Surface Induced Spin-Lattice Relaxation of Water in Tricalcium Silicate Gels

F. Milia, Y. Bakopoulos
N.R.C. "Demokritos", Institute of Material Sciences 153 10 Ag. Paraskevi Attikis, Athens, Greece

Lj. Miljkovic
Department of Physics, Faculty of Sciences University of Nis, Yugoslavia

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The water proton spin-lattice relaxation time and recovery function of exchangeable water was measured in tricalcium silicate (C_3S) gels. The measurements were carried out as a function of the hydration time and grain size. Results show that the hydration of (C_3S) is a two stage process. A model is developped.

I. Introduction

The interaction of water with the surface in porous systems is of interest for many applications, among others also for cement hardening. It has been generally shown that the fluid in a porous solid will have a shorter spin-lattice relaxation time T_1 than the corresponding bulk fluid. The shortening of the water T_1 is assumed to depend on the ratio between the pore surface area and pore volume. The above effect has been recently used for the study of cement hardening [1–5].

In order to check this effect quantitatively we decided to measure the water proton spin-lattice relaxation time T_1 and recovery function of exchangeable water in tricalcium silicate (C_3S) gels as a function of the hydration time and grain size. The pore size and time development of the internal surface of (C_3S) have been studied before [4, 5].

II. Experimental

All experiments have been performed with samples sealed in glass tubes so that the water/(C_3S) ratio – which was 0.5 – did not change during the measurement. Two grain size distributions P_1 (mesh number between 53 μ–105 μ) and P_2 (mesh number ≤ 53 μ) centered around 70 μ and 30 μ, respectively, have been used. The (C_3S) samples contained about 63 μg of Fe per g. The spin-lattice relaxation times have been measured by a $90°$-τ-$90°$ pulse sequence technique at a Larmor frequency of 32 MHz.

III. Results and Discussion

Whereas the proton magnetization recovery in (C_3S) is mono-exponential in the early stages of hydration, it becomes non-exponential at long enough hydration times. The time evolution of the T_1 is shown in Fig. 1 and the time evolution of the proton magnetization recovery in Figure 2.

Similarly as in ordinary Portland cement (OPC) samples [1, 6, 7], T_1 is nearly constant and of the order of 400–500 ms in the dormant period which extends up to 3 hrs after mixing. T_1 rapidly decreases in the period between 4 hrs and 10 hrs, shows a small maximum and then continues to decrease slowly with increasing hydration time down to 4 ms. T_1 of the fine (C_3S) is 20–30% shorter than T_1 of the more coarsely grained (C_3S). After 800–900 hrs the magnetization recovery is a stretched exponential plus a component with a larger T_1. The onset of the stretched exponential behaviour thus takes place at larger hydration times than in OPC samples [5].

The above results must be compared with scanning electron microscopy studies [8], which show that the hydration of (C_3S) is a two-stage process involving (i) the formation of the initial coating of calcium silicate hydrate gel around the anhydrous grain and (ii) the growth of hollow or tubular "silica garden" fibrils, the interlocking of which results in a finite compressive

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Reprint requests to Dr. F. Milia, Institute of Material Sciences, N.R.C. "Demokritos", 153 10 Ag. Paraskevi Attikis, Athen, Greece.

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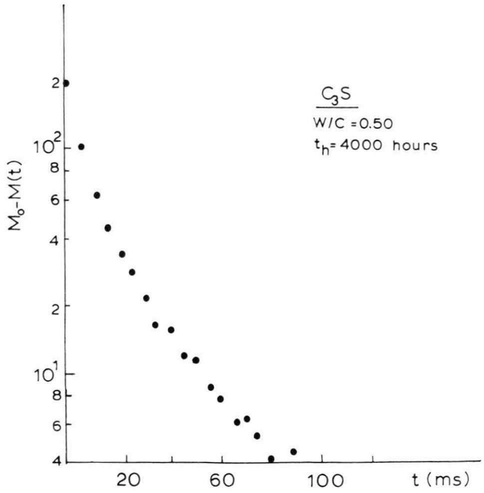

Fig. 1. Proton magnetization relaxation recovery of exchangeable water in (C_3S) (grain size distribution P_1).

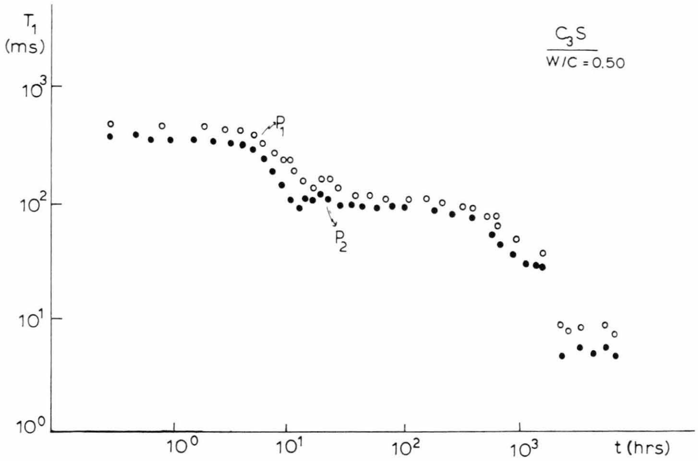

Fig. 2. Proton T_1 of exchangeable water as a function of time in (C_3S) with a) grain size distribution P_1, and b) grain size distribution P_2.

strength of the material. The growth of the "silica tubes" involves osmosis through the initial gelatinous coating and level ruptures of the semi-permeable gelatinous membrane.

The "dormant" period can be correlated with the formation of the gel coating of the grains, and the fast decrease in T_1 with the formation of the "silica gardens" and the resulting increase in the pore surface to volume ratio.

The T_1 data can be described by the following "model": Within a given pore there is a fast exchange between molecules in the free "bulk" water and molecules "bonded" to the surface resulting in a unique T_1 characterizing protons in different environments.

$$1/T_1=(1/T_1)_b\,\eta+(1/T_1)_f\,(1-\eta), \tag{1}$$

where $\eta=\tau_b/(\tau_b+\tau_f)$ is proportional to the surface to volume ratio. τ_b is the time the molecules spend bonded to the surface and τ_f the time the molecules spend in the "free" bulk water.

If the relaxation time of the gel is shorter than that of the bonded water molecules, $T_{1g}<T_{1b}$, the molecules bonded to the surface relax via cross-relaxation to the gel protons.

The cross-relaxation time $\tau_{\text{cross}}=\tau_{bg}$ is of the order of $(M_{2\text{gel-surf.pr.}})^{-1/2}\simeq 10^{-4}$ sec.

In such a case one has for the two components of the proton magnetization:

$$\frac{d}{dt}M_b=-\frac{1}{T_{1b}}(M_b-M_{b\infty})-\frac{1}{\tau_{bg}}M_b+\frac{1}{\tau_{gb}}M_g, \tag{2}$$

$$\frac{d}{dt}M_g=-\frac{1}{T_{1g}}(M_g-M_{g\infty})-\frac{1}{\tau_{gb}}M_g+\frac{1}{\tau_{bg}}M_b, \tag{3}$$

where the equilibrium values $M_{g\infty}$ and $M_{b\infty}$ and exchange rates τ_{bg} and τ_{gb} are related by

$$\tau_{bg}\,M_{b\infty}=\tau_{gb}\,M_{g\infty}\,. \tag{4}$$

Under certain conditions ($\tau_{gb}^{-1}\ll T_{1g}^{-1}$, $T_{1b}^{-1}\ll\tau_{bg}^{-1}$, $\tau_{gb}^{-1}\ll\tau_{bg}^{-1}$) one finds

$$m_b=A\exp\{-t/T_{1g}\}+B\exp\{-t/\tau_{bg}\} \tag{5a}$$

and

$$m_g=m_{g0}\exp\{-t/T_{1g}\}\,. \tag{5b}$$

Here

$$m_i=(M_i-M_{i\infty})/M_{i\infty}\,. \qquad i=b,\,g \tag{5c}$$

is the reduced nuclear magnetization along the magnetic field, T_{1g} is the relaxation time of the gel and τ_{bg} is the cross-relaxation time between the gel and the bonded water molecules.

IV. Conclusion

In the above case we thus find a biexponential magnetization recovery for the water proton within a given pore.

Since exchange of water between different pores becomes slow at larger stages of hydration, one gets a distribution of T_1^{-1} values $P(T_1^{-1})$ reflecting the pore size distribution $g(\xi)$. Finally one has [9]

$$\frac{M_0 - M(t)}{M_0} = \int P(T_1^{-1})\, \mathrm{e}^{-t/T_1}\, \mathrm{d}(T_1^{-1}), \tag{6}$$

where

$$P(T_1^{-1})\, \mathrm{d}(T_1^{-1}) = g(\xi)\, \mathrm{d}\xi \tag{7}$$

and ξ is the reduced size of the pore.

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