

HYDRATION KINETICS OF CEMENT PASTE FOLLOWED BY QUASI-ELASTIC NEUTRON SCATTERING

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A key to improve the properties (strength and durability) of a cement material is to understand and control its hydration.

The major component of ordinary Portland cement is tricalcium silicate (Ca_3SiO_5 or " C_3S "). When water is added to C_3S , the hydration reaction generates calcium-silicate-hydrate ("CSH") and $\text{Ca}(\text{OH})_2$ in a semi-crystalline-amorphous gel form surrounding colloidal cement particles. CSH is the main factor in the setting and hardening of the cement paste.

We have shown that the hydration kinetics of C_3S can be followed quantitatively by quasi-elastic neutron scattering (QENS). Indeed, the incoherent QENS cross-section is extremely sensitive to hydrogen, and therefore reveals as a unique technique to study the translational diffusion of water.

The studied samples consisted of a paste obtained by mixing pure crystalline C_3S powder with water (65% in weight). The effect of a retarder additive ("Dequest 1086") was also studied. QENS experiments were performed on the time-of-flight spectrometer MIBEMOL at LLB, at high energy

resolution (28 μeV), and the quasi-elastic spectra were recorded each hour of the ageing process at 30 and at 15°C. Figure 1 shows the obtained spectra after ageing times ranging from 1 hour to 42 days at 30°C. The analysis of spectra has been realized using a dynamical model (see caption of Fig. 1), taking into account the existence of two types of water : "immobile water" (non detectable at the time-scale of Mibemol, 2 ps $< t <$ 50 ps) which is bound inside the colloidal cement particles, and "glassy water" which is incorporated in the gel region between the colloidal particles (1). At one hour delay time, only a single quasi-elastic component was appreciated, which is attributed to glassy water rather than to free water. An additional elastic peak appears at larger delay times, and its amplitude gradually increases as the cement paste ages. **We interpret the drying process as a transformation from "glassy" to "immobile" water.** The fraction p of immobile water and the relaxation time of "glassy water" can be obtained as a function of ageing time of the cement paste.

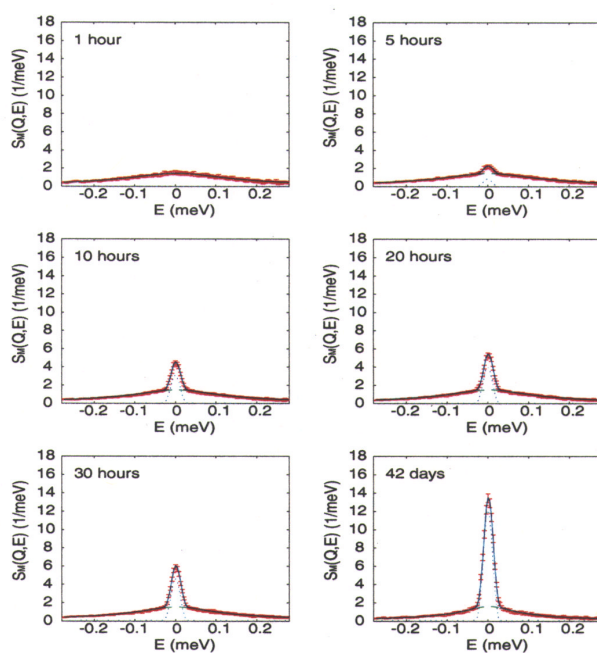


Figure 1. Time evolution of quasi-elastic incoherent neutron scattering spectra of a hydrated cement paste, for $Q=1.04 \text{ \AA}^{-1}$ and $T=30^\circ\text{C}$. The data fitting is made with an elastic peak and the Fourier transform of a stretched exponential characterised by the relaxation time τ and the exponent β .

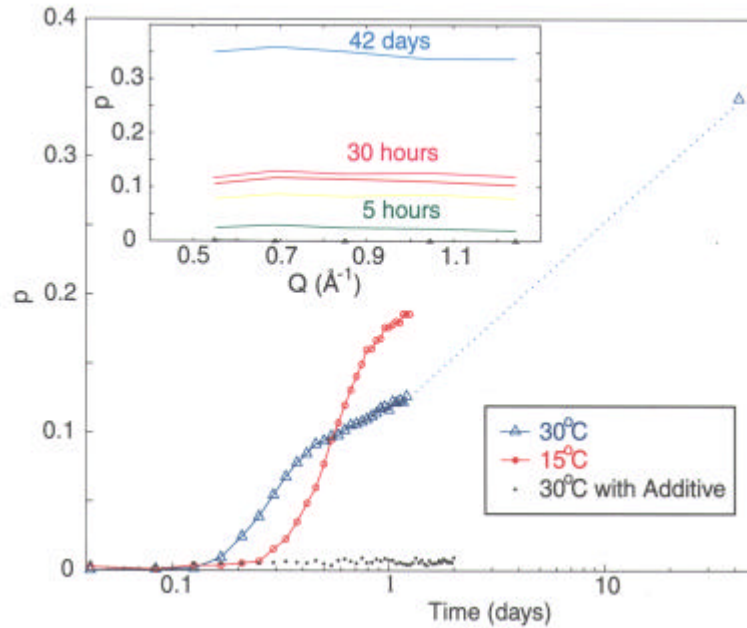


Figure 2. Time evolution of the fraction p of immobile water for different ageing conditions. The inset shows the dependence of p on magnitude of the scattering vector Q for different ageing times at 30°C.

From the evolution of p as a function of time (fig. 2), one could follow the kinetics of the hydration réaction. The dependence of p versus $\log(t)$ is in good agreement with a three-stage (induction, acceleration and diffusional periods) kinetic model reported in the literature (2).

The time evolution of the average relaxation time τ of water is depicted on figure 3. It clearly indicates a slowing down of the relaxation time of the "glassy" water as a function of age, which depends on temperature (4).

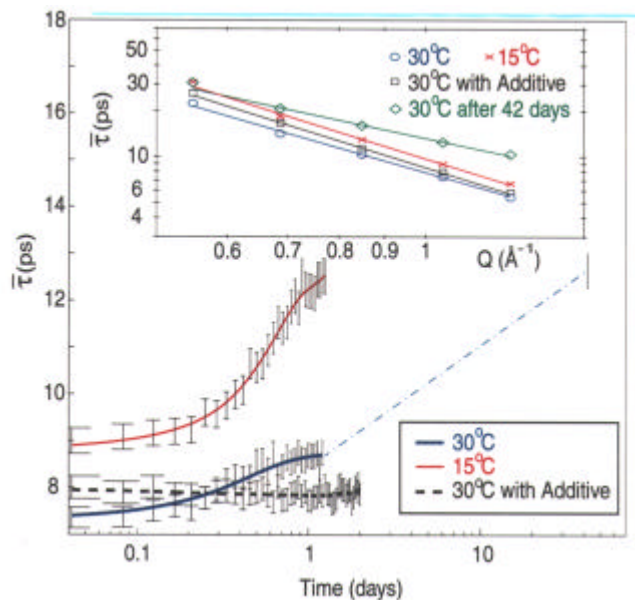


Figure 3. Time evolution of the average relaxation time of vitreous water, τ , obtained for $Q=1.04 \text{ \AA}^{-1}$. The inset shows that τ follows a power-law Q dependence characteristic of "glassy" or super-cooled water (3).

- (1) Jennings, M. H. : *Cem. Conc. Res.* **30**, 101-116 (2000).
- (2) Taylor, H.W.F. : *Cement Chemistry* (Academic Press, London, 1990)
- (3) Bellissent-Funel, M.C., et al. : *Phys. Rev. Lett.* **85**, 3644-3647 (2000).
- (4) Fratini, E., et al. : *Phys. Rev. E* **64**, (2001).

