



HAL
open science

Nuclear magnetic relaxation dispersion investigations of water retention mechanism by cellulose ethers in mortars

Laetitia Patural, Jean-Pierre Korb, Alexandre Govin, Philippe Grosseau,
Bertrand Ruot, Olivier Devès

► To cite this version:

Laetitia Patural, Jean-Pierre Korb, Alexandre Govin, Philippe Grosseau, Bertrand Ruot, et al.. Nuclear magnetic relaxation dispersion investigations of water retention mechanism by cellulose ethers in mortars. Cement and Concrete Research, 2012, 42 (10), pp.1371-1378. 10.1016/j.cemconres.2012.06.002 . hal-00762106

HAL Id: hal-00762106

<https://hal.science/hal-00762106>

Submitted on 30 Jan 2013

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Nuclear magnetic relaxation dispersion investigations**
2 **of water retention mechanism by cellulose ethers in mortars**

3
4 **LAETITIA PATURAL⁽¹⁾, JEAN-PIERRE KORB^{(2)*}, ALEXANDRE GOVIN⁽¹⁾, PHILIPPE**
5 **GROSSEAU⁽¹⁾, BERTRAND RUOT⁽³⁾, OLIVIER DEVÈS⁽³⁾**

6
7 ⁽¹⁾ *École Nationale Supérieure des Mines de Saint-Étienne ; Centre SPIN, LPMG FRE 3312*
8 *158 Cours Fauriel, 42023 Saint-Étienne Cedex 2, France*

9 ⁽²⁾ *Physique de la Matière Condensée, Ecole Polytechnique-CNRS, Route de Saclay,*
10 *91128 Palaiseau Cedex, France*

11 ⁽³⁾ *Université Paris-Est, Centre Scientifique et Technique du Bâtiment ; Département*
12 *Enveloppe et Revêtements / Division Enduits, Mortiers et Colles, 84 avenue Jean Jaurès,*
13 *77447 Marne-la-Vallée Cedex 2, France*

14
15
16
17
18
19
20 * Corresponding author: jean-pierre.korb@polytechnique.fr

21

22 **ABSTRACT**

23

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

34

35

36

37

38 **KEYWORDS:** *cellulose ether, cement paste, NMR relaxometry, surface diffusion coefficient,*
39 *water retention.*

40

41

42 1. Introduction

43 Cellulose ethers (*CE*) are well known water-soluble semi-synthetic polymers derived from
44 cellulose, the most abundant polysaccharide in nature. This polymer is build up from 1,4-
45 anhydroglucose units linked through β -1,4 glycoside bonds. Among the various derivatives of
46 this polymer, hydroxypropyl methyl cellulose (HPMC, Fig. 1a), hydroxyethyl methyl
47 cellulose (HEMC, Fig. 1b) and hydroxyethyl cellulose (HEC, Fig. 1c) are extensively used in
48 the formulation of various industrial products encountered in food stuffs, pharmaceuticals and
49 building materials. For instance, the presence of cellulose ethers (*CE*) in mortars enhances
50 drastically the water-retention [1]. Some experimental devices have been designed to
51 evidence such water retention **on a macroscopic lengthscale** (Fig. 2). This specific property of
52 *CE* is crucial to achieve sufficient mortar-substrate adhesion **when the mortar is applied in**
53 **thin layers on highly absorbent substrates**. Other properties are also affected by *CE*, such as
54 the delay of hydration and setting [2-3]. Some HPMC, HEMC and HEC were characterized in
55 terms of their effect on mortar water retention [4-5]. A few recent works have been concerned
56 with the remarkable mechanism of water retention capacity. A significant influence of the
57 polymer molecular parameters like molecular weight and substitution degrees was evidenced
58 [5], but no clear water retention mechanism could be clearly identified. During evaporation,
59 no admixture loss is occurring, due to the very low vapour pressure of this admixture and a
60 decrease in the water chemical potential occurs [6]. A decrease of water mobility due to the
61 jamming of the diffusion space by the polymer molecules is even expected [7, 8]. However, a
62 recent pulsed gradient field NMR study proved that the macroscopic bulk water self diffusion
63 coefficient is not modified in *CE* solution or in admixed cement pastes [9]. Moreover, the
64 interdiffusion imaging experiments demonstrated also that the water diffusion at the paste
65 interface is not affected by the presence of cellulosic admixture [9]. So, the possibility of a
66 potential microscopic diffusion barrier specifically at the cement hydrates interfaces is still

67 controversial and the origin of the mechanism of water retention due to *CE* admixture is still
68 an open question.

69 The aim of the present work is precisely to answer the latter question and to propose a
70 realistic mechanism for the water retention in presence of *CE* in mortars. To limit the
71 interaction between mineral components, the system was reduced to a white cement paste. We
72 propose another NMR measurement to sense the proton species dynamics specifically at the
73 solid interface. Our primary measurement here is the magnetic field dependence or relaxation
74 dispersion of the proton spin-lattice relaxation rate constant $1/T_1$ (NMRD, [10, 11]) in neat
75 (without *CE*) and *CE*-admixed white cement pastes. For cement pastes, the NMRD technique
76 is neither invasive nor destructive because one measures only the proton NMR response
77 coming from the mixing water itself. This technique has proven useful to give a direct reliable
78 value of the specific surface area of a cement-based material [12]. The remarkable features of
79 the relaxation dispersion support an interpretation in terms of coupled solid/liquid relaxation
80 at pore interfaces, surface diffusion and nuclear paramagnetic relaxation. The measurement is
81 sufficiently fast to be applied continuously during the progressive hydration and setting of the
82 material. In this study, we show the time evolution of the NMR-based specific surface area
83 and the amount of water transiently present at the solid and growing interface. We also
84 discuss the effects of the different *CE* and Starch Ether (*SE*) used on the surface diffusion
85 coefficient and on the relative amount of water transiently present at the solid and growing
86 interface.

87 2. Experiments

88 2.1. Mineral and organic products

89 Cement pastes were prepared with white cement in order to facilitate NMR relaxation
90 experiments. However, we showed before by electronic spin resonance (ESR) that

91 paramagnetic Fe^{3+} ions were clearly present in white cement (see Fig. 6 in ref. [12]). The
92 amount of such paramagnetic ferric ions was quantitatively evaluated through a double
93 integration of this calibrated ESR spectrum [12]. Chemical analysis of this cement was
94 performed by X-ray fluorescence spectroscopy (XRF). The phase compositions were
95 calculated using Bogue's formula with a correction on CaO due to sulfates [13]. The cement
96 composition is given in **Table 1**.

97 The admixtures used are cellulose ethers (*CE*) of chemical structures given in Fig. 1. The
98 admixture amount was equal to 0.27% (compared to cement). The characteristics of the main
99 physical-chemistry properties and labels used for the cellulose ethers studied are summarized
100 in **Table 2**. The number of substituted hydroxyl groups per anhydroglucose unit is expressed
101 as degree of substitution (*DS*). Moreover the molar ratio of alkoxy groups in the side chains to
102 cellulose is expressed as the average molecular substitution (*MS*) [14]. The cellulose ether
103 weight-average molecular mass (\bar{M}_w) was determined using size exclusion chromatography
104 [5, 15]. We have prepared different samples with increased molecular mass $\bar{M}_w =$
105 {225, 630, 910} *kDa* labeled J1, J2 and J3, respectively (**Table 2**). Others starch ethers were
106 also investigated, those are polymers providing very different water retentions (**Table 3**).

107 2.2. Water retention

108 For water retention measurements, mortars were prepared according to the CEReM
109 mixture proportions consisting in 65% sand, 30% ordinary Portland cement (CEM I 52.5 R),
110 5% calcareous filler with a water to cement ratio $w/c=1$ [16]. Mixing procedure was in
111 accordance with EN 196-1 [17]. Admixture amount (0.27%) was in addition to the total dry
112 mixture (*i.e.* cement, sand and filler). The water retention capacity was assessed using the test
113 from an American standard (ASTM C1506-09), based on application of an air depression
114 [18]. It is also used in France for assessing one-coat renderings [19].

115 The experimental device to measure water retention is shown in Fig. 2. It is composed
116 of a perforated dish attached to a vacuum assembly by a funnel. The dish was filled in with
117 the freshly mixed mortar and the vacuum was adjusted to maintain a depression of 50 mm Hg
118 for 15 min. The initial weight of mixing water is labeled as W_0 . Its loss (W_1) is weighted after
119 the depression period. Hence, the water retention WR was defined by the following equation:

$$120 \quad WR (\%) = \frac{W_0 - W_1}{W_0} \times 100 \quad (1)$$

121

122 *2.3. Experiments of proton nuclear magnetic relaxation dispersion (NMRD) in admixed* 123 *cement pastes*

124 We performed proton nuclear magnetic relaxation dispersion (NMRD) on a fast-field
125 cycling spectrometer from *Stelar s.r.l., Mede, Italy*, where the polarization magnetic field is
126 0.5 T while the evolution magnetic field ranges from 0.25 mT to 0.5 T. All samples were
127 introduced into a 7 mm-tube which was inserted into a 10 mm-diameter standard NMR tube.
128 Cement pastes were prepared with a water/cement ratio $w/c=0.4$ in order to have an
129 appropriate consistency and for facilitating the NMR measurements at low fields. The proton
130 nuclear magnetization originally at thermal equilibrium is oriented toward the external steady
131 polarized magnetic field (typically 0.5 T). The external field is instantaneously decreased (in
132 about 3ms) at an evolution magnetic field chosen in the range from 0.25 mT to 0.5 T in which
133 the magnetization relaxes, then the magnetic field is fixed to 0.25T in which a classical **free**
134 **induced longitudinal magnetization decay measurement is then** achieved by applying a $\pi/2$
135 pulse. **Such a fast field cycling sequence is very well documented [10, 11].** The temperature
136 was fixed at 298K. The experiment was repeated over a large range of proton Larmor
137 frequencies $\omega/2\pi$ (10 kHz - 20 MHz) in order to obtain the complete dispersion profile of the
138 longitudinal spin-lattice relaxation rate $R_1(\omega)=1/T_1(\omega)$.

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

146 We propose two kinds of NMRD experiments for white admixed cement pastes. The first
147 experiment consists of measuring the magnetic field dependence of the proton spin-lattice
148 relaxation rate $R_1(\omega_l) = 1/T_1(\omega_l)$ of various admixtures of different CE (Figs. 3, 4). The
149 second experiment consists in probing continuously the spin-lattice relaxation rate $1/T_1$
150 ($\omega_l = 2\pi \times 10\text{kHz}$, t_{hydr}) at a fixed and low frequency (10kHz) during the inducing period of
151 cement paste with various admixtures of different CE (Figs. 5, 7- 9). During this period, we
152 observe a monoexponential longitudinal magnetization decay that rules out any distribution of
153 T_1 , the non exponential relaxation only appearing after ten hours of hydration [see Fig. 7 of
154 12]. The continuous measurement of $1/T_1(\omega_l = 2\pi \times 10\text{kHz}, t_{hydr})$ in presence of various
155 admixtures of cellulose ethers allows us to monitor the evolution of the specific surface area
156 $S(t_{hydr})/V$, of the material during the hydration.

157 3. Theory of nuclear magnetic relaxation dispersion (NMRD) in cement pastes

158 We proposed previously a theoretical model necessary for interpreting all the NMRD
159 relaxation features reported in Figs. 3 and 4 [12, 20-22]. In the following, we just present a
160 self-contained outline of the basic hypothesis and equations of the model needed for probing
161 the specific surface area and the water surface diffusion coefficient at the growing interface of
162 the adjuvanted cement paste.

163 (i) Basically, when considering the nuclear relaxation of water embedded in solid hydrated
 164 cement, there are coupled relaxation equations for the solid and liquid magnetizations at
 165 pore interfaces. The return to equilibrium of either solid or liquid proton spin
 166 magnetization is thus a bilinear combination of exponentials with the rate constants for
 167 slow (R_{slow}) and fast (R_{fast}) components [23, 24] given by:

$$168 \quad R_{slow} = \frac{1}{2} \left\{ R_{1,s} + R_{1,w} + k(1+1/F) \mp \left[\left[R_{1,s} - R_{1,w} - k(1-1/F) \right]^2 + 4k^2/F \right]^{1/2} \right\} \quad (2)$$

169 Here $R_{1,s}=1/T_{1,s}$ and $R_{1,w}(\omega_l)$ are the spin-lattice relaxation rate constants associated to
 170 solid protons and confined liquid proton-water, respectively. k is the dipolar cross-
 171 relaxation rate from the water protons to the solid proton species and F is the ratio of the
 172 solid-proton magnetization to the liquid-proton population at equilibrium: $F = m_s^{eq} / m_w^{eq}$.

173 (ii) In most applications of field cycling experiments, the rapidly decaying component R_{fast} of
 174 the bi-exponential decay is not detected because of instrumental limitations and the
 175 slowly decaying component R_{slow} dominates the observations. Moreover, for the confined
 176 liquid, the intermolecular dipole-dipole interaction couples the water spin relaxation to
 177 that of the solid and the magnetic field dependence of the immobilized solid spin system.

178 (iii) The molecular exchange between the solid and liquid phases is sufficiently fast compared
 179 to their respective individual proton relaxation times that a single $R_{1,w}(\omega_l)$ exists given by
 180 a linear combination of a bulk and a surface contributions [25]. The latter is weighted by
 181 the surface to volume ratio S/V present at a given time of hydration at the solid/liquid
 182 interface [20].

183 (iv) The spin-lattice relaxation rate $R_{1,w}(\omega_l)$ for the confined proton-liquid has a bilogarithmic
 184 frequency dependence [26] that comes unambiguously from the two dimensional
 185 diffusion of the water molecules along the pore surface modulating the dipole-dipole
 186 interaction between the proton species and the paramagnetic Fe^{3+} ions fixed at the surface

187 [12, 20-22]. On the contrary, in the frequency range studied, the spin-lattice relaxation
 188 rate for the solid protons $R_{I,s}$ does not depend on the frequency [20] and the bulk
 189 relaxation rate $R_{I,bulk}$ is frequency independent [27].

190 (v) At high frequencies (10-100 MHz), the nuclear paramagnetic relaxation controls the
 191 proton relaxation [28]. This gives a typical bump in the NMRD profiles in this frequency
 192 range [29] that is not seen here.

193 (vi) The conservation of these frequency dependencies during the progressive hydration and
 194 the evolution of $1/T_1(\omega_I, t_{hydr})$ with the hydration time allowed us to renormalize the
 195 NMRD data to a single master curve $1/T_1(\omega_I, t_{hydr}) \propto [S_{p,NMR}(t_{hydr})]f(\omega_I)$ [20],
 196 where $S_{p,NMR}$ is a NMR-based specific surface area of the hydrated cement that appears to
 197 be directly proportional to the degree of advancement of chemical reaction [20].

198 Taking these considerations into account, we find that the following theoretical analytical
 199 expression of $R_{I,w}$ allows us to reproduce all the observed frequency features:

200

$$\begin{aligned}
 R_{I,w}(\omega_I > \omega_d) = & R_{I,bulk} + \frac{x\mathcal{E}}{60} \sigma_S \rho_w S_{p,NMR} (\gamma_I \gamma_S \hbar)^2 S(S+1) \times \\
 & \left[\frac{\pi}{\mathcal{E}^4} \tau_m \left[3 \ln \left(\frac{1 + \omega_I^2 \tau_m^2}{(\tau_m/\tau_s)^2 + \omega_I^2 \tau_m^2} \right) + 7 \ln \left(\frac{1 + \omega_S^2 \tau_m^2}{(\tau_m/\tau_s)^2 + \omega_S^2 \tau_m^2} \right) \right] \right. \\
 & \left. + \frac{8n\mathcal{E}^2}{r_{IS}^6} \tau_c \left[\frac{7}{1 + \omega_S^2 \tau_c^2} + \frac{3}{1 + \omega_I^2 \tau_c^2} \right] \right] \quad (3)
 \end{aligned}$$

202

203 where ρ_w is the density of the water, $\mathcal{E} = 3.0 \text{ \AA}$ is the water molecule size, $x\mathcal{E} \sim 10 \text{ \AA}$ is an
 204 interfacial water layer according to previous calorimetry studies [30] and $r_{IS} = 2.7 \text{ \AA}$ is the
 205 distance of minimal approach between I and S spins. The electronic spin $S = 5/2$ for Fe^{3+} ; $n \approx$
 206 I is the number of bounded water molecules in the ligand field of the Fe^{3+} ions. Since the
 207 gyromagnetic ratio of the electron, γ_S , is much larger than that of the proton, γ_I ($\gamma_S = 658.21$

208 γ), the electronic frequency is $\omega_S=658.21 \omega$. In Eq. 3, $N_S/N = x\varepsilon \rho_w S_{p,NMR}$ represents the ratio
209 of the number of water molecules transiently present at the pore surface, N_S , to the total
210 number, N , of exchangeable water molecules in the sample. Also in Eq. (3), τ_m is the
211 correlation time characterizing the two-dimensional diffusion of the proton species at the
212 surface of the pores. We introduce also the effects of the finite time of residence $\tau_S \gg \tau_m$ for
213 the mobile proton species at the surface of the pores by an exponential cut-off in the time
214 dependence of the pair correlations IS . The correlation time τ_c of the nuclear paramagnetic
215 relaxation is given by $1/\tau_c = 1/\tau_{ex} + 1/T_{1Fe} \approx 1/T_{1Fe}$ where τ_{ex} ($\tau_{ex} \gg T_{1Fe}$) is the lifetime of water
216 in the ligand field of the ferric ions. The electronic spin-lattice relaxation time of the
217 paramagnetic impurity T_{1Fe} (of the order of $2 \cdot 10^{-11}$ s) is constant at low frequency and has a
218 frequency dependence at higher frequency defined in ref [12, 20, 28]. The relaxation rate in
219 the bulk phase, $R_{Ibulk} \sim 0.3 \text{ s}^{-1}$ is caused by the fast molecular reorientations and translations
220 and is independent of frequency in the low field range studied [27]. Last, Substituting Eq. (3)
221 into Eq. (2) gives the theoretical expression that we can compare with the experiments in Figs.
222 3 and 4.

223 4. Results and discussion

224 4.1. Water retention of freshly-mixed mortars

225 The water retention capacity of each admixed mortar was evaluated; the results are
226 presented in **Table 2 and 3**. The cellulose ethers improved water retention up to 98.9% for
227 HPMC J3. With respect to the water retention capacity of the non-admixed mortar (64.5%),
228 this represents a very large increase. However the starch ethers procure very different water
229 retention capacities ranging from 66.2% to 92.6%.

230 4.2. Surface diffusion coefficient

231 The surface diffusion coefficient is obtained from a fitting procedure with Eqs. (2) and (3)
232 on the NMRD profiles of Figs. 3 and 4. Fig. 3a shows the NMRD profiles for the neat
233 (without CE) white cement paste. Fig. 3b shows the NMRD profiles of a white cement paste
234 admixed with HPMC J3. On both cases, we have varied the duration of the experiments by
235 changing the number of frequencies explored. Using thirty points takes some time (about 5
236 minutes per point) and we note that frequency profiles were affected by the kinetics of cement
237 hydration. Indeed, the time needed to register one complete profile is about 2h30. In
238 consequence, we could not observe the characteristic 10/3 slope ratio of the bilogarithmic
239 frequency dependence usually found in cement based materials [20]. A simple procedure that
240 allows limiting such a kinetic effect during the measurements is to decrease the number of
241 frequency points on the profiles. One observes on Figs. 3a, b that reducing the experimental
242 time to 45 minutes allows decreasing the kinetic effect. For instance, we observe that the first
243 12 points almost merge at high frequency, then, the gap between the two profiles increases
244 with time. In consequence, all NMRD dispersion curves of this work were obtained with
245 twelve different and logarithmically spaced frequency values between 0.01 and 15 MHz to
246 avoid the problems due to kinetics of cement hydration. This procedure allows a quite
247 reasonable fit of the plateau dependence at low frequency and the bilogarithmic dependence at
248 higher frequency (Figs. 3 and 4).

249 Fig. 4a presents the proton NMRD data obtained for different admixed cement pastes with
250 three HPMC (J1, J2 and J3). The correlation time τ_m is determined using the model described
251 above. For these four different cement pastes, we find similar results for the translational
252 surface diffusion approximately equal to $\tau_m \approx 1ns$ and $\tau_s \approx 10 \mu s$. This suggests a pore scale
253 invariance of water dynamics at the pore surface in C-S-H whatever the paste composition.
254 This value of τ_m is in agreement with previous studies performed on cement pastes or on

255 mortars [20, 21]. The translational diffusion coefficient D_{surf} at the pore surface can be
256 deduced from the Stokes-Einstein relationship: $D_{surf} = \varepsilon^2 / (4\tau_m)$ where $\varepsilon = 3\text{\AA}$ is the water
257 molecules size. For all cement pastes (admixed or not), the surface diffusion coefficient is
258 about $D = 2.25 \cdot 10^{-11} \text{m}^2 \cdot \text{s}^{-1}$ *i.e.* about 1/100 of that of bulk water at 23°C. In consequence,
259 the presence of cellulose ethers in cement paste does not modify the surface diffusion
260 coefficient at the pore surface. This result is similar to those obtained in the macroscopic scale
261 by pulsed field gradient NMR showing that the CE does not modify the diffusion coefficient
262 of water in the bulk [9].

263 The effect of starch ethers was also investigated with M1 and M4. These polymers provide
264 very different water retentions (92.6% and 66.2% respectively). The protocol was identical to
265 that of cement pastes containing cellulose ethers. The results are shown on Fig. 4b. The
266 translational correlation times are also $\tau_m \approx 1 \text{ns}$ and $\tau_s \approx 10 \mu\text{s}$ for the admixed cement paste
267 with M1 and M4 respectively. This demonstrates that the translational diffusion coefficient at
268 the surface of the solid interfaces is not affected by starch ether's presence.

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

272 4.3. Specific surface area and relative quantity of water transiently present at pore surface

273 On Figs. 3 and 4, one observes a constant value for $1/T_1$ when the proton frequency
274 becomes $\omega_l < \omega_d = 2\pi \times 30 \text{ kHz}$. Such a cross-over frequency ω_d is of the order of the dipolar
275 interaction in the solid state between two protons separated by 0.155 nm. On this low
276 frequency range, the confined proton liquid explores relaxation processes induced by
277 characterized long correlation times encountered in the solid state: $\tau_{rigid} = 1/\omega_d = 5.3 \mu\text{s}$. We
278 have shown in Section 3 (i) that owing to the cross relaxation process, the intermolecular
279 dipole-dipole interaction then couples the water spin relaxation to that of the solid and the

280 magnetic field dependence of the immobilized spin system. From a mathematical point of
 281 view, Eq. (2) tends to the constant relaxation rate of the solid matrix R_{I_s} when the dipolar
 282 cross-relaxation rate is lower than the individual relaxation
 283 rates, *i. e.*: $k \ll R_{1,w}, R_{1,s}$ and $|R_{1,w} - R_{1,s}|$ and providing that $F \ll 1$ and $k/F > k$:

284

$$285 \quad R_{slow}(\omega_I < \omega_d) \approx R_{1,s} + k/F, \text{ with } R_{1,s} \equiv R_{1,w}(\omega_I = \omega_d) = Cte \quad (4)$$

286

287 The observed data presented in Fig. 5 confirm the plateau observed at low frequency (at 10
 288 kHz) for R_{slow} during the first hundred minutes. Then, relaxation rate increases due to cement
 289 hydration and development of the specific surface area. Moreover, a zoom on the Fig. 5
 290 shows that small but significant differences exist between each adjuvanted cement pastes.
 291 The observed plateau for frequency below ω_d is thus characteristic of the rigid-lattice limit of
 292 the solid-proton hydrates. The absolute value of such a plateau, measured for instance at 10
 293 kHz, is thus indicative of the specific surface area precisely at the solid-liquid interface:

$$294 \quad R_{slow}(\omega_I = 2\pi \times 10kHz, t_{hydr}) \approx R_{1,s}(t_{hydr}) \approx R_{1,w}(\omega_I = \omega_d, t_{hydr}) \quad (5)$$

295 As the correlation times τ_m and τ_s are constants whatever the cement paste composition, the
 296 continuous measurement of $R_{slow}(t_{hydr})$ at a fixed and low frequency $\omega_I = 2\pi \times 10kHz$, allows
 297 to probe directly the time evolution of the specific surface area of the cement paste $S_{p,NMR}$:

298

$$299 \quad S_{p,NMR}(t_{hydr}) = \frac{1/T_{1,observed}(10kHz, t_{hydr})}{\frac{x\epsilon\pi}{60\epsilon^4} \sigma_S \rho_w (\gamma_I \gamma_S \hbar)^2 S(S+1)\tau_m \left[3 \ln \left(\frac{1 + \omega_d^2 \tau_m^2}{(\tau_m/\tau_s)^2 + \omega_d^2 \tau_m^2} \right) + 7 \ln \left(\frac{1 + 659^2 \omega_d^2 \tau_m^2}{(\tau_m/\tau_s)^2 + 659^2 \omega_S^2 \tau_m^2} \right) \right]} \quad (6)$$

300

301 The continuous measurement of $1/T_1(\omega_f=2\pi\times 10\text{kHz}, t_{hydr})$ in presence of various
302 admixtures of cellulose ethers thus allows to monitor the evolution of the specific surface area
303 $S_{P,NMR}(t_{hydr})$, of the material during the hydration.

304

305 4.4. How NMR relaxation can elucidate water retention mechanisms

306

307 In the very early aged of the hydration, the amount of CSH is not very large and the
308 admixed polymer is still in the interstitial solution within the pores of the paste, even if the
309 cellulose ethers are rather large. The relaxation of the mobile proton-water thus will be
310 influenced by the presence of the polymer. We show that measuring the time evolution of the
311 spin-lattice relaxation rate $R_{slow}(10\text{ kHz}, t_{hydr})$ at 10 kHz, especially in the first minutes of
312 hydration allows probing quantitatively the relative population of water transiently present at
313 the solid hydrate surfaces $N_S/N(t_{hydr})$.

314 On Fig. 5, the continuous lines exhibit the time evolution of $R_{slow}(10\text{ kHz}, t_{hydr})$ for the non
315 adjuvanted (neat) white cement and with HPMC J1, J2, J3 admixtures. The periods d_{CE}
316 during which the plateau remains constant are evidenced (d_0 is related to neat cement) and
317 ordered as followed:

$$318 \quad d_0 = 11\text{ min} < d_{J3} = 60\text{ min} < d_{J2} = 79\text{ min} < d_{J1} = 107\text{ min}.$$

319 This period d_{CE} , measured at low frequency, is a clear indicator of the delay of hydration
320 induced by the CE polymer introduced into the material. The fact that d_0 stays much smaller
321 than the other d_{CE} is a clear indication of the delayed hydration and setting induced by the
322 HPMC J1, J2, J3 admixtures. We show on Fig. 6, that one can correlate these delays of
323 hydration measured by NMRD to the ones measured from isotherm calorimetry
324 measurements (determined using the method described in ref. [31]) on similar materials. The
325 quasi linear dependence ($r^2=0.99$) shows very good accuracy between the microscopic
326 (NMRD) and macroscopic (calorimetry) measurements.

327 Another important parameter can be extracted from the behaviour of the time evolution of
 328 $R_{slow}(10\text{ kHz}, t_{hydr})$ during the first 100 minutes of hydration. This is the value of the plateau
 329 itself, noted, $R_{CE} = R_{slow,observed}(10\text{kHz}, t_{hydr})$ which depends critically on the nature of the
 330 admixtures. The results found for the neat white cement paste and HPMC-admixed cement
 331 pastes J1, J2, J3 are ordered as followed:

$$R_0 = 30\text{ s}^{-1} < R_{J1} = 35,9\text{ s}^{-1} < R_{J2} = 36,3\text{ s}^{-1} < R_{J3} = 37,6\text{ s}^{-1}$$

332 where R_0 is the value of the low-frequency plateau for neat cement. According to Eqs. (2) and
 333 (3), R_{CE} is proportional to the correlation time τ_m and directly related to the relative amount
 334 of water N_S/N transiently present during the first 100 minutes at proximity of solid interfaces
 335 that is proportional to the specific surface area:

$$337 \frac{N_S(t_{hydr} < d_{CE})}{N} = x\varepsilon\rho_w S_{p,NMR}(t_{hydr} < d_{CE}) \quad (7)$$

338
 339 where $S_{p,NMR}(t_{hydr})$ is defined in Eq. (6). Substitution of all the parameters measured or defined
 340 above in Eq. (7) and owing to the observation that $\tau_m \approx 1\text{ ns}$ and $\tau_s \approx 10\ \mu\text{s}$ are universal for all
 341 the cement-based materials, one obtains a proportion $N_S(t_{hydr}=2\text{ min})/N = 1.06\%$ for the neat
 342 white cement paste and $N_S(t_{hydr}=2\text{ min})/N = 1.36\%$ for the admixed cement pastes with
 343 HPMC J3. One obtains intermediate values for the other admixtures HPMC J1 and HPMC J2.
 344 The fact to probe, in the first minutes of cement hydration, the fraction of mobile water
 345 molecules transiently present at solid interfaces N_S/N in presence of different nature and
 346 quantity of cellulose ethers is a key result of this study that can be directly linked to the
 347 relative amount of water retained on the pores surface.

348 We have applied the same NMRD method for starch ethers M1, M4 (Fig. 7) and found the
 349 following results: $d_0 = 11\text{ min} < d_{M4} = 19\text{ min} < d_{M1} = 22\text{ min}$ and $R_0 = 30\text{ s}^{-1} <$

350 $R_{M4} = 33.6 \text{ s}^{-1} < R_{M1} = 35.2 \text{ s}^{-1}$ that reveal a much weaker microscopic water retention
351 effect than the ones obtained with *CE* polymers.

352 Moreover, the effect of the substitution of *CE* on the water transiently present at the solid
353 interfaces for HEMC C4 and HEC N7 molecules is shown on Fig. 8. These two polymers
354 have been chosen to evidence the effect of hydrophobic methoxyl groups present on HEMC
355 and absent on HEC. We check that the ASTM method cannot discriminate the important
356 water retention (WR=98.8%) for the cements adjuvanted by these two polymers [31]. We
357 remind that this discrimination is limited by the depression imposed by the method (50
358 mmHg). To improve the sensibility of the ASTM method, one should increase largely such a
359 depression. On the contrary, we show here that the NMRD data can indeed discriminate the
360 observed value $R_{CE}=39 \text{ s}^{-1}$ for the hydrophilic HEC N7 molecule and $R_{CE}=37\text{s}^{-1}$ for the
361 hydrophobic HEMC molecule, because NMR is very sensitive to the local environment of the
362 proton spins. So the macroscopic ASTM measurement is not able to distinguish polymer's
363 effect while NMRD is more sensitive to the local physical-chemistry at the solid interfaces.

364 Last, Fig. 9 shows the NMRD results for HPMC J1 with two different concentrations
365 namely 0.1 and 0.4% giving 82.3 and 98.0% macroscopic water retention, respectively. As
366 expected, the value of the plateau R_{CE} increases significantly with the concentration of
367 admixture. Finally, on Fig. 10, the linear correlation ($r^2 = 0.93$) of R_{CE} and water retention of
368 mortar admixed with three different concentrations 0.1, 0.27 and 0.4% of HPMC J1 proves
369 that our microscopic NMRD measurements on cement pastes could be correlated with the
370 macroscopic water retention on mortars.

371 5. Conclusion

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

375 The first application of NMRD probes directly the proton-water surface dynamics from the
376 magnetic field dependence of the nuclear spin-lattice relaxation rate. In spite of modifications
377 of the solution's viscosity, we find that the cellulosic derivatives do not modify the surface
378 diffusion coefficient of water that is about two orders of magnitude smaller than that of bulk
379 water.

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

393

394 **Acknowledgements**

395 The authors acknowledge all the industrial and academic CERE M members
396 (<http://cerem.cstb.fr>).

397

- 399 [1] S. Mansoutre, P. Colombet, H. Van Damme. *Water retention and granular rheological*
400 *behavior of fresh C3S paste as a function of concentration.* Cem. Concr. Res., **29** (1999)
401 1441-1453.
- 402 [2] A. Peschard, A. Govin, P. Grosseau, B. Guilhot, R. Guyonnet. *Effect of polysaccharides*
403 *on the hydration of cement paste at early ages.* Cem. Concr. Res., **34** (2004) 2153–2158.
- 404 [3] J. Pourchez, A. Peschard, P. Grosseau, R. Guyonnet, B. Guilhot, F. Vallée. *HPMC and*
405 *HEMC influence on cement hydration.* Cem. Concr. Res., **36** (2006) 1777-1780.
- 406 [4] J. Pourchez, B. Ruot, J. Debayle, E. Pourchez, P. Grosseau. *Some aspects of cellulose*
407 *ethers influence on water transport and porous structure of cement-based materials.*
408 Cem. Concr. Res., **40** (2010) 242-252.
- 409 [5] L. Patural, P. Marchal, A. Govin, P. Grosseau, B. Ruot, O. Devès. *Cellulose ethers*
410 *influence on water retention and consistency in cement-based mortars.* Cem. Concr.
411 Res., **41** (2011) 46-55.
- 412 [6] H. Kuhn, D. H. Waldeck, H.-D. Försterling. *Principles of Physical Chemistry.* Wiley-
413 Interscience (2009).
- 414 [7] B. Penke, S. Kinsey, S. J. Gibbs, T. S. Moerland, B. R. Locke. *Proton Diffusion and T1*
415 *Relaxation in Polyacrylamide Gels: A Unified Approach Using Volume Averaging.* J.
416 Magn. Reson., **132** (1998) 240-258.
- 417 [8] N. Nestle, A. Kühn, K. Friedemann, C. Horch, F. Stallmach, G. Herth, *Water balance*
418 *and pore structure development in cement materials in internal curing with modified*
419 *superabsorbent polymer studied by NMR, Microporous and Mesoporous Materials* **125**
420 *(2009) 51-57.*
- 421 [9] L. Patural, P. Porion, H. Van Damme, A. Govin, Ph. Grosseau, B. Ruot, O. Devès, A
422 *pulsed field gradient and NMR imaging investigations of the water retention*

- 423 *mechanism by cellulose ethers in mortars*, Cem. Concr. Res., **40** (2010) 1378-1385.
- 424 [10] A. G. Redfield, W. Fite, H.E. Bleich, *Precision high speed current regulators for*
425 *occasionally switched inductive loads*, Rev. Sci. Instrum., **39** (1968) 710-715.
- 426 [11] F. Noack, *Basic and novel aspects of NMR field-cycling spectroscopy*, Bull. Ampere,
427 **175** (1994) 18-35.
- 428 [12] J.-P. Korb, L. Monteilhet, P.J. McDonald, J. Mitchell. *Microstructure and texture of*
429 *hydrated cement-based materials: A proton field cycling relaxometry approach*. Cem.
430 Concr. Res., **37** (2007) 295-302
- 431 [13] H.F.W. Taylor, *Cement Chemistry, 2nd edition*, Academic Press Thomas Telford (2007).
- 432 [14] F. Crössmann, W. Klaus. *Wasserlösliche Celluloseäther im Spiegel der*
433 *Anwendungstechnik*. Collection of publication of a group of authors of Kalle, branch of
434 Hoechst AG, Wiesbaden-Biebrich (1974).
- 435 [15] C. Clasen, W.-M. Kulicke. *Determination of viscoelastic and rheo-optical material*
436 *functions of water-soluble cellulose derivatives*. Prog. Polym. Sci., **26** (2001) 1839-1919.
- 437 [16] B. Ruot, T. Goto, J. Pourchez. *Some aspects of cellulose ethers and latexes influence on*
438 *the properties of cement-based materials - Examples of results obtained within the*
439 *CEReM*. Proceedings of the VII SBTA (7^o Symposio Brasileiro De Tecnologia Das
440 Argamassas), (2007).
- 441 [17] EN 196-1. *Methods of testing cement — Part 1: Determination of strength*. (2006).
- 442 [18] Standard C1506-09. *Standard test Method fo Water Retention of Hydraulic Cement-*
443 *Based Mortars and Plasters*. Am. Soc. Test. Mat. (2009).
- 444 [19] *Certifié CSTB Certified des enduits monocouches d'imperméabilisation – Modalités*
445 *d'essais, DT 9 du 10 avril 2008*.
- 446 [20] F. Barberon, J.-P. Korb, D. Petit, V. Morin, E. Bermejo. *Probing the surface area of a*
447 *cement-based material by nuclear magnetic relaxation dispersion*. Phys. Rev. Lett., **90**

- 448 (2003) 116103-116104.
- 449 [21] J.-P. Korb. *NMR and nuclear spin relaxation of cement and concrete materials*.
450 *Curr. Opin. in Coll. Int. Sci.*, **14** (2009) 192-202.
- 451 [22] J.-P. Korb. *Microstructure and texture of cementitious porous materials*. *Magn. Res.*
452 *Imag.*, **25** (2007) 466-469.
- 453 [23] I. Solomon, *Relaxation processes in a system of two spins*, *Phys. Rev.* **99**, (1955) 559-
454 **565**.
- 455 [24] R.G. Bryant, D. A. Mendelson, C. Coolbaugh Lester, *The magnetic field dependence of*
456 *proton spin relaxation in tissues*, *Magn. Reson. in Medicine* **21**, (1991) 117-126.
- 457 [25] K. R. Brownstein and C. E. Tarr, *Importance of classical diffusion in NMR studies of*
458 *water in biological cells*, *Phys. Rev. A*, **19**, (1979) 2446-2453.
- 459 [26] J.-P. Korb, M. Whaley-Hodges, R. G. Bryant. *Translational diffusion of liquids at*
460 *surfaces of microporous materials: Theoretical analysis of field-cycling magnetic*
461 *relaxation measurements*. *Phys. Rev. E*, **56** (1997) 1934-1945.
- 462 [27] A. Abragam, *The principles of Nuclear Magnetism*, Ch 8, (Clarendon, Oxford, 1961).
- 463 [28] N. Bloembergen and L. O. Morgan, *Proton relaxation times in paramagnetic solutions;*
464 *effects of electron spin relaxation*, *J. Chem. Phys.*, **34**, 842 (1961).
- 465 [29] A. Plassais, M.-P. Pomies, N. Lequeux, J.-P. Korb, D. Petit, F. Barberon,
466 *Microstructure evolution of hydrated cement pastes*, *Phys. Rev. E*, **72** (2005) 041401-
467 041408.
- 468 [30] J. J. Fripiat, M. Letellier, and P. Levitz, *Interaction of Water with Clay Surfaces*, *Phil.*
469 *Trans. R. Soc. A*, **311** (1984) 287-299.
- 470 [31] L. Patural, PhD Thesis, ENSM (2011).

471 **Table 1.** Phase composition of the white cement.

| Phases | C ₃ S | C ₂ S | C ₃ A | C ₄ AF | Sulfates |
|-----------------------|------------------|------------------|------------------|-------------------|-----------|
| Phase composition (%) | 68.8 ± 0.3 | 10.4 ± 0.7 | 10.5 ± 0.1 | 1.0 ± 0.1 | 7.5 ± 0.1 |

472 **Table 2.** Molecular parameters and water retention for cellulose ethers used in this work.

| CE | \overline{M}_w (kDa) | OCH ₃ (%) ^a | DS | OC ₂ H ₄ OH (%) ^a | OC ₃ H ₆ OH (%) ^a | MS | Water retention (%) |
|---------|---------------------------|--------------------------------------|-----|---|---|------|------------------------|
| HEMC C4 | 380 | 27.4 | 1.7 | 4.80 | - | 0.15 | 98.8 |
| HPMC J1 | 225 | 28.2 | 1.8 | - | 2.98 | 0.10 | 96.8 |
| HPMC J2 | 630 | 28.2 | 1.8 | - | 2.98 | 0.10 | 98.6 |
| HPMC J3 | 910 | 28.2 | 1.8 | - | 2.98 | 0.10 | 98.9 |
| HEC N7 | 2 900 | - | - | 56.0 | - | 2.5 | 98.8 |

473 ^a Informations provided by the manufacturer.

474 Mw=Cellulose ether weight-average molecular mass determined using size exclusion chromatography

475 DS= Number of substituted hydroxyl groups per anhydroglucose unit expressed as degree of substitution

476 MS=Molar ratio of alkoxy groups in the side chains to cellulose expressed as the average molecular substitution

477 OCH₃= Methoxy group

478 OC₂H₄OH= Hydroxyethyl group

479 OC₃H₆=Hydroxypropyl group

480 **Table 3.** Molecular parameters and water retention for starch ethers (SE) used in this work.

| SE | \overline{M}_w (kDa) | Amylopectin / amylose ratio ^a | Degrees of polymerization ^a | | Water retention (%) |
|-------|---------------------------|---|--|-------------|------------------------|
| | | | Amylose | Amylopectin | |
| SE M1 | 860 | 80 / 20 | 4 000 | 2 000 000 | 92.6 |
| SE M4 | 830 | 80 / 20 | 4 000 | 2 000 000 | 66.2 |

481 ^a Informations provided by the manufacturer.

482

483

Figure captions

484 **Fig. 1.** Structure of cellulose ethers (a): HPMC, (b): HEMC, (c): HEC. Substituent positions
485 are arbitrary; they may differ slightly from one molecule to another.

486 **Fig. 2.** Experimental device to measure water retention with ASTM C1506-09 standard.

487 **Fig. 3.** Measured water ^1H magnetic relaxation dispersion profiles for hydrated white cement
488 paste ($w/c=0.4$) as a function of the proton Larmor frequency. The experiments have been
489 realized in the early hydration period (0-45 min, filled circles) and on a larger hydration time
490 (up to few hours, filled squares) for neat (without *CE*) cement (**a**) and cement admixed with
491 HPMC J3 (**b**). The continuous lines are the best fits obtained with Eqs. (2) and (3).

492 **Fig. 4.** Measured water ^1H spin-lattice relaxation rates of hydrated white cement pastes
493 ($w/c=0.4$) as a function of the proton Larmor frequency. (a) Effect of three cellulose ethers
494 (HPMC J1, J2, J3). The J3 data sets are the same as those in Fig. 3. (b) Effect of two starch
495 ethers (M1 and M4). In both cases, we have reported the results obtained with the neat white
496 cement paste. The continuous lines are the best fits obtained with Eqs. (2) and (3).

497 **Fig. 5.** Water ^1H spin-lattice relaxation rates of hydrated cement pastes ($w/c=0.4$) as a
498 function of hydrating time measured at a Larmor frequency of 10 kHz. Effect of three
499 cellulose ethers (HPMC, J1, J2, J3). The inset represents a zoom on the frequency range of the
500 plateau.

501 **Fig. 6.** Correlation between the delays obtained by the NMRD and isotherm calorimetry.
502

503 **Fig. 7.** Water ^1H spin-lattice relaxation rates of hydrated cement pastes ($w/c=0.4$) as a function
504 of hydrating time measured at a Larmor frequency of 10 kHz. Effect of three cellulose ethers

505 (Neat, starch CE: M1, M4). The inset represents a zoom on the frequency range of the ,
506 plateau.

507 **Fig. 8.** Comparison of the water ^1H spin-lattice relaxation rates of hydrated cement pastes
508 ($w/c=0.4$) as a function of hydrating time measured at a Larmor frequency of 10 kHz. Effect
509 of different cellulose ethers (Neat, HEC N7, HEMC C).

510 **Fig. 9.** Comparison of the water ^1H spin-lattice relaxation rates of hydrated cement pastes
511 ($w/c=0.4$) as a function of hydrating time measured at a Larmor frequency of 10 kHz. Effect
512 of the *CE* concentration of HPMC.

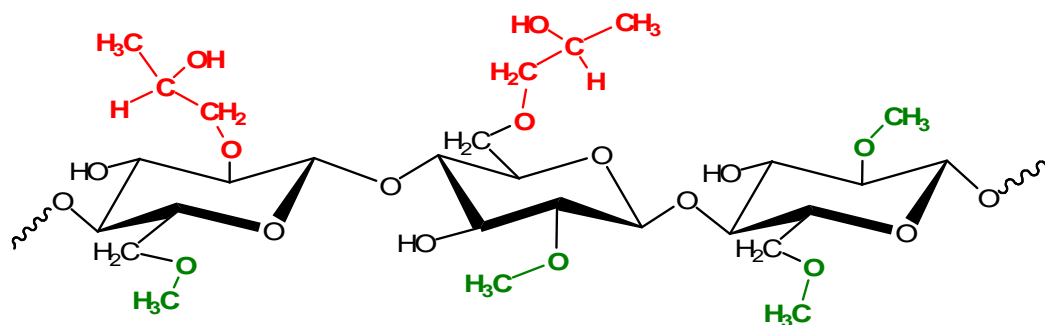
513 **Fig. 10.** Correlation between the water retention evidenced from the macroscopic
514 measurement described in Fig. 2 (ASTM C1506-09 standard) and the NMRD method. The
515 different concentrations of HPMC J1 are indicated.

516

517

518

(a)

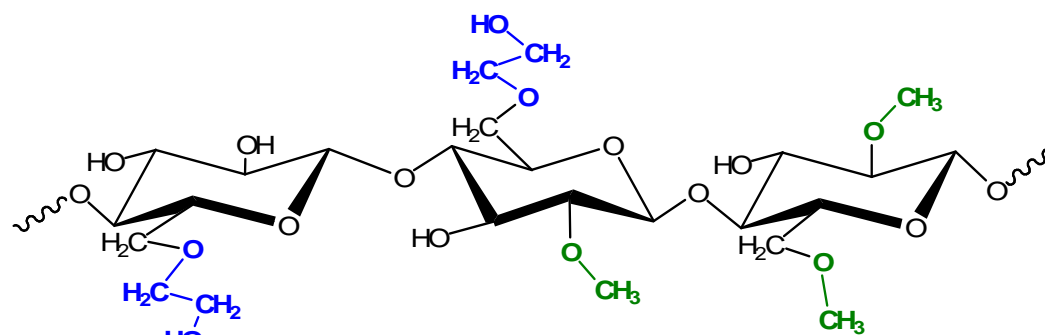


519

520

521

(b)

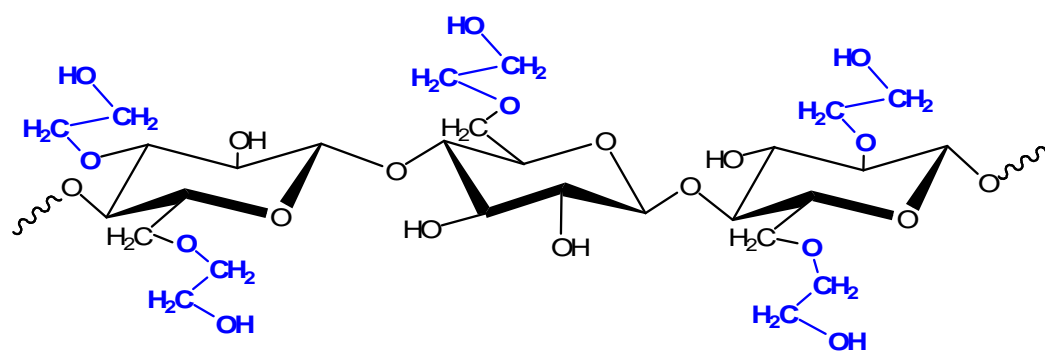


522

523

524

(c)

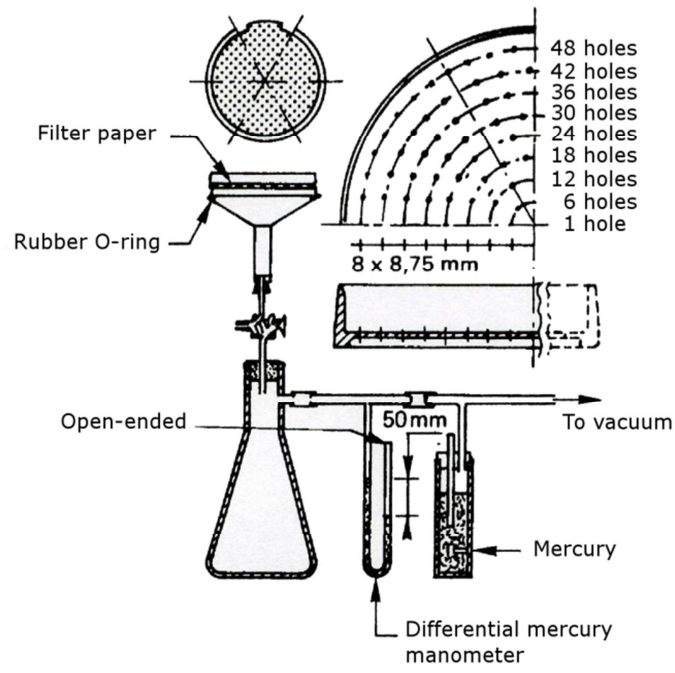


525

526

Fig. 1

527

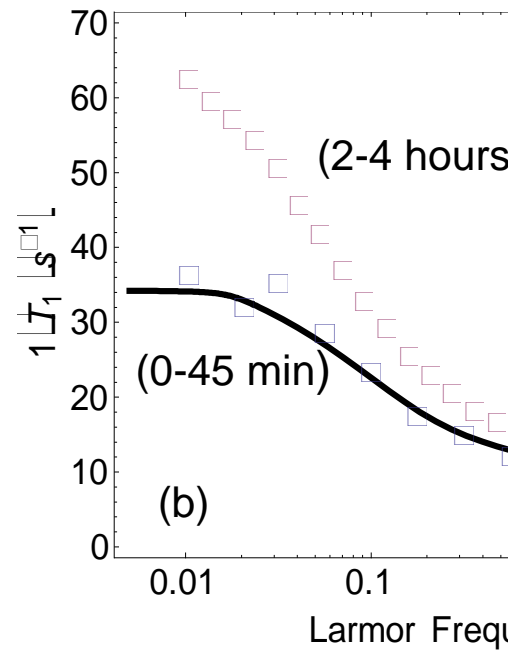
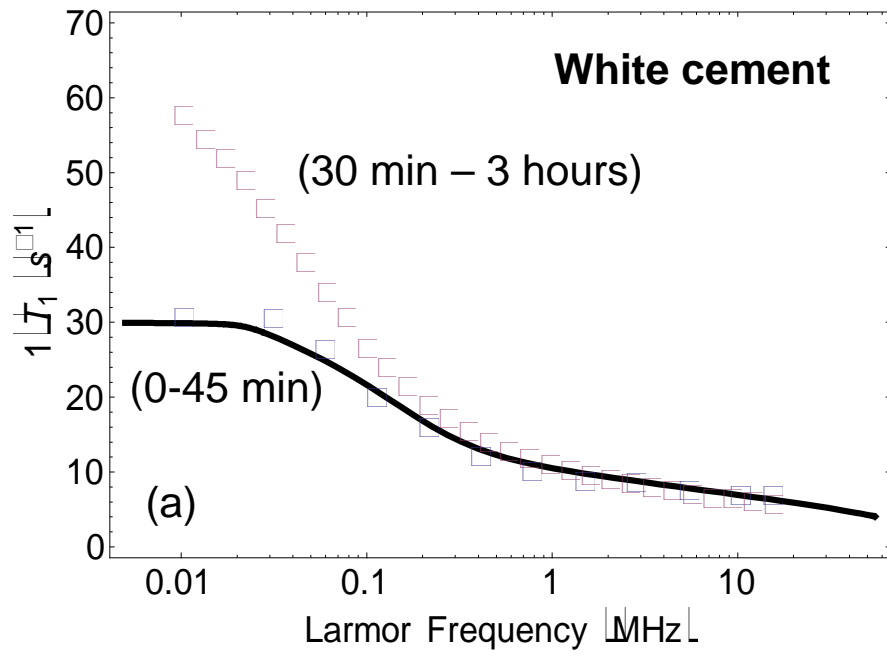


528

529

530

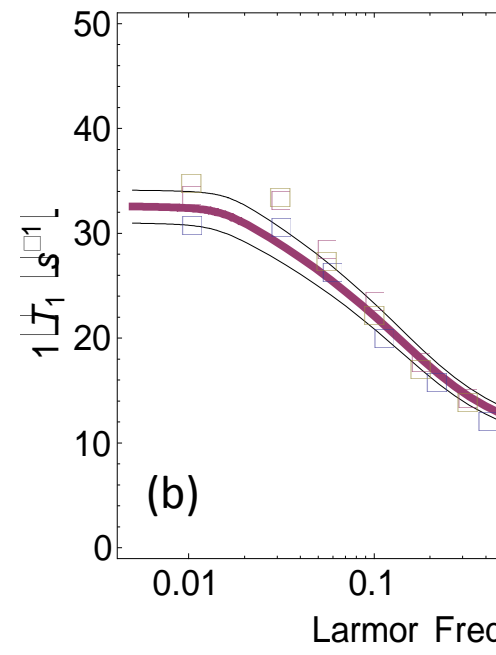
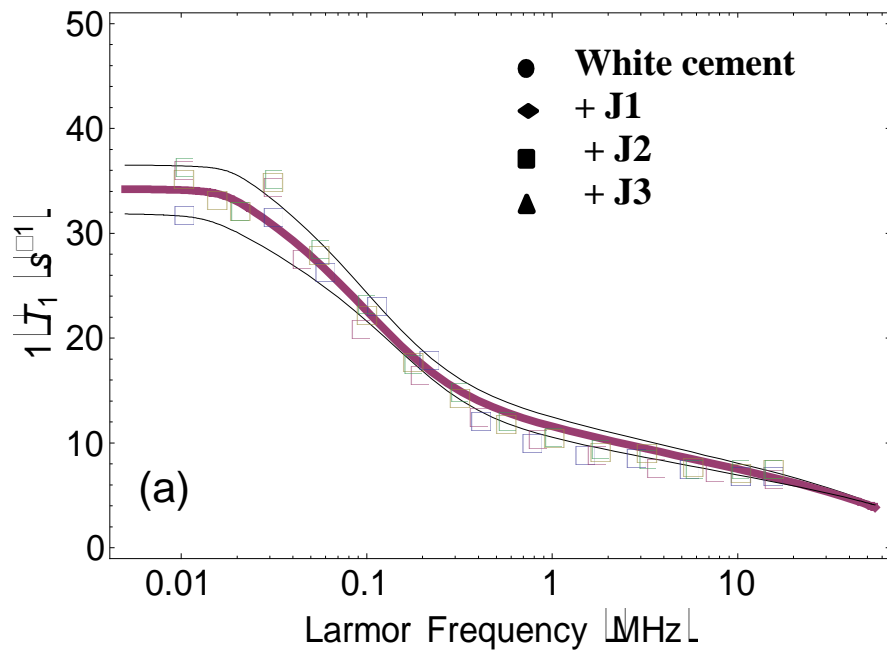
Fig.2



531
532

Fig. 3

533



535
536
537
538
539
540

Fig.4

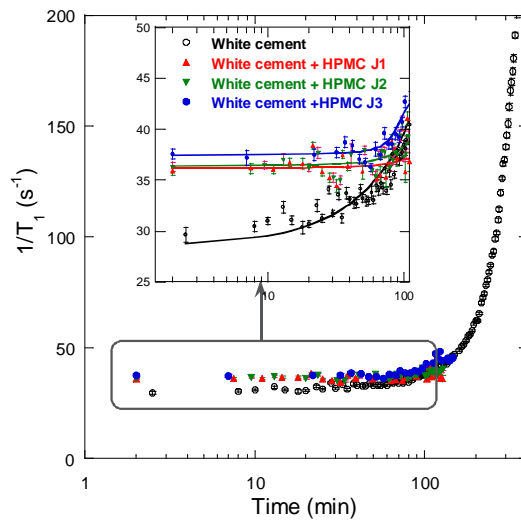
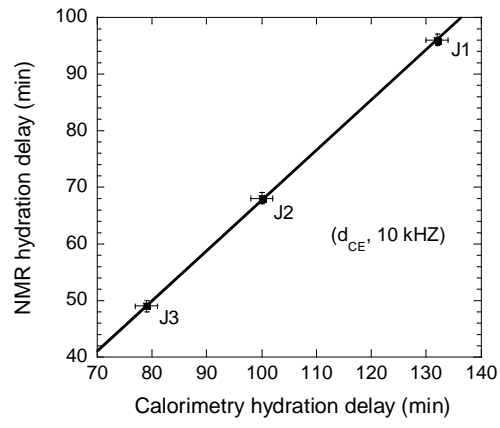


Fig. 5

541
542
543

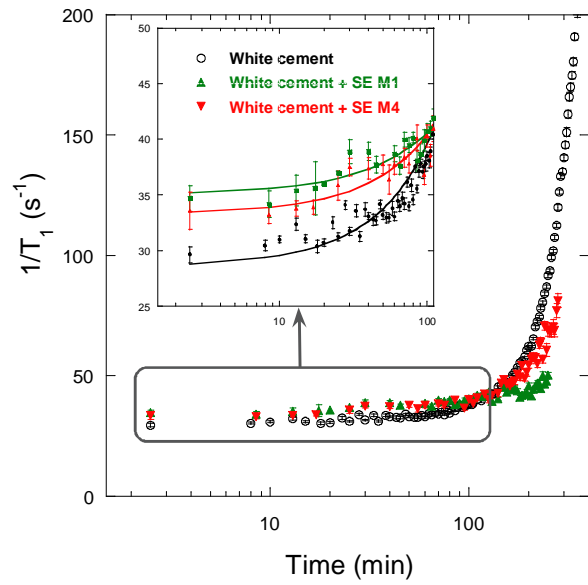


544

545

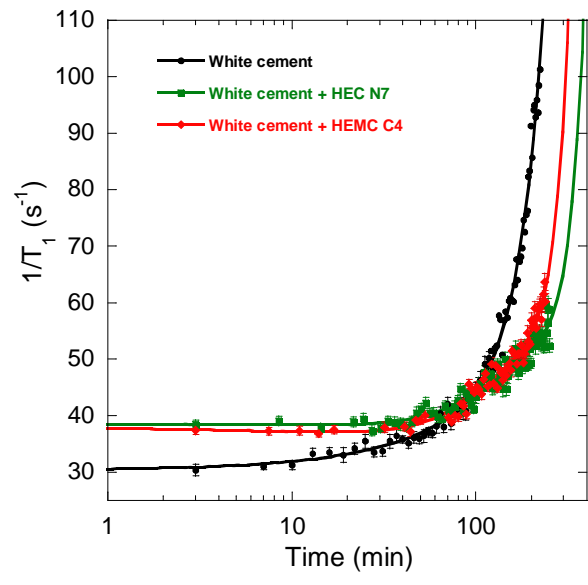
546

Fig. 6



547
 548
 549
 550

Fig. 7



551
 552
 553
 554

Fig. 8

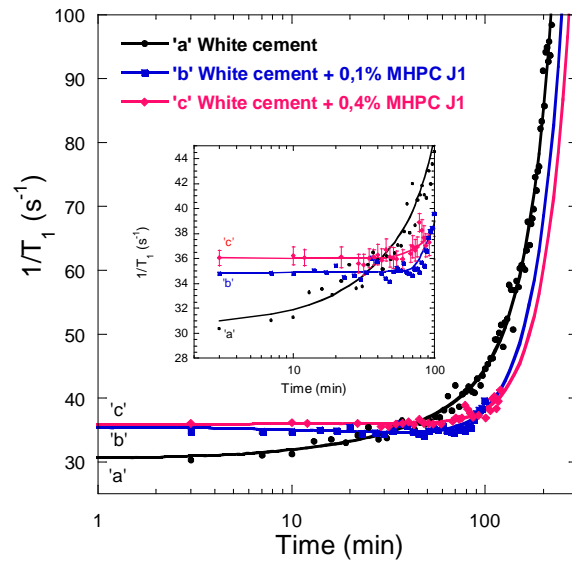
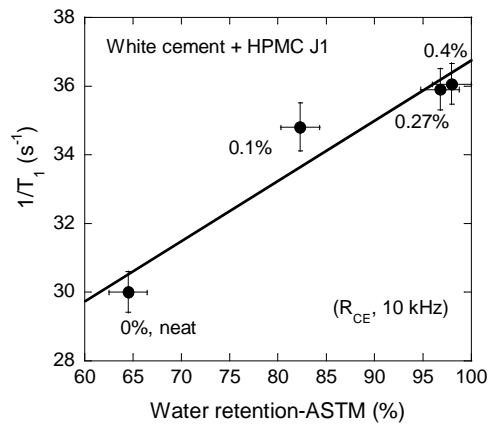


Fig. 9

555
556
557



558

559

560

Fig. 10