DETERMINATION OF THE DIFFUSIVE MOTION OF WATER MOLECULES IN HYDRATED CEMENT PASTE BY QUASIELASTIC NEUTRON SCATTERING

C.A. DRAGOLICI [1], R. KAHN [2], F. DRAGOLICI [1]

[1] "Horia-Hulubei" National Institute for Physics and Nuclear Engineering, P.O.Box MG-6, RO-077125 Bucharest-Magurele, Romania, E-mail: adrag@nipne.ro, Email: fdrag@nipne.ro
[2] Laboratoire Léon Brillouin (CEA-CNRS), CEA Saclay, 91191 Gif-sur-Yvette, France, E-mail: kahn@llb.saclay.cea.fr

Abstract. The microscopic motions involved in diffusion of hydrogen containing molecules can be most effectively studied by quasielastic incoherent neutron scattering. In this paper we report the results of our high resolution quasielastic incoherent neutron scattering experiment on the translational dynamics of water molecules contained in the structure of the cement paste. Based on the accumulated data we try to outline the diffusion of water molecules at the microscopic level. The spectra from the confined H_2O are first analyzed in terms of half with at half maximum over the studied Q range to obtain the diffusion constant. Age dependent dynamics of water in hydrated cement paste has been studied as function of integrated intensity.

Key words: cement, neutron scattering, hydration, diffusion.

1. INTRODUCTION

Water dynamics in the cement paste have been the subject of many studies.

It's of great economic importance to control macroscopic proprieties like strength and durability of this material. To achieve this goal an important number of workers have studied the process of cement hydration by a variety of tools but many details remain unclear because of the complexity of the cement system.

Among these, quasielastic neutron scattering (QENS) provides a convenient method to study the status of the water in the cement paste and its important role during the hydration process. It is well known from literature [1], that water in the cement paste is continuously active and produces modifications inside the material even long time after mixing. When anhydrous powder of ordinary Portland cement (OPC) is mixed with water, the overall hydration chemical reaction generates calcium silicate hydrate (C-S-H) in a gel form. The cement paste, contain pore water and hydration products very rich in hydrogen atoms making this material

desirable for examination by means of neutrons. Quasielastic neutron scattering measurements can directly quantify the ratio of chemically bound water in the sample [2]. Usually, the hydration process is considered in terms of early, middle and late periods of hydration. Appropriate divisions of these hydration periods are approximately at 3 and after 24 hours after mixing [1]. QENS do not suffer any limitation to be applied in the study of slow diffusion limited processes on a long time scale. The obtained data can be expressed as a free water index (FWI) or bound water index (BWI) [3] or, can be modelled as "glassy water" [4] or "interfacial water" [5]. C-S-H gel of the cement paste has a layer structure, and that, together with a pore solution, it forms a rigid gel in which the pores varies in size from macroscopic to enlarged interlayer spaces of nanometre dimensions. The most highly hydrated state is that existing in a saturated paste i.e. one in which the pores are totally filled with water. Chemically bound water is most reasonably defined as included in the interlayer spaces or small pores, or more firmly bound, but not that present in large pores. The distinction between interlayer space and micropores is not sharp. The water in a hydrated cement paste can be defined as non-evaporable water, chemically bound water and water required to the formation of the hydration products in a saturated paste. Water retained, known as non-evaporable water, has often been wrongly identified with chemically bound water.

It excludes much of the interlayer water in C-S-H. It is often used as a measure of the fraction of the cement that has reacted, but can only be approximate in this respect, because the clinker phases react at different rates and yield products containing different amounts of non-evaporable water. Fully hydrated cement pastes typically contain about 23% of non-evaporable water, referred to the ignited mass.

Many aspects of the cement hydration process remain unexplained. It's still unclear the real stoichiometry of the C-S-H gel, which changes during the reaction and affect the microstructure of the sample.

2. EXPERIMENT

The neutron scattering experiment was performed at the Laboratoire Léon Brillouin (LLB) in Saclay, France, using the high resolution time of flight spectrometer MIBEMOL. In order to achieve a good energy resolution (28 μeV) in the investigated Q range, an incident neutron wave length of 9 Å was selected.

Here $Q=(4\pi/\lambda)\sin(\theta/2)$ represent the magnitude of wave-vector momentum transfer in the scattering process, λ is the wavelength of the incident neutrons and θ is the scattering angle. In this way we were able to cover a Q range between 0.21 Å^{-1} until 1.28 Å^{-1}. The scattered energy was measured by time of flight of the scattered neutrons over the 3.58 m of flight path between the sample and the 71 detectors. The measured spectra were reduced by regrouping the 71 detectors in 10 (standard grouping) and normalized to the monitor. Corrections were applied by

subtraction of the dry cement powder spectra and standardized to the spectra obtained with a thin vanadium plate. The conversion to differential scattering cross section was performed using LLB standard computer programs. The typical data collection time for this experiment was about 6 hours. An ordinary Portland cement powder having the specific Blaine fineness of 3 200 cm^2/g and the density of 3.05 g/cm^3 has been used in performance of our experiment. The samples for this study were made by mixing the OPC with de-ionized water at 0.4 water-to-cement ratio by mass.

After mixing, the obtained cement paste was poured in the specimen holder.

The specimen holder is a steel ring frame having the inner diameter of about 18 mm and the thickness of 0.5 mm. The ring frame is glued to a thin disk of pure nuclear grade aluminium having the same dimensions with the ring frame. After the cement paste was carefully poured in the specimen holder, filling evenly the whole space, a second thin aluminium disk was glued to the frame ring creating a sealed compact disk. Because the pore water in the cement paste is strongly basic even within a few minutes after mixing, the use of Al for the specimen holder is not suitable. The formed cement paste is extremely corrosive and quickly attacks the aluminium forming pits of corrosion products at the interface which could affect the reaction rates. To avoid this, the Al disks were coated with a thin film layer of about 1 μm of Ti. The coating was performed by evaporation under high vacuum. The Ti layer protects very well the Al disks against any aggression from the cement paste. No corrosion, reaction products or pits were noticed during hydration reaction or even at long times, after one year or more. The specimen holder and the cement paste form a thin cell that makes multiple scattering corrections not necessary.

3. RESULTS AND DISCUSSIONS

In a quasielastic experiment, usually the measured intensity is given by a convolution of the scattering function $S(Q,\omega)$ and the the resolution function $R(Q,\omega)$ of the spectrometer [6]. This can be written in the following form:

$$I(Q,\omega) = S(Q,\omega) \otimes R(Q,\omega). \tag{1}$$

The energy transfer in the scattering process is $\hbar\omega = E_0 - E$, were E_0 is the energy of the monochromated incident neutrons and E that of scattered neutrons.

As described in [7] the diffusion constant (D) is given by:

$$D = \frac{\langle l^2 \rangle}{6\tau_0}, \tag{2}$$

were l is the distance covered in the time τ_0.

Taking into account the above equation, the dynamic structure factor has the following expression:

$$S_S\left(Q,\omega\right) = \frac{1}{\pi}\frac{DQ^2}{\omega^2+(DQ^2)^2}\ .$$ (3)

The full with at half maximum (*hwhm*) of this function is $2DQ^2$, and if is measured at a number of fixed values of Q, a graphical representation of the with as a function of Q should be a straight line of slope $2D$.

We followed the evolution of the samples in runs of every 6 hours from their set up (a few minutes after mixing) until 31 days, at a constant temperature of 25ºC. To study the time evolution of translational dynamics of hydration water in the curing cement paste, the best fit to the following analytic form of the integrated intensity:

$$I_{tot}=\left[I_{ela}\times\Delta\left(n-n_0\right)+I_{lor}\times\frac{\Gamma}{\Gamma^2+\omega^2}\right],$$ (3)

convoluted with the resolution function is obtained.

Here I_{ela} represent the integrated intensity of the elastic peak, Δ is the channel with, n is the channel number, n_0 is the channel number for zero energy transfer, I_{lor} is the integrated intensity of the quasielastic lorentzian peak, Γ is the half with at half maximum (*hwhm*) of the quasielastic peak and ω is the energy transfer. In this manner, for each run six coefficients are obtained plus two coefficients for the "inclined background" witch take in account all the inelastic (phonons) and large quasielastic (rotation of H_2O) components.

The fit is a good approximation of the obtained data. First result is shown in Fig. 1, and it gives the Q dependence of the fitted *hwhm* for 7 runs, after first 6 hours, between 6 and 12 hours, between 12 and 18 hours, between 18 and 24 hours, between 24 and 30 hours, after 30 to 36 hours and after 31 days.

Clearly it appears that even 31 days after sample preparation, long distance translational movement still occurs and the diffusion constant D (at small $Q < 0.5$ Å^{-1}) varies a little or not at all. A linear fit gives $D = 3.5 \times 10^{-5}$ cm^2/s.

The second result represented in Fig. 2 show that for the fitted coefficients there is not Q dependence either of the integrated intensity of the elastic component, nor of the integrated intensity of the quassielastic component.
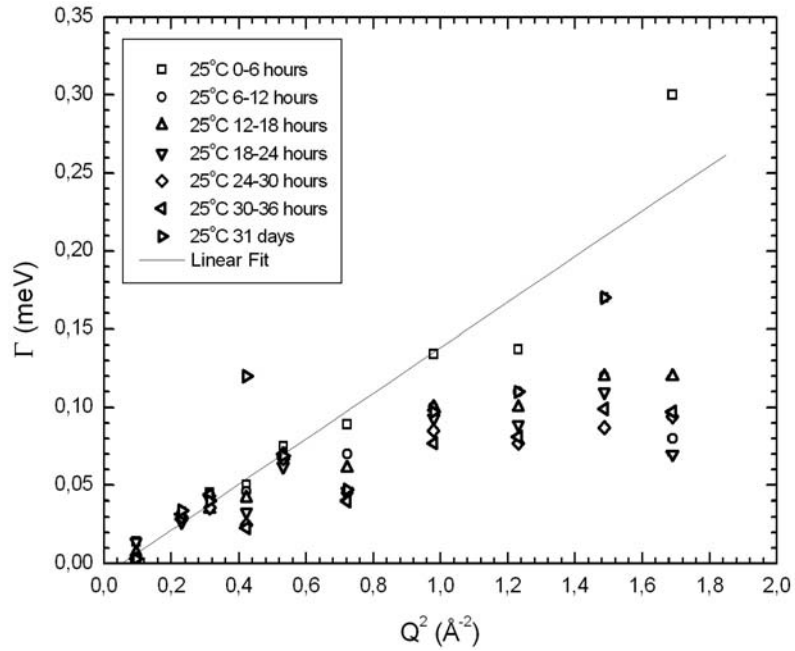
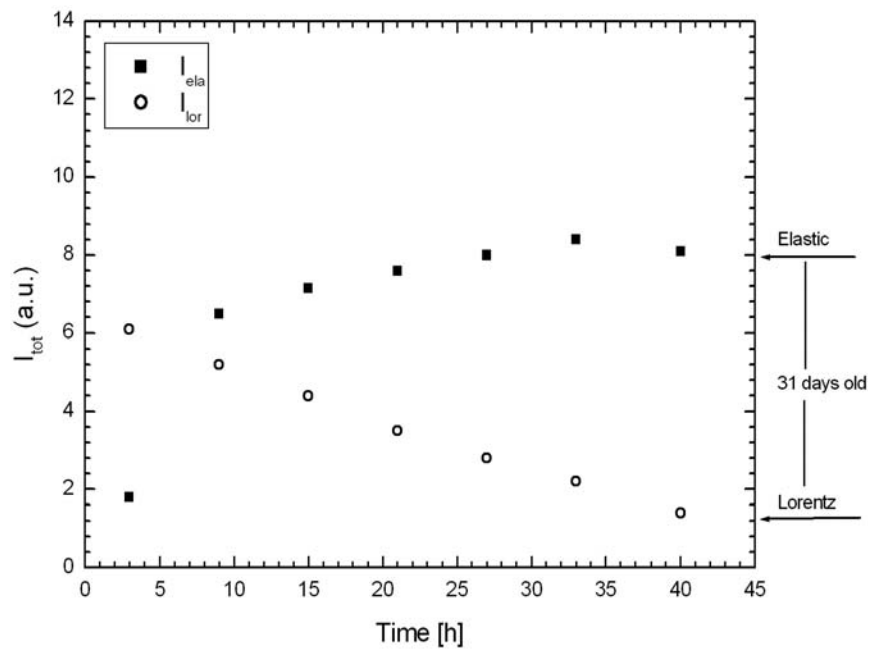Fig. 1 – Linear fit of the data gives the diffusion constant *D*.

Fig. 2 – The integrated intensity of every component.

Here, the intensity (the mean value over Q) is represented as a function of the elapsed time since the sample preparation. It appears that there is a clear decrease of the quasielastic intensity and an increase of the elastic component. This means that, if there is no variation of the diffusion constant, the number of mobile H_2O molecules decrease with time. As the 31 days old sample still present a quasielastic component, at that time, we can say that after a "rapid decrease" of the number of mobile water molecules, there remains a population of still mobile molecules in a metastable state (pore water, interlayer water or interfacial water) that is trapped for ever in the material. This water is not like bound water and is different from bulk water. If is detected at low temperatures is called supercooled water.

4. CONCLUSIONS

The obtained results of the diffusion coefficient are in good agreement with the theory [7] and with the achievements of other workers [8-9]. Also, the interpretation of the data by the mean of integrated intensity gives us a complementary picture of translational diffusion of water molecules in the hydrated cement paste. The consequence of aging on diffusion dynamics of water in cement paste can be viewed as a process of continuous conversion of the free water into the immobile water. The immobilization of water can arise from incorporation of free water into interior of colloidal particles, saturating different types of phases or as a part of crystalline water. This water is embedded in the amorphous gel-like region, where the effective pore sizes of the gel is decreasing as the cement ages. On the other hand, water molecules dispersed in the C-S-H gel matrix have a slow dynamics significantly different from that of bulk water at the same temperature. As cement ages, the water in C-S-H gel penetrates continuously into the colloidal particles and thus increases the immobile fraction except some amount characterized by a quasi-free state.

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