



Impact of wettability on moisture transport at mesoscale in porous materials

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ABSTRACT

A multiscale NMR method is used for probing the proton dynamics in control pore glasses (CPG) standing in the meso and macro scale ranges. The porous material has been synthesized in our laboratory following the sol–gel route as well as spinodal decomposition. Special heat treatment has modified the proton species at the pore surface. ¹H high field NMR spectroscopy has been realized under controlled relative humidity conditions. This has allowed a clear identification of the different proton species present during the kinetics of hydration from RH = 0% up to 98%. We focused on the nuclear magnetic relaxation dispersion experiments to probe specifically the proton dynamics in CPG pores with and without methyl groups at the surface. A detailed analysis of the frequency dependences of the longitudinal relaxation rates in these two materials evidences the impact of microscopic wettability on moisture transport in meso- and macro-porous materials. The surface modification has allowed a frequency rescaling such that different regimes of relaxation dependence can be fully explored in a larger frequency range than that explored by FFC relaxometry. We believe that such an NMR study realized on model porous materials is of particular importance for studying the moisture transport between the meso- and macro-porous networks of cement-based materials.

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1. Introduction

Concrete is a porous material composed of cement (commonly Portland cement) as well as aggregates, sand, water and chemical admixtures such as silica fume and adjuvants [1]. Concrete solidifies and hardens after mixing with water and placement due to a chemical process known as hydration [2]. The water reacts with the anhydrous cement, which bonds the other components with hydrates and forms a hardened cement paste known as the main ingredient of concrete. The important mechanical performances and durability of concrete are mainly due to the high compactness of this material but also to the microstructure of hydrated cement paste. NMR methods have proven useful for probing microstructure including different mesoscopic properties such as: porosity [3], specific surface area [4], distribution and connectivity of pore sizes [5] as well as tortuosity factor [6,7]. However, general questions still exist concerning the multiscale character of such highly disordered hydrated and porous materials. For instance, the moisture transport efficiency and aggressive agents involve all the other mixed classes of porosity from micro- to macro-lengthscales [8]. An important example is encountered in nuclear waste storage

[9]. A better control on physical properties on such multiscale structures is thus absolutely needed in each class of porosity.

A promising way to study the moisture transport of such multiscale materials is to restrict the study to well defined materials belonging to each class of porosity. Here, we present a multiscale NMR study of moisture transport in “Controlled Silicate Pore Glass” (CPG) having a meso- and macro-porosity and where one controls the surface reactivity. In the following sections, we outline the synthesis of these materials and discuss the main results obtained concerning the impact of the wettability on moisture transport.

2. Materials and methods

2.1. Samples

We use a synthesis [10] involving competition between sol–gel route and spinodal decomposition for controlling the macro-porosity of silica controlled pore glass (CPG) material [11]. The silica skeleton at the macroscale presents micro- and meso-porosity characterized by nitrogen adsorption [10]. Basically, the method consists in mixing three different reactive products: an alkoxyde, the tetramethoxysilane (TMOS); a polymer, the polyethylene-glycol (PEG) and a diluted acetic acid at pH 3.5 to initiate a hydrolyse-condensation reaction in acidic conditions. Then this reaction is kept at 0 °C for controlling the competition between the sol–gel

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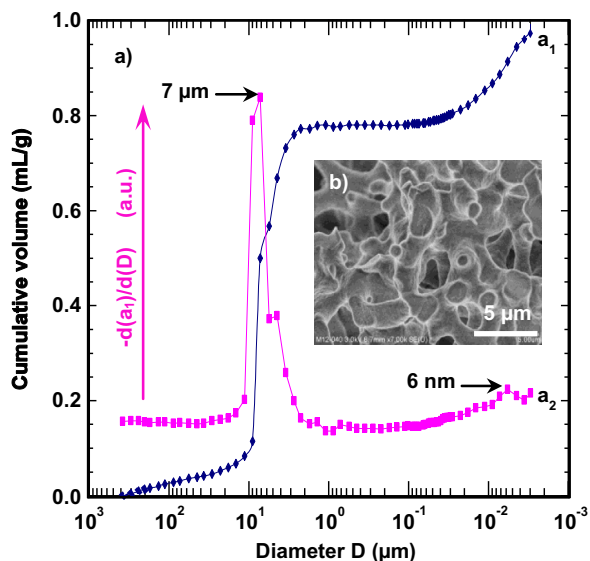


Fig. 1. Mercury intrusion in raw CPG sample. (a) The continuous curve a_1 represents the cumulative invasion volume. The continuous curve a_2 is the numerical derivative of curve a_1 . (b) MEB image of the studied CPG sample.

process and a spinodal decomposition leading to a phase separation between an enriched phase in silica and the different solvents (water and methanol). After, the polycondensation, the sample is maintained at 40 °C during 24 h for removing the solvents. We used the “soxhlet” method for obtaining CPG with different macro-pore sizes depending on the relative quantity of PEG. After a supercritical drying, one has a multiscale porous material with micro-, meso- and macro-porosities. Finally, a thermal treatment allows closing of the micro-porosity. We show in the inset (b) of Fig. 1, a MEB picture of the silica network of CPG. The curve (a_1) reports the cumulative mercury invasion volume vs. pore diameters in the main Fig. 1. As usual in the mercury invasion technique, the numerical derivative (a_2) enhances the singularities evidencing an average macro-pore size of 7 μm and a meso-pore contribution at about 6 nm.

2.2. Methods

We used, in parallel with the usual methods of material characterization [10], a non-invasive multiscale NMR method including high field spectroscopy with high power probes, fast field cycling relaxometry (FFC) and diffusometry by the pulsed field gradient (PFG) method. Other complementary techniques like conductivity and X-ray tomography were also used. A key point of our work is the *in situ* control of the relative humidity (RH) during the different NMR experiments. For instance, we follow continuously the kinetics of water filling in pores. Here, we focus on the high field NMR spectroscopy and FFC relaxometry.

3. Experimental results, data treatment and discussion

3.1. Characterization of proton species by high field NMR and continuous control of kinetics of water adsorption

We present in Fig. 2 the high field ^1H NMR spectroscopic data of a raw CPG sample at 360 MHz in a static probe bearing our control relative humidity device. We show in Fig. 2a the raw experimental spectrum (1) of the dry sample and the analysis based on the sum (2) of two Voigt- profiles components (3 and 4). The peak (3) is an almost Lorentzian peak of relative intensity 57% characteristic of a

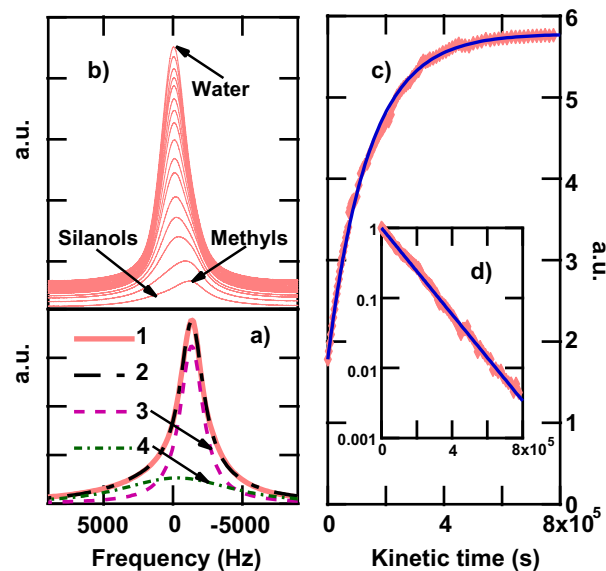


Fig. 2. ^1H NMR results of raw CPG sample at 360 MHz and 25 °C. (a) Static spectrum of the dry raw CPG sample (1) and the computed curve (2) composed of two components (3, 4) obtained through a Voigt deconvolution procedure. (b) Kinetic evolution of NMR spectrum from dry state to full equilibrium at RH = 98%. The arrows indicate the silanol and methyl contributions in the dry state as well as the one of water at RH = 98%. (c) Kinetic evolution of the intensities at the time origin of the FID. (d) Semi logarithmic plot showing the return to equilibrium of the normalized data displayed in (c). The continuous lines in (c, d) obtained are the best fits achieved with a mono-exponential decay with a characteristic time of 39 h.

fast molecular motion. However, the linewidth of 2 kHz of such a peak is not compatible with a liquid line shape. The peak (4) is almost a Gaussian peak of 4.7 kHz line width typical of static dipolar interaction. We have shown that these two populations relax with a unique $T_1 = 0.61$ s [10]. This reveals an efficient spin diffusion process for achieving a unique spin temperature. Fig. 2b reports the NMR spectrum evolution of the same sample from its dry state (Fig. 2a – spectrum 1), at time zero, up to an equilibrium state at RH = 98% after 9 days. In this latter state, the frequency position of the maximum is mainly controlled by water. So, the full evolution of the NMR spectrum allows assigning at each step the different proton species. This analysis ends with a contribution of methyl group species for the Lorentzian peak (3) and a contribution of silanol groups for the Gaussian ones (4). Finally, we report in Fig. 2c, the kinetic evolution of the free induction decay (FID) intensity corresponding to the surface area of spectra displayed in Fig. 2b. This figure thus covers the evolution from non-zero initial dry state with contributions of methyls and silanols (31.0% of total protons) to the final hydrated equilibrium state where the main contribution is due to water (69.0% of total protons). During this kinetics, the silanol and water protons are in fast exchange regime. The semi logarithmic plot of the water contribution displayed in Fig. 2d shows a pure exponential behavior with a characteristic time of 39 h. Last, one can make the two following remarks. (i) The plateau in Fig. 2c achieved at long time proves that one reaches an equilibrium between the adsorbed and gas moisture phases. (ii) In the raw dry sample, the protons are mainly associated with methyl groups.

3.2. Dynamical and structural information on moisture transport in raw CPG

We use the nuclear magnetic relaxation dispersion (NMRD) of longitudinal relaxation rate $R_1 = 1/T_1$ for studying the dynamics of the proton species at mesoscale close to the solid/liquid

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