A Study of Portland Cement Hydration by Paramagnetic Iron Suppression of Proton Magnetic Resonance

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The dynamics of the hydration of a white cement with negligible iron content and of Portland cement with a considerable amount of iron has been studied by proton magnetic resonance. The presence of iron in Portland cement results in the protons close to the free electron spins of iron being out of resonance and their signal being suppressed. The evolution in time of the percentage of protons out of resonance in a Portland cement and the growth of the solid component have been determined as a function of hydration time.

I. Introduction

Nuclear magnetic resonance (NMR) has often been used to study the hydration of various systems [1–3], particularly of cements [4–7]. The effects of paramagnetic iron suppression of the proton NMR in cements, however, have not yet been considered. A comparative NMR study of a white cement (negligible iron content) and a Portland cement (containing Fe_2O_3) was therefore undertaken.

The total amount of water in a cement paste at a given hydration time can be monitored by weighing the sample. NMR determinations of the total proton magnetization through measurement of the Free Induction Decay (FID) should yield the amount of "liquid like" water present at a given hydration time. However, paramagnetic centres in the sample may make some of the protons unobservable. NMR techniques such as FID measurements and spin echo measurements using variations of the Carr-Purcell (CP) pulse sequences, can also give information on the spin-spin relaxation times, T_2, of the protons in the cements. These time constants can be used to characterize the environment of the protons (see Table 1) for some examples). In fact, the CP technique can also be used to measure directly the fraction of water which exists in a "liquid-like" environment (i.e., with $T_2 > 1$ ms) at a given hydration time.

Table 1. NMR relaxation times for protons in various materials [4].

State of water	T_2 (μs)
Bulk water	2 500 000
Physically absorbed water	1000 – 3000
Zeolitic water	100 – 1000
Interlayer-clay water	100 – 1000
Ice	7
Hydrogen in calcium hydroxide	4 – 7

II. Experiment

The dry type 10 normal Portland and white cements with compositions given in Table 2, were obtained from Canada Cement Lafarge Ltd. (Belleville, Ontario). Doubly distilled water was mixed with the dry cement powder in the ratio 0.42 g water/g dry cement. The cement paste was then put into 8 mm OD glass NMR tubes. To simulate hydration under normal conditions the sample tubes were left open for the duration of the experiments. The NMR measurements were performed with a Bruker SXP pulse spectrometer (Bruker Instruments Inc., Billerica Mass.) operating at a frequency of 40 MHz. All experiments were performed at 20 °C.

The spin-spin relaxation measurements were made using two techniques. The FID was measured

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Table 2. Oxide composition of Lafarge Canada Portland No. 10 and white cement powders [13].

Oxide	Weight percent	
	Portland No. 10	White cement
CaO	63.38	65.65
SiO_2	20.94	23.12
Al_2O_3	4.60	4.74
SO_3	3.89	3.37
MgO	2.33	0.88
Fe_2O_3	2.05	0.03
K_2O	1.06	0.08
L.O.I.	1.05	1.69
Free CaO	0.60	0.07
Na_2O	0.52	0.04
TiO_2	0.17	0.21
SrO	0.14	0.04
P_2O_5	0.12	0.08

directly after a 90° r.f. pulse; this gave T_2 of the solid. The FID was recorded at 110 positions along the decay. Carr-Purcell Meiboom-Gill (CPMG) modified spin-echo experiments [8] were also performed to determine T_2 and the magnetization fraction of protons in the liquid-like environment, with $T_2 > 1$ ms. Typically 100 signals were averaged using a Biomation 805 transient waveform recorder (Biomation; Cupertina, CA). The true equilibrium magnetization for the samples was determined by fitting the FID and extrapolating back to zero time immediately following the r.f. pulse. The magnetization fraction for the liquid-like spins was obtained from the $t = 0$ extrapolation of the spin echo decay normalized to the total magnetization as determined by the total FID, recorded with the first 90° pulse of the CPMG sequence. The FID and CPMG experiments were performed at various hydration times. The weight loss of the samples was also recorded. The observed total magnetizations and weights of the samples during hydration were normalized to those measured at the start of hydration; the magnetization of the liquid-like protons was normalized to the total magnetization determined from the FID experiments.

III. Results

The weight loss, and the magnetization loss from the FID and CPMG measurements, for the Portland # 10 cement and the white cement as they hardened, are shown in Figs. 1 and 2, respectively. In Fig. 3 the growth of the solid component of these cements as well as the evolution in time of the percentage of protons out of resonance in the Portland cement due to paramagnetic iron suppression is depicted. In Fig. 4 shows the hydration time-dependence of the T_2 for the two samples.

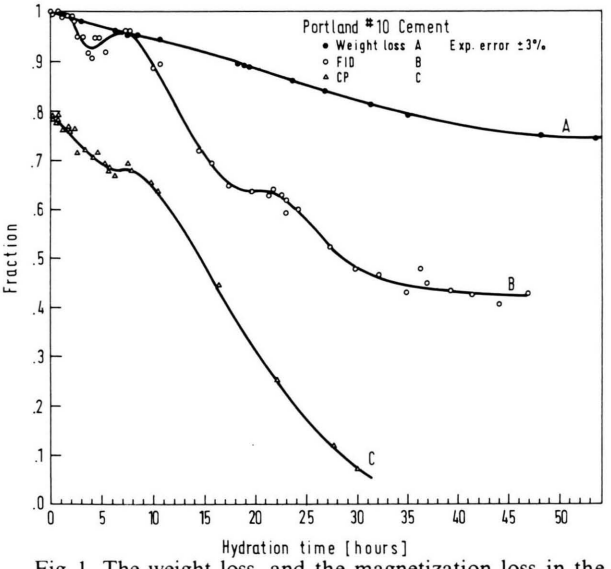

Fig. 1. The weight loss, and the magnetization loss in the FID and CPMG measurements for Portland # 10 cement.

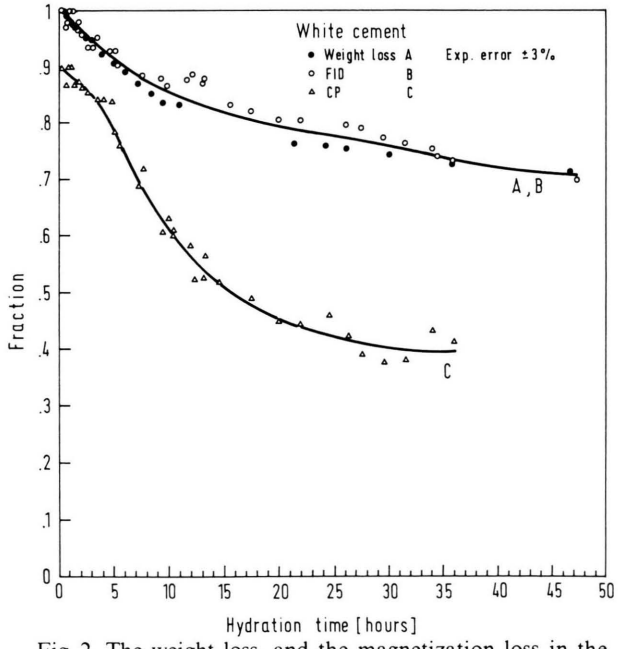

Fig. 2. The weight loss, and the magnetization loss in the FID and CPMG measurements for white cement.

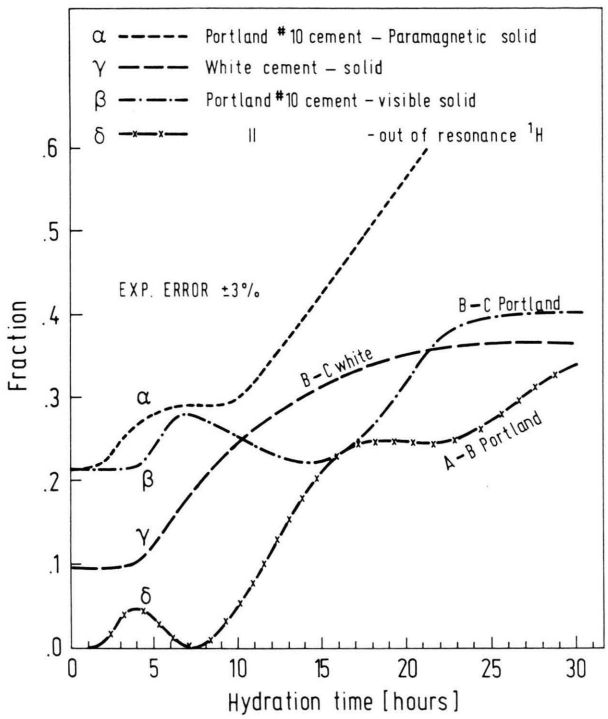

Fig. 3. Fractions of the proton magnetization of the solid environments of the cements and fraction of protons out of resonance in the Portland cement sample vs. hydration time. The curves A, B, and C are shown in Figs. 1 and 2.

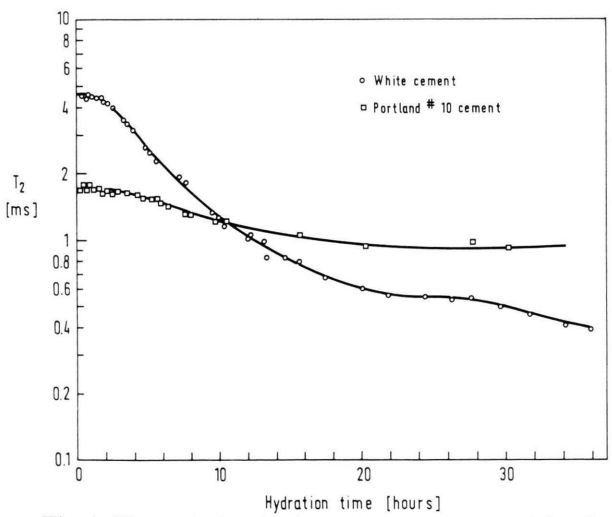

Fig. 4. The evolution in time of T_2 as measured by the CP method. The solid T_2, which is on the order of 10 μs, is essentially constant and is not shown.

IV. Discussion

Prior to the addition of water, both the Portland No. 10 and white cement clinkers were found to contain $(4 \pm 3)\%$ water by mass in a solid-like environment, and no water in a liquid-like environment. A few minutes after the beginning of the hydration (time $t = 0$) the percentage of protons in the solid milieu seemed to be $(20\% \pm 3\%)$ for the Portland cement and $(10\% \pm 3\%)$ for the white cement (cf. Figure 3). This difference, however, is to be explained by the presence of iron in the Portland cement since any protons in close proximity with iron free electron spins in a solid or liquid matrix will not be observed. Evidently up to $\sim 10\%$ of the protons in the Portland cement experience such an effect at time $t \sim 0$.

As hydration progresses, more and more water becomes associated with rigid environments as the crystallization of gel compounds increases (Fig. 3, curves α and γ). Note that this growth appears to be negligible until after ~ 1 h in Portland and ~ 3 h in white cement. In Portland cement a dormant period is apparent between 5 and 9 h hydration time. Apart from these divergences the solid growth appears to be smooth in both cases, showing no structure. In white cement at 30 h hydration time the solid component makes up $\sim 35\%$ of the total magnetization while the "visible solid" component of Portland cement makes up $\sim 40\%$.

The samples were kept in open tubes with a free contact area of $\sim \frac{1}{2}$ cm^2 and, therefore, water was able to evaporate during the hardening process. This is evident from the weight-loss curves of Figs. 1 and 2. The rate of water loss from the white cement sample was somewhat greater than that of the Portland during the first 30 h, particularly during the first 10 h. This implies that the amount of water available for evaporation in Portland cement decreased more rapidly with time than that in white cement, as supported by the greater rate of structural development in Portland cement indicated in Figure 3. The amount of water loss in both cements appears to approach $\sim 30\%$ at large hydration times.

The loss of signal from protons in the liquid-like environment in Portland cement (Fig. 1, curve C) is extremely different from the corresponding loss in white cement (Fig. 2, curve C). For example, at 30 h hydration time the liquid-like proton signal in Portland cement is only about 7% of the initial proton

NMR signal. On the other hand the liquid water signal in white cement amounts to still 40% at 30 h. The difference between the liquid water signals from these two samples is the result of the strong magnetic interaction [9] between an Fe atom's electron spin and the water in its vicinity. As a result of this interaction, the water proton Larmor frequency becomes vastly different from the Proton Larmor frequency in the external field H_0 ($\omega_0 = \gamma H_0$ where γ is the proton gyromagnetic ratio); it is shifted considerably into the wings of the NMR absorption spectrum. Therefore some of this water is not even excited by the r.f. irradiation at ω_0. However, because a spread in this frequency occurs as a result of the short (high power) 90° pulses used, some of this paramagnetically suppressed water may still be excited. The FID of such water though would occur in a fraction of a microsecond, and would thus be lost in the dead time ($\sim 8\,\mu s$) of the receiver of the NMR spectrometer. Therefore, the paramagnetically suppressed water is simply not observed.

As a result of the extreme loss of this liquid water proton NMR signal (Fig. 1, curve C), the Portland cement paste exhibits a dramatically different total proton signal intensity (Fig. 1, curve B). The difference between these two curves (Fig. 3, curve β) represents the apparent relative intensity of the NMR signal of protons in solid-like environments. This function shows structure with a peak at 7 h, and an apparent acceleration of the rate of growth of the solid-like phase between 14 and 18 h hydration time. The unusual character of this function reflects the transfer of Fe between the solid-like and liquid-like environments. The percentage of protons that are out of resonance and hence unobservable is contingent primarily upon the amount of iron in the liquid-like milieu, and is depicted in Fig. 3, curve δ. The peak in this curve at 4 h hydration time indicates that between approximately 4 and 7 h, more water was finding its way into a solid matrix of relatively low iron content than iron was dissolving into solution. During this period therefore, relatively rapid hydration of e.g. the calcium silicate phases must occur in an environment isolated from iron.

This may correspond to the so-called stage of inter-granular fibrillar growth [10] during which finger-like protuberances of both iron-free and iron-containing hydrates [11] crystallize on the surface of the cement grains.

As there are no paramagnetic impurities in white cement, its solid proton component (Fig. 3, curve γ) reflects directly the amount of solid present at a given time. The growth of this component is a monotonous function of time, depicting the fastest rate between 5 and 10 h, and apparent cessation of growth at about 26 h hydration time.

The time-evolutions of T_2 of the two samples differ markedly (Figure 4). The T_2 of white cement decreases gradually from about 5 ms at $t \approx 0$ to about 0.5 ms at 30 h hydration time. Its shape is correlative of that of the solid proton growth curve of Fig. 3 (curve γ) during this time. That T_2 is only 5 ms at $t \sim 0$ indicates that there is no bulk water present in the white cement paste, since bulk water has a T_2 on the order of a second. The water is however still in a liquid-like state but with the correlation times for translational and rotational diffusion longer by about three orders of magnitude, as the relaxation rate for water is proportional to the correlation time.

V. Conclusions

Paramagnetic iron suppression of proton magnetic resonance augments the capacity of NMR to non-invasively monitor the evolution in time of the constituent solid and liquid components of hydrating cement pastes. The effects of paramagnetic impurities on the results of NMR studies of cement are profound and have hitherto not been observed. The dynamics of hydration of the two cements studied as seen by paramagnetically suppressed proton NMR differed markedly. Some implications of these differences have been discussed in the text. Paramagnetic iron suppression of proton magnetic resonane can be a useful tool in enhancing the NMR resolution of heterogeneous systems and in NMR imaging. In order to better investigate the subtleties of cement hydration a comparative study of white and Portland cements by NMR methods [12] is currently underway.

Acknowledgements

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