diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

# Impact of Multi-Scale Moisture Transport on Durability of Hardened Cement Pastes

*H. Chemmi, D. Petit, P. Levitz, J.-P. Korb, M. Bérard*

Physique de la Matière Condensée, Ecole Polytechnique, CNRS, Palaiseau 91128, France.

Corresponding author: Houria Chemmi, Laboratoire de Physique de la Matière Condensée, Ecole Polytechnique, CNRS, Palaiseau 91128, France, houria.chemmi@polytechnique.edu

(received 14 July 2008, accepted 27 January 2009)

## Abstract

We report on proton NMR relaxation of hardened Grey CEM I paste with two controlled degree of relative humidity. The comparison between these two aged materials evidences that the moisture transport only occurs on the meso and capillary scales. The proton population distribution *vs* $T_1$ follows power laws with a negative exponent in the nanopore-mesopore pore scale, and a positive exponent in the mesopore-capillary pore scale. This opposite exponent sign shows that the spatial hierarchical proton distribution behaves like a surface and volume distribution on short and large scales, respectively.

## Keywords

Durability, Cement, Moisture transport, Confinement, Longitudinal nuclear relaxation,

## 1. Introduction

Improving sustainability and performance of cements is a key point to limit $CO_2$ emission. Long term durability is closely related to unsaturated moisture transport on different length scales of these materials. In our study, hardened cement pastes exhibit threefold hierarchy: intra-CSH (hydraulic binder) nanopore, mesopore structure at a scale ranging from 3 nm to 20 nm and capillary (macro) pore network above 100 nm. The moisture transport at different water filling controlled by temperature and relative humidity ratio is followed by a proton NMR multi-scale approach using PFG diffusometry, field cycling relaxometry and spectroscopy correlated with $T_1$, $T_2$ and $T_{1\rho}$ measurements. In parallel, a similar study is conducted in three types of reference pore network, having nano, meso and macro pore networks MCM41, Vycor, and Controlled Pore Glass CPG, respectively. Here, we report, a proton NMR relaxation study of a hardened Grey CEM I paste (Portland cement) with different controlled relative humidities. This study leads to two main results. First, the comparison between these different aged situations evidences that the moisture transport only occurs at the meso and capillary scales. Second, in the nanopore-mesopore range, the proton population distribution *vs* $T_1$ follows a power law with a negative exponent. On the contrary,

in the mesopore-capillary pore scale, the proton population distribution follows another power law with a positive exponent. This drastic change in these exponents shows that the spatial proton distribution behaves like a surface hierarchical distribution at short scale and a volume hierarchical distribution at large scale.

## 2. Materials and experiments

A cement paste is prepared at 20°C by mixing anhydrous grey CEM I powder and distilled water with water-to-cement mass ratio w/c = 0.5. After 24 h, the material is kept in saturated lime water solution. Then, longitudinal relaxation NMR experiments by inversion recovery are performed at 360 MHz proton Larmor frequency on this material in three different conditions. Evolutions of longitudinal proton magnetizations are analysed by a "curve-peeling" method as illustrated on Fig.1. At first, (condition 1) the material is used after a 5 days setting delay, then (condition 2) this material is dried during 3 days under vacuum in a drying oven after an aging period of 2 months at 25°C and R.H. = 50 %, and finally, (condition 3) the same material is hydrated again during one month at 25°C and R.H. = 90 % using a saturated water solution by $BaCl_2$ salt.

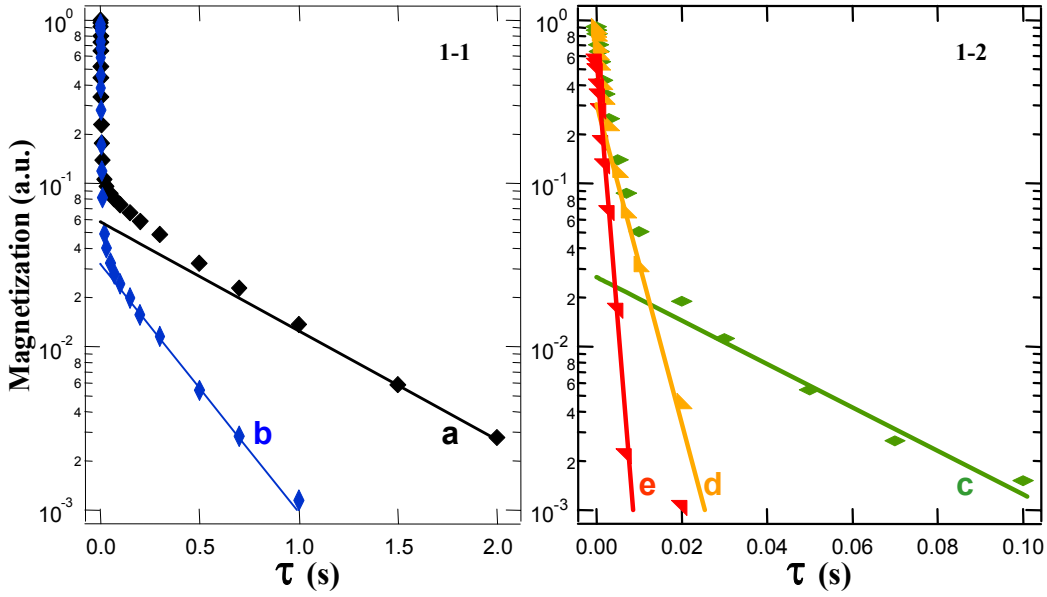


**Fig. 1:** Different steps of the "curve-peeling" method are used to extract successively five exponential components from the magnetization raw data (curve 1-1-a) of a grey CEM I paste hydrated 5 days with w/c = 0.5 at 20°C and shown on semi logarithmic plots. At the first step, a single exponential is subtracted to the raw data 1-1-a. The result leads to curve 1-1-b. The same method is iteratively applied up to the fifth step (Fig. 1-2). The continuous lines show the best fits of the 5 exponential components leading to sets of 5 weight factors $A_i$ and 5 relaxation times $T_{1i}$.

## 3. Results and discussion

From a logarithmic plot of the weighting factors $A_i$ set *vs* the longitudinal relaxation times $T_{1i}$ set, we follow the evolution of the $T_1$ dependence of proton population distribution ($^1$H-P.D.) for the grey CEM I paste in the three conditions 1, 2, 3 described above and shown on Figs. 2-1, 2-2 and 2-3, respectively. On Fig 2-2 the vertical dashed line gives the longest $T_1$ for pure liquid water and then the $T_1 \sim 20$ s only can be explained by vapour phase of water or some solid phases like portlandite. In this cement paste the nuclear relaxation process is mainly controlled by paramagnetic ferric ions [1] and well understood in this porous media using a biphasic fast-exchange model [2] leading to a proportionality relation between $T_1$ and the volume to surface ratio of pores $V/S$ which defines an average NMR pore radius

$\langle R\rangle_{NMR} \propto T_1$ [1, 3]. Thus $^1$H-P.D. can be seen as a surface or volume distribution of the pore size *vs* $\langle R\rangle_{NMR}$. $^1$H-P.D. leads to structural information of this porous material as underlined by ellipses on Fig 2. The main results shown on Fig. 2 are the evolution of $^1$H-pore distribution (P.D) under the three conditions defined above. There is practically no modification at the nanopore scale of $^1$H-P.D. showing that nanopores do not participate to moisture transport. Mesopores can be filled (Fig. 2-1 & 2-3) or empted (Fig. 2-2) on the contrary of the macropores showing the participation of these two scales to moisture transport.

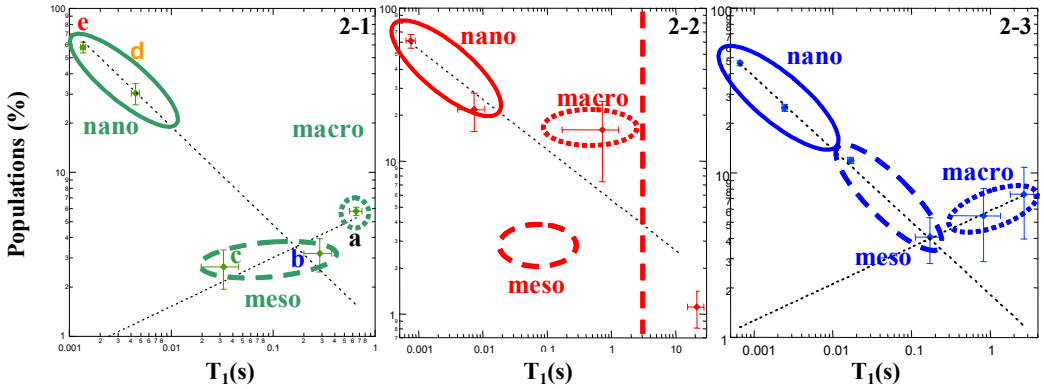


**Fig. 2:** Logarithmic plots of the proton population distribution though the weight factors $A_i$ versus the relaxation times $T_{1i}$ as illustrated by the point set {a,b,c,d,e} on Fig. 2-1 and coming from the mono exponential components drawn on Fig. 1. Fig. 2 reports successively proton distributions of a 5 days setting grey CEM I (Fig. 2-1), then of the same material dried 2 months later (Fig. 2-2), and finally of the same dried material hydrated at R.H. = 90 % during one month (Fig. 2-3). The dotted lines underline the power law behavior of the proton distributions.

On Fig. 2, the dotted lines show the power law behavior of $^1$H-P.D. which is a consequence of the well known hierarchical distribution of the pore size in this material. The exponent sign of these power laws are negative in the nano to meso scale (region 1) and positive in the meso to macro scale (region 2). We can understand this change in the exponent sign by a surface proton distribution $S(R)=\langle R\rangle^{2-Df}$ in region 1 and a volume proton distribution $V(R)=\langle R\rangle^{3-Df}$ in region 2 with the fractal dimension $D_f$ between 2 and 3 [3].

## 3. Conclusions

The main results of this study are twofold. First, the moisture transport in grey CEM I occurs in the range of meso and capillary scales. Second, the spatial $^1$H distribution follows a surface (volume) distribution on short (large) scales.

## References

[1]F. Barberon, J.-P. Korb, D. Petit, V. Morin and E. Bermejo, Phys. Rev. Lett. **90** (2003) 116103.

[2]K.R. Brownstein and C. E. Tarr, Phys. Rev. A **19** (1979) 2446.

[3]A. Plassais, M.-P. Pomiès, N. Lequeux, J.-P. Korb, D. Petit, F. Barberon and B. Bresson, Phys. Rev. E. **72** (2005) 041401.