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Age-dependent dynamics of water in hydrated cement paste

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Self-dynamics of water molecules has been studied in hydrated tricalcium silicate as functions of temperature, aging, and in the presence of an additive. A dynamical model taking into account the existence of ‘‘immobile water’’ and ‘‘glassy water’’ has been used to analyze quasielastic neutron spectrometer spectra. We deduced the fraction of the immobile water (p), the stretch exponent (β), and the average relaxation time $(\overline{\tau})$ of the glassy water. A quantitative picture for an aspect of the kinetics of the curing process and the structural relaxation parameters of the glassy water have been established.

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Understanding the state of hydration water in cement materials and the way to control it, is likely the key for the improvement of its ultimate strength and durability. Tricalcium silicate is the major component of ordinary Portland cement (OPC), and for this reason it has been often used as a model system to study schematic hydration reactions occurring in an ordinary cement paste [1]. According to the literature [2], when water is added to tricalcium silicate, Ca_3SiO_5 (abbreviated as C_3S), the overall hydration chemical reaction generates calcium-silicate-hydrate in a gel form, generally indicated as C-S-H, and calcium hydroxide, $Ca(OH)_2$, as a secondary product. The real stoichiometry of the calcium-silicate-hydrate gel is still not clear, and it changes during the course of the reaction and throughout the sample. However, it has been proven that C-S-H is the principal factor in the setting and hardening of the cement paste. It appears as semicrystalline amorphous material in x-ray diffraction [3], and for this reason it is very difficult to obtain useful information about its nanometric structure. Small-angle neutron scattering (SANS) experiments [4] have shown that in the hydrated cement paste a bimodal distribution of colloidal particles is present just after the mixing. The main component has a diameter of about 50 Å, and a second component with a diameter of 100 Å is also present. These dimensions do not change during the curing and have been confirmed unambiguously by transmission electron microscopy [5]. Very recently, a structural model of the calcium silicate hydrate has been proposed [6] using as basic unit a bigger colloidal globule formed by the aggregation of smaller units [4,5]. The globules can pack together in a close packing arrangement (high density cluster) and in a more open arrangement (low density cluster) [7]. If we accept the above picture for the micro-structure of cured cement, the aggregated colloidal particles must be dispersed in some sort of amorphous matrix of gel-like material, which contains calcium, hydroxide, and silicate ions. As for the dynamics of water embedded in this porous structure, the fraction of water incorporated into the colloidal particles must be immobile in the time scale of our measurements $(2\ \mathrm{ps}<t<50\ \mathrm{ps})$. However, the water incorporated in the gel region could be considered as an interfacial or glassy water [8], and its dynamics can be significantly different from bulk water depending on the concentrations of ions and the gel matrix structure [9,10]. Furthermore, motions of water molecules in the first and second hydration shells of the colloidal particles could be significantly slowed down. As cement ages, the glassy water penetrates continuously into the colloidal particles and thus increases the immobile fraction. According to their dynamics it is reasonable to divide water molecules in a cement paste into two categories: an immobile water or bound water having a fraction p, and a mobile but glassy water having a fraction $1\text{-}p$. In this Rapid Communication we formulate the translational part of the intermediate scattering function (ISF) of a water molecule explicitly according to the above picture. We show that the model accounts for the experimental spectra quite well, allowing us to deduce the fraction p as well as the relaxational parameters for the glassy water as a function of aging of the cement paste, temperature, and additive. Our model for ISF, taking into account both elastic and quasi-elastic scattering, is

$$F(Q,t)=p+(1-p)F_v(Q,t)\exp[-(t/\tau)^{\beta}], \tag{1}$$

where p is the immobile water fraction and $F_v(Q,t)\exp[-(t/\tau)^{\beta}]$ the relaxation function of the glassy water according to the ‘‘relaxing cage model’’ previously given for supercooled water [11]. The model treats the short-time dynamics as vibrations of water molecules in an ensemble of harmonic wells arising from the cage effect, described by the factor $F_v(Q,t)=\exp[-Q^2\Gamma(t)]$, which,

$$\Gamma(t)=v_0^2\left[\frac{1-C}{\omega_1^2}(1-e^{-\omega_1^2t^2/2})+\frac{C}{\omega_2^2}(1-e^{-\omega_2^2t^2/2})\right], \quad (2)$$

where $\hbar\omega_1$ and $\hbar\omega_2$ are the peak positions of the translational density of states of water [12] and C their relative strength. The long-time dynamics of cages is described by the "α relaxation" (the stretched exponential factor), which follows from the "mode coupling theory" [13,14]. This model was shown to fit an extensive set of ISF generated by computer molecular dynamics simulation of the extended simple point charge (SPC/E) [15] model supercooled water [16]. It was previously argued with some experimental evidence that the long-time dynamics of interfacial water behaves similarly to that of a bulk supercooled water at a lower temperature [8]. In this paper, we therefore use parameters ω_1, ω_2, and C taken from the previous fits to MD data on supercooled water [11].

The quasielastic neutron scattering experiments were carried out at the Laboratoire Léon Brillouin (LLB) in Saclay (France) using the high-resolution time-of-flight spectrometer MIBEMOL. The incident neutron wavelength was chosen as 9.0 Å (1.01 meV) to achieve a good energy resolution in the investigated Q range. The energy resolution [full width at half maximum (FWHM)] at the elastic position was about 28 μeV. Only detectors situated in the reflection geometry were taken into account. To obtain an adequate statistics in an hour of counting time, we grouped spectra from close-by detectors, excluding detectors situated at Bragg peaks. The Q range covered in our measurements was from 0.55 to 1.24 Å^{-1}, having a set of five spectra resulting from the grouping. Since for each hour we have five different spectra at five different average $\overline{Q}$ values, we analyzed more than 150 spectra in each series. In practice, the scattered energy is measured by time of flight of the scattered neutron over 3.58 m of flight path between the sample and detectors. The time-of-flight spectra thus measured were corrected for scattering from the same sample holder containing dry C_3S powder and standardized by dividing by a scattering intensity from a thin vanadium plate and converted to the differential scattering cross section by using standard routines available at LLB. The measured spectral intensity is fitted by the following equation: $S_M(Q,\omega)=S(Q,\omega)\otimes R(\omega)$, where $R(\omega)$ represents the normalized vanadium spectral intensity and $S(Q,\omega)$ the theoretical dynamic structure factor obtained by Fourier transform of ISF given in Eq. (1). In practice, it is important that the total spectral area of $S_M(Q,\omega)$ which is obtained experimentally is normalized to unity. A standard nonlinear least squares minimization has been implemented to obtain the phenomenological parameters p, β, and τ.

In each sample about 1.5 g of pure crystalline C_3S powder (specific surface area 0.92 m^2/g, BLAINE) were mixed with about 1 g of bidistilled water to produce a paste with a 0.65 water/C_3S weight ratio. The paste so obtained was spread evenly into a rectangular aluminum cell making a layer of 0.5 mm thickness. The volume fraction of water in the sample was 0.62, making a film of H_2O of an effective thickness of 0.31 mm, so the multiple scattering correction was not necessary. The cell was reassembled and sealed by means of an indium wire used as a gasket. This insures a negligible loss of water as well as no contamination of the paste by carbon dioxide during the experiment. The interior of the cell was coated completely by Teflon to prevent contact of the paste with aluminum sample holder, in order to prevent interference with the hydration process.

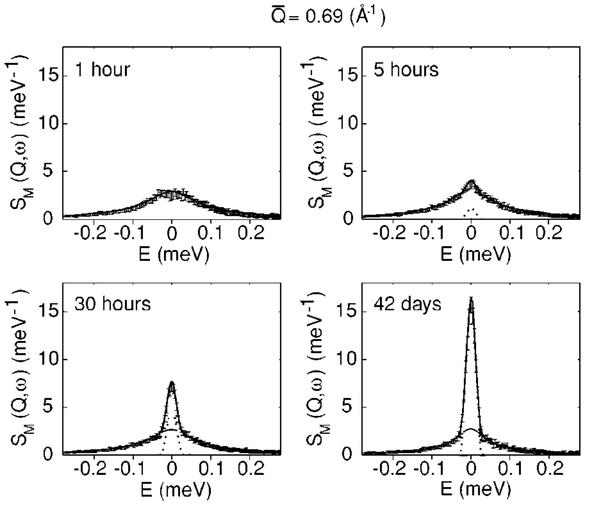

FIG. 1. Typical examples out of several hundred spectra we have measured and analyzed in this work. This figure shows time evolution of quasielastic incoherent neutron scattering spectra at $\overline{Q}$ equal to 0.69±0.10 Å^{-1}. The points with error bars represent the normalized experimental spectra, solid lines are the fitted theoretical spectra, thin solid lines and dotted lines are the quasielastic and elastic components [see Eq. (1)] respectively convoluted with the resolution function.

Figure 1 presents the quasielastic neutron scattering spectra at four different delay times during the cement hydration for the 30 °C sample. In each case we collected a spectra for 60 min from the beginning of the delay time. We followed the evolution every hour for at least 30 h. At 1 h delay time, only a quasielastic component was appreciable. However, the line shape of the quasielastic peak was already definitely non-Lorenzian ($\beta=0.79$), showing the presence of glassy water instead of free water. An additional elastic component gradually increases in time as the cement paste ages, indicating that part of the glassy water is converted into immobile water as time passes. Since the total spectral area is normalized to unity, we can define the fraction of immobile water (p) as the area of the elastic peak and the fraction of glassy water as the area of the quasielastic component.

From the time evolution of p it is possible to follow the kinetic of the hydration reaction (Fig. 2). The inset of Fig. 2 presents the flat dependence of p on the scattering vector. This result indicates that immobile water molecules are highly localized (less than 1 Å) in the colloidal particles [17]. The time behavior of p, characterized by three different slopes in the p versus $\log(t)$ curve, agrees with the three stage kinetic model already reported in the literature [1]. In fact p

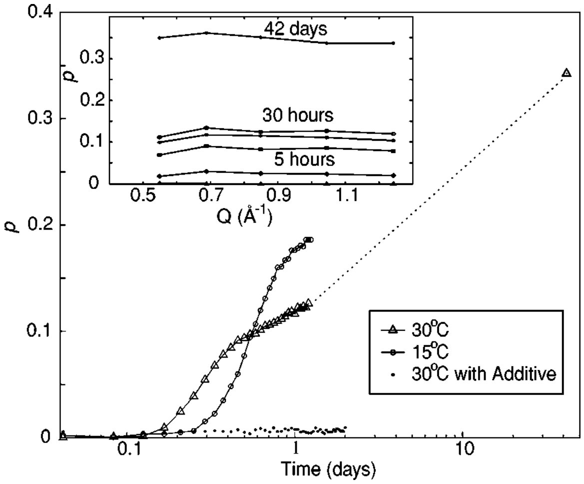

FIG. 2. Time evolution of the fraction of immobile water at two temperatures, 30 °C (△), 15 °C (○) and 30 °C with an additive (·). The inset shows the dependence of p on magnitude of the scattering vector $Q=(4\pi/\lambda)\sin(\theta/2)$, where $\lambda=9$ Å and θ is the scattering angle.

increases only after an induction period that is temperature dependent. The second stage of the kinetic is the so-called acceleration period, and the third stage is called diffusional period. The experiment at 30 °C was repeated using an organo-phosphonate retarder additive (1,5,9,13-tetra-aza-tridecane-1,1',5,9,13,13'-methylen-phosphonic acid, $C_{15}H_{42}N_4O_{18}P_6$, known commercially as Dequest 2086) solubilized in water having a concentration of 2000 ppm. The phosphonate molecules directly interact with the C_3S nuclei [18], slowing down the growth process by increasing the induction period. It can be seen that the effect of the additive is to retard the conversion of glassy water to immobile water by more than 48 h.

Figure 3 depicts the time evolution of the stretch exponent β. According to computer simulation of the SPC/E model of supercooled water [11] $\beta=0.75$ at $Q=1$ Å^{-1} at 47 K below the temperature of maximum density which is 4 °C in real water. In this sense we can call the water in cement paste a glassy water much like a deeply supercooled bulk water. Previous neutron scattering experiments established without any doubt that the translational quasielastic scattering line-shape of room temperature bulk water is Lorenzian, namely, $\beta=1$ (see for example, Ref. [12]). It can be seen that the glassy water becomes ''glassier'' as time goes on, indicating the increasing degree of confinement of water incorporated in the amorphous gel region. The change of slope of β versus log(t) also mirrors roughly the three stage kinetics governing p. Again the additive case shows that the glassy dynamics of water is preserved in time for the duration of observation.

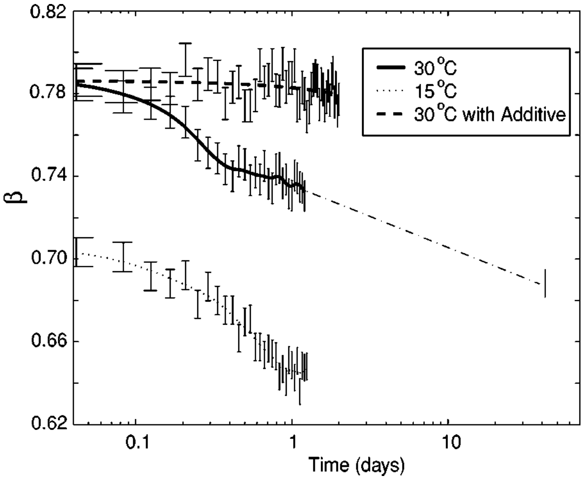

FIG. 3. Time evolution of the stretch exponent β at two temperatures, 30 °C (solid line), 15 °C (dotted line), and 30 °C with an additive (dashed line). Since the dependence of β on Q is weak the average values have been plotted.

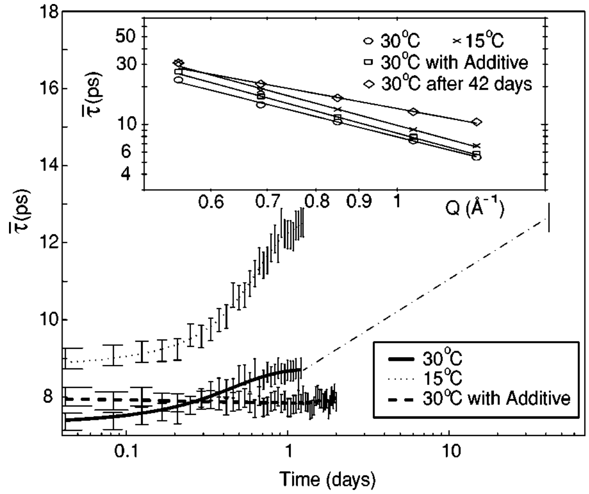

FIG. 4. Time evolution of the average relaxation time, $\bar{\tau}=(\tau/\beta)\Gamma(1/\beta)$ [9], at two temperatures, 30 °C (solid line), 15 °C (dotted line), and 30 °C with an additive (dashed line) obtained using the values at $\bar{Q}=1.0\pm0.10$ Å^{-1}. The inset shows a power law Q-dependence $\bar{\tau}\propto Q^{-\gamma}$, $\gamma=1.7\pm0.1$ for 30 °C (○), $\gamma=1.8\pm0.1$ for 15 °C (×), $\gamma=1.8\pm0.1$ for 30 °C with additive (□), and $\gamma=1.2\pm0.1$ for 30 °C after 42 days (◇).

Figure 4 presents a plot of $\bar{\tau}$ versus log(t). The slowing down of the average structural relaxation time as function of age is obvious. The inset clearly indicates that the average relaxation time has a power law dependence in Q, agreeing with our previous finding in the case of water confined in Vycor glass [9] and analysis of computer molecular dynamics data of a bulk supercooled water [11]. It is observed that as far as γ is concerned, aging for a cement paste has a similar effect as lowering of the temperature in the case of a bulk supercooled water [11] or water in Vycor [9].

Previous neutron scattering studies [19,20] elucidated kinetics of a parameter related to p. However, their numerical values do not agree with ours, possibly due to the poorer resolution of their instruments and to the different model implemented to fit the spectra. Owing to this limitation they were not able to get the information with regard to the line shape and the relaxation time associated with it.

In conclusion the consequence of aging on diffusional dynamics of water in cement paste can be viewed as a process of continuous conversion of the glassy water into the immobile water. The immobilization of water can arise from incorporation of glassy water into interior of colloidal particles, perhaps as a part of crystalline water. The glassy water is the component of water embedded in the amorphous gel-like region, where the effective pore sizes of the gel is decreasing as the cement paste ages [21].

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