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NMR investigations of water retention mechanism by cellulose ethers in cement-based materials

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ABSTRACT

We show how nuclear magnetic spin-lattice relaxation dispersion of proton-water (*NMRD*) can be used to elucidate the effect of cellulose ethers on water retention and hydration delay of freshly-mixed white cement pastes. *NMRD* is useful to determine the surface diffusion coefficient of water, the specific surface area and the hydration kinetics of the cement-based material. In spite of modifications of the solution's viscosity, we show that the cellulosic derivatives do not modify the surface diffusion coefficient of water. Thus, the mobility of water present inside the medium is not affected by the presence of polymer. However, these admixtures modify significantly the surface fraction of mobile water molecules transiently present at solid surfaces. This quantity measured, for the first time, for all admixed cement pastes is thus relevant to explain the water retention mechanism.

INTRODUCTION

It is known that the presence of cellulose ethers (*CE*) in mortars enhances drastically the water-retention (Mansoutre). Cellulose ethers (*CE*) are water soluble semi-synthetic polymers derived from cellulose, the most abundant polysaccharide in nature. This specific property of *CE* is crucial to achieve sufficient mortar-substrate adhesion when the mortar is applied in thin layers on highly absorbent substrates. Other properties are also affected by *CE*, such as the delay of hydration and setting (Peschard). A significant influence of the polymer molecular parameters like molecular weight and substitution degrees was evidenced (Pourchez, 2006), but no clear water retention mechanism could be clearly identified. During evaporation, no admixture loss is occurring, due to the very low vapor pressure of this admixture and a decrease in the water chemical potential occurs (Pourchez, 2010). A decrease of water mobility due to the jamming of the diffusion space by the polymer molecules is even expected (Patural, 2011). However, a recent pulsed gradient field *NMR* study proved that the macroscopic bulk water self diffusion coefficient is not modified in *CE* solution or in admixed cement pastes (Patural, 2010). Moreover, the interdiffusion

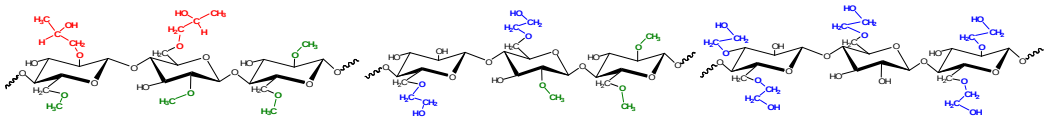
imaging experiments demonstrated also that the water diffusion at the paste interface is not affected by the presence of cellulosic admixture (Patural, 2010). So, the possibility of a potential microscopic diffusion barrier specifically at the cement hydrates interfaces is still controversial and the origin of the mechanism of water retention due to *CE* admixture is still an open question.

Our aim here is precisely to answer the latter question and to propose a realistic mechanism for the water retention in presence of *CE* in mortars and cements. For that purpose, we show how nuclear magnetic spin-lattice relaxation dispersion of protons-water *(NMRD)* can be used to elucidate the effect of cellulose ethers on water retention and hydration delay of freshly-mixed white cement pastes (Patural 2012).

EXPERIMENTS

Mineral and organic products. Cement pastes were prepared with white cement in order to facilitate *NMR* relaxation experiments. However, we showed before by electronic spin resonance (*ESR*) that paramagnetic Fe^{3+} ions were clearly present in white cement (see Figure 6 in (Korb, 2007)). The admixtures used are cellulose ethers (*CE)* of chemical structures given in Figure 1. All the characteristics of the main physical-chemistry properties and labels used for the cellulose ethers studied are described in (Patural, Thesis 2011). Admixture amount (0.27%) was in addition to the total dry mixture (*i.e.* cement, sand and filler). The cellulose ether weight-average molecular mass ($\bar{M}_w$) was determined using size exclusion chromatography. We have prepared different samples with increased molecular mass $\bar{M}_w = \{225, 630, 910\}\, kDa$ labeled *J1*, *J2* and *J3*, respectively. Others starch ethers were also investigated, those are polymers providing very different water retentions

Water retention. For water retention measurements, mortars were prepared according to the *CEReM* mixture proportions consisting in 65% sand, 30% ordinary Portland cement (*CEM I 52.5 R*), 5% calcareous filler with a water to cement ratio w/c=1.



(a) (b) (c)

Figure 1. Structures of cellulose ethers (a) *HPMC*, (b): *HEMC*, (c): *HEC*

The experimental device and way of probing water retention *WR(%)* have been described in (Patural, Thesis 2011). The cellulose ethers improved water retention up to *WR*=98.9% for *HPMC J3*. With respect to the water retention capacity of the non-admixed mortar (64.5%), this represents a very large increase. However the starch ethers procure very different water retention capacities ranging from 66.2% to 92.6%.

Experiments of *NMRD* in admixed cement pastes. We performed proton nuclear magnetic relaxation dispersion (*NMRD*) on a fast-field cycling spectrometer from *Stelar s.r.l., Mede, Italy*, where the polarization magnetic field is 0.5 T while the evolution magnetic field ranges from 0.25 mT to 0.5 T. All samples were introduced into a 7 mm-tube which was inserted into a 10 mm-diameter standard *NMR* tube. Cement pastes were prepared with a water/cement ratio *w/c=0.4* in order to have an appropriate consistency and for facilitating the *NMR* measurements at low fields. The *NMRD* sequence is very well documented (Kimmich). The experiments were repeated over a large range of proton Larmor frequencies $\omega_I/2\pi$ (10kHz-20MHz) in order to obtain the complete dispersion profile of the longitudinal spin-lattice relaxation rate $1/T_1(\omega_I)$. The temperature was fixed at 298K.

Basically, proton NMR relaxation is a stimulated (non spontaneous) phenomenon driven by the coupling of the proton spins to the magnetic noise induced by molecular motions (translation, rotation, exchange, etc). Varying the magnetic field changes the proton Larmor frequency $\omega_I/2\pi$, and thus allows exploring the time scales of the magnetic fluctuations (noise) to which the nuclear spin relaxation is sensitive. For diffusive liquids, *NMRD* gives also a rich source of dynamical information over a large range of length scales, from localized and fast motions at large frequency to a delocalized and slow motions at low frequency.

We propose two kinds of NMRD experiments for white admixed cement pastes. The first experiment consists of measuring the magnetic field dependence of $1/T_1(\omega_I)$ of various admixtures of different *CE* (Figure 2).

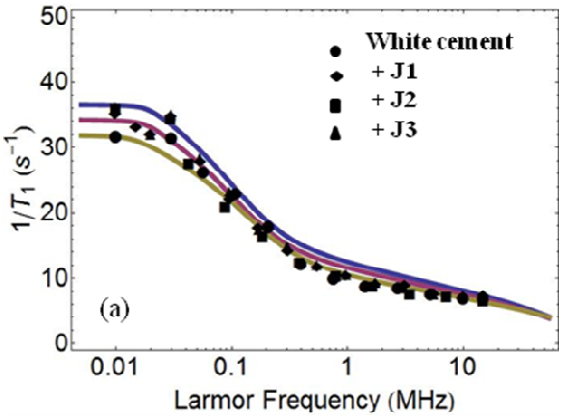


Figure 2. Measured water ^{1}H magnetic relaxation dispersion profiles $1/T_1(\omega_I)$ for hydrated white cement paste (w/c=0.4) as a function of the proton Larmor frequency. The experiments have been realized in the early hydration period (0-45 min). Effect of three cellulose ethers (*HPMC J1, J2 and J3*) compared to the neat white cement paste. The continuous lines are the best fits obtained with our theory of surface relaxation (Barberon and Korb 2009).

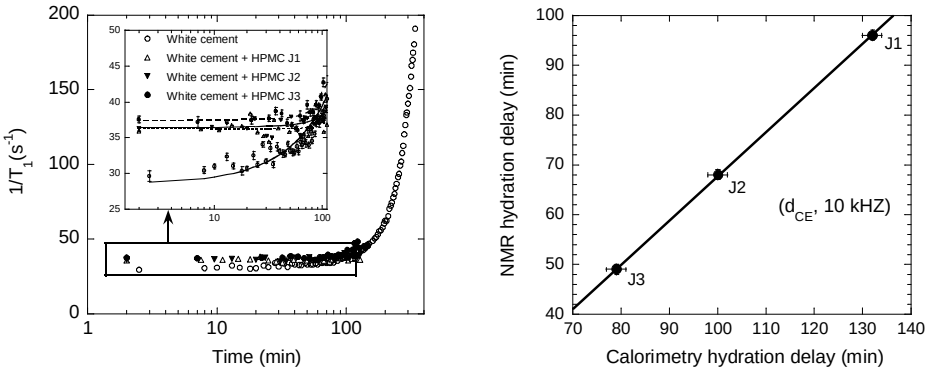
The second experiment consists in probing continuously $1/T_1(\omega_I=2\pi\times 10kHz, t_{hydr})$ at a fixed and low frequency (10kHz) during the inducing period t_{hydr} of cement paste with various admixtures of different *CE* (Figures 3a, 4a). During this period, we observe a monoexponential longitudinal magnetization decay that rules out any

distribution of T_1, the non exponential relaxation only appearing after ten hours of hydration [see Figure 7 of (Korb, 2007)]. The continuous measurement of $1/T_1(\omega_I=2\pi\times 10kHz, t_{hydr})$ in presence of various admixtures of cellulose ethers allows us to monitor the evolution of the specific surface area $S(t_{hydr})/V$, of the material during the hydration.

RESULTS AND DISCUSSION

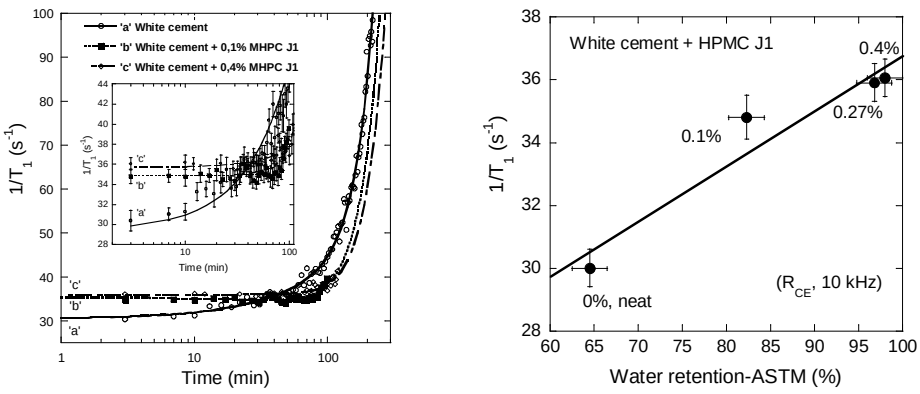
We proposed previously a theoretical model necessary for interpreting all the *NMRD* relaxation features reported in Figure 2, 3a and 4a (Barberon and Korb 2009). Here, we just outline the basic hypothesis of the model needed for probing the specific surface area and the water surface diffusion coefficients at the growing interface of the admixed and neat cement pastes. Basically, the molecular exchange between the solid and liquid phases is sufficiently fast compared to their respective individual proton relaxation times that a single $1/T_{1,w}(\omega_I)$ exists given by a linear combination of a bulk and a surface contributions. The latter is weighted by the surface to volume ratio S/V present at a given time of hydration at the solid/liquid interface. $1/T_{1,w}(\omega_I)$ for the confined proton-liquid has a bilogarithmic frequency dependence (Barberon and Korb 2009) that comes unambiguously from the two dimensional diffusion of the water molecules along the pore surface modulating the dipole-dipole interaction between the proton species and the paramagnetic Fe^{3+} ions fixed at the surface of the pores. On the contrary, in the frequency range studied, the spin-lattice relaxation rate for the solid protons does not depend on the frequency and the bulk relaxation rate $1/T_{1,bulk}$ is frequency independent. The conservation of these frequency dependencies during the progressive hydration and the evolution of $1/T_1(\omega_I, t_{hydr})$ with the hydration time allowed us to renormalize the *NMRD* data to a single master curve $1/T_1(\omega_I, t_{hydr}) \propto [S_{P,NMR}(t_{hydr})]f(\omega_I)$ (Barberon and Korb 2009), where $S_{p,NMR}$ is a *NMR*-based specific surface area of the hydrated cement that appears to be directly proportional to the degree of advancement of chemical reaction.

Surface diffusion coefficient. The surface diffusion coefficient is obtained from a fitting procedure of the *NMRD* profiles of Figure 2 which shows the *NMRD* profiles for different admixed cement pastes with three *HPMC (J1, J2* and *J3)* and neat (without *CE*) white cement pastes. In order to limit the kinetics effect during the measurements, we have decreased the number of frequency points on the profiles. This procedure allows a quite reasonable fit of the plateau dependence at low frequency and the bilogarithmic dependence at higher frequency (Figure 2). The correlation time τ_m for translational diffusion of water-proton is determined using the model described in (Barberon and Korb 2009).



(a) (b)

Figure 3. (a) Water ^{1}H $1/T_1(\omega_l)$ of hydrated cement pastes (w/c=0.4) as a function of hydrating time measured at a Larmor frequency of 10kHz. Effect of three cellulose ethers (*HPMC J1*, *J2* and *J3*). The inset represents a zoom on the frequency range of the plateau. (b) Correlation between the delays obtained by the *NMRD* and isotherm calorimetry.



(a) (b)

Figure 4. (a) Comparison of the water ^{1}H $1/T_1(\omega_l)$ of hydrated cement pastes (w/c=0.4) as a function of hydrating time measured at a Larmor frequency of 10kHz. Effect of the *CE* concentration of *HPMC J1*. (b) Correlation between the water retention evidenced from the *NMRD* technique and the macroscopic measurement described in the text (ASTM C1506-09 standard). The different concentrations of *HPMC J1* are indicated.

For these four different cement pastes, we find similar results for the translational surface diffusion $\tau_m \approx 1ns$ and for the time of residence $\tau_s \approx 10\ \mu s$. This suggests a pore scale invariance of water dynamics at the pore surface in *CSH* whatever the paste composition. This value of τ_m is in agreement with previous studies performed on cement pastes or on mortars (Barberon and Korb 2009). The translational diffusion coefficient D_{surf} at the pore surface can be deduced from the Stokes-Einstein relationship: $D_{surf} = \varepsilon^2/(4\tau_m)$ where $\varepsilon = 3\text{Å}$ is the water-molecule size. For all cement pastes (admixed or not), the surface diffusion coefficient is about $D = 2.25\ 10^{-11} m^2.s^{-1}$ *i.e.* about 1/100 of that of bulk water at 23°C. In consequence, the presence of cellulose ethers in cement paste does not modify the surface diffusion coefficient at the pore surface. This result is similar to those obtained in the macroscopic scale by pulsed field gradient *NMR* showing that the *CE*

does not modify the diffusion coefficient of water in the bulk (Patural 2010). We found similar results for starch ethers that present very different water retentions (92.6% and 66.2% respectively). This demonstrates that the translational diffusion coefficient at the surface of the solid interfaces is not affected by starch ether's presence.

These experiments thus demonstrate that cellulose and starch derivatives do not change the surface diffusion coefficient of water. The water mobility at pore surface is thus not modified in presence of such polymers.

Specific surface area and relative quantity of water transiently present at pore surface. On Figure 2, one observes a constant value for $1/T_1(\omega_I)$ when the proton frequency becomes $\omega_I < \omega_d = 2\pi \times 30$ *kHz*. Such a cross-over frequency ω_d is of the order of the dipolar interaction in the solid state between two protons separated by *0.155 nm*. On this low frequency range, the confined proton liquid explores relaxation processes induced by characterized long correlation times encountered in the solid state: $\tau_{rigid} = 1/\omega_d = 5.3\mu s$. We have shown in (Barberon and Korb 2009) that owing to the cross relaxation process, the intermolecular dipole-dipole interaction then couples the water spin relaxation to that of the solid and the magnetic field dependence of the immobilized spin system. The observed data presented in Figure 2 confirms the plateau observed at low frequency (at 10 kHz) for $1/T_1$ during the first hundred minutes. Then, relaxation rate increases due to cement hydration and development of the specific surface area. Moreover, a zoom on the Figure 3a shows that small but significative differences exist between each admixed cement pastes. The observed plateau for frequency below ω_d is thus characteristic of the rigid-lattice limit of the solid-proton hydrates. The absolute value of such a plateau, measured for instance at 10 kHz, is thus indicative of the specific surface area precisely at the solid-liquid interface. The continuous measurement of $1/T_1(\omega_I = 2\pi \times 10kHz, t_{hydr})$ in presence of various admixtures of cellulose ethers thus allows to monitor the evolution of the specific surface area $S_{P,NMR}(t_{hydr})$, of the material during the hydration.

How NMR relaxation can elucidate water retention mechanisms? In the very early aged of the hydration, the amount of *CSH* is not very large and the admixed polymer is still in the interstitial solution within the pores of the paste, even if the cellulose ethers are rather large. The relaxation of the mobile proton-water thus will be influenced by the presence of the polymer. We show that measuring the time evolution of the spin-lattice relaxation rate $1/T_1(10\ kHz, t_{hydr})$ at 10 kHz, especially in the first minutes of hydration allows probing quantitatively the relative population of water transiently present at the solid hydrate surfaces $N_S/N(t_{hydr})$.

On Figure 3a, the continuous lines exhibit the time evolution of $1/T_1(10\ kHz, t_{hydr})$ for the non admixed (neat) white cement and with *HPMC J1, J2, J3* admixtures. The periods d_{CE} during which the plateau remains constant are evidenced (d_0 is related to neat cement) and ordered as followed:

$$d_0 = 11\ min < d_{J3} = 60\ min < d_{J2} = 79\ min < d_{J1} = 107\ min.$$

This period d_{CE}, measured at low frequency, is a clear indicator of the delay of hydration induced by the *CE* polymer introduced into the material. The fact that d_0 stays much smaller than the other d_{CE} is a clear indication of the delayed hydration and setting induced by the *HPMC J1, J2, J3* admixtures. We show on Figure 3b, that one can correlate these delays of hydration measured by *NMRD* to the ones measured from isotherm calorimetry measurements (determined using the method described in Patural Thesis 2011) on similar materials. The quasi linear dependence (r^2=0.99) shows the very good accuracy between the microscopic (NMRD) and macroscopic (calorimetry) measurements.

Another important parameter can be extracted from the behavior of the time evolution of $1/T_1(10\ kHz,\ t_{hydr})$ during the first 100 minutes of hydration. This is the value of the plateau itself, noted, $1/T_{1,CE} = 1/T_{1,observed}(10kHz, t_{hydr})$ which depends critically on the nature of the admixtures. The results found for the neat white cement paste and *HPMC*-admixed cement pastes *J1, J2, J3* are ordered as followed: $1/T_{1,0} = 30s^{-1} < 1/T_{1,J1} = 35.9s^{-1} < 1/T_{1,J2} = 36.3s^{-1} < 1/T_{1,J3} = 37.6s^{-1}$, where $1/T_{1,0}$ is the value of the low-frequency plateau for neat cement. $1/T_{1,CE}$ is proportional to the correlation time τ_m and directly related to the relative amount of water N_s/N transiently present during the first 100 minutes at proximity of solid interfaces that is proportional to the specific surface area. Owing to the observation that $\tau_m \approx 1ns$ and $\tau_s \approx 10\mu s$ are universal for all the cement-based materials, one obtains a proportion $N_S(t_{hydr}=2\ min)/N=1.06\%$ for the neat white cement paste and $N_S(t_{hydr}=2\ min)/N$=1.36% for the admixed cement pastes with *HPMC J3*. One obtains intermediate values for the other admixtures *HPMC J1* and *HPMC J2*.

The fact to probe, in the first minutes of cement hydration, the fraction of mobile water molecules transiently present at solid interfaces N_s/N in presence of different nature and quantity of cellulose ethers is a key result of this study that can be directly linked to the relative amount of water retained on the pores surface.

We have applied the same *NMRD* method for *HPMC J1* with two different concentrations namely 0.1 and 0.4% giving 82.3 and 98.0% macroscopic water retention, respectively (Figure 4a). As expected, the value of the plateau $1/T_{1,CE}$ increases significantly with the concentration of admixture. Finally, on Figure 4b the linear correlation (r^2 = 0.93) of $1/T_{1,CE}$ and water retention of mortar admixed with three different concentrations 0.1, 0.27 and 0.4% of *HPMC J1* proves that our microscopic *NMRD* measurements on cement pastes could be correlated with the macroscopic water retention on mortars.

CONCLUSION

An original method based on two different applications of proton-water magnetic relaxation dispersion (*NMRD*) has been proposed to elucidate the effect of cellulose ethers (*CE*) on water retention of freshly-mixed white cement paste.

The first application of *NMRD* probes directly the proton-water surface dynamics from the magnetic field dependence of the nuclear spin-lattice relaxation rate. In spite

of modifications of the solution's viscosity, we find that the cellulosic derivatives do not modify the surface diffusion coefficient of water that is about two orders of magnitude smaller than that of bulk water.

The second application of *NMRD* concerns the continuous measurements of the spin-lattice relaxation rates at a fixed and very low Larmor frequency. At the very early ages, this application probes continuously and for the first time, the relative population of water transiently present at the surface of the time-growing solid hydrate interfaces. Compared to neat white cement, the *CE* modifies significantly the surface fraction of mobile water molecules transiently present initially at solid surfaces. Our results show that the larger the fraction, the better water-retention capacity of the hydrated cement or mortar samples at proximity of a solid support. This quantity measured for all admixed cement pastes is thus relevant to explain the water retention mechanism. Furthermore, a linear correlation is found between the *NMR* surface fraction and the standard *ASTM* method used by the mortar industry to estimate the water retention capacity of admixed mortars. However for very strong water retention, it seems that the *ASTM* is not able to distinguish polymer's effect while *NMRD* enables to make the difference between two admixtures.

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