution of the pore size distribution coming from the high density CSH formed after.

In conclusion, this experiment shows, for the first time, how proton NMRD can provide continuously a direct measurement of the surface area of a cement-based material. Based on our results, we estimate that the method is relevant to other chemically reactive porous media.

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