Probing Water Phases in Cement Blends using [1]H Nuclear Magnetic Resonance Relaxometry

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Introduction

The nuclear industry uses blended cement systems to encapsulate low and intermediate level nuclear wastes. These systems use high substitution of ordinary Portland cement (OPC) with ground granulated Blast Furnace Slag (BFS) to reduce heat output and improve immobilisation capability[1]. Some nuclear wastes include metals such as aluminium and Magnox, which corrode in the high pH environment of the cement blend matrices and depend on free water to drive the corrosion. In the long term, the volume increase due to the formation of corrosion products creates mechanical stress in the cementing matrix which could reduce its immobilisation capabilities over time.

This project aims to identify and quantify the water phases present in hardened cement blends in the long term. [1]H Nuclear Magnetic Resonance (NMR) relaxometry is used for this study. This technique is non-invasive (no need to introduce a molecular dye as ^{1}H from liquid water present within the cement microstructure is used as the active NMR probe), non-destructive and multiple measurements can be undertaken over time on the same specimen.

Materials

OPC blends containing high replacement levels of BFS were prepared by varying either the BFS to OPC weight ratio (BFS:OPC), the curing temperature or the water to solid weight ratio (w:s). Pastes were poured into 1 cm OD diameter glass test tubes, vibrated to remove entrapped air before sealing and then rotated horizontally for about 12 hours at room temperature to reduce water bleeding. NMR data have been recorded for samples cured for 1, 3, 7, 14, 28 and 90 days. Results obtained from different cement blends are compared to a reference sample prepared as follow: BFS:OPC of 3:1, w:s of 0.37 and cured at 20ºC. Samples discussed here are listed in Table 1.

Table 1: sample identification and composition.

Sample Name	Paste Composition	Water to Solid Ratio	Water Content Vol.%	Curing Temperature
B1	BFS:OPC 9:1	0.37	52	20ºC
B2	BFS:OPC 3:1	0.32	49	20ºC
B3 reference	BFS:OPC 3:1	0.37	52	20ºC
B4	BFS:OPC 3:1	0.37	52	60ºC

Experimental
Carr-Purcell-Meiboom-Gill (CPMG) and Free Induction Decay (FID) signals were recorded on a permanent magnet spectrometer (0.5 T tuned to 20 MHz) from Resonance Instruments Ltd. The CPMG sequence is used to refocus magnetisation dephasing as a result of local field inhomogeneities due to variations in magnetic susceptibility. The signal is additionally attenuated by water diffusion through pore space field gradients. Hence, measurements at several pulse gaps (τ = 25 – 200 μs) have been made. Relaxation times presented here are obtained by extrapolation of data to zero. Bi-exponential decays were used to model CPMG signals, the primary objective being to identify capillary water and calcium silicate hydrate (C-S-H) gel water. Amplitudes of the bi-exponential decays were used to estimate their relative content. Relative content of chemically bound water was estimated by subtracting the CPMG amplitudes from the FID amplitudes[2]. Water content (vol.%) was obtained by normalisation using a standard (test tube filled with water). Values of water content displays in figures are averages (over up to four sample repeats). Error bars in figures represent the standard deviations calculated from measurements made on sample repeats.

Magnetisation relaxation mechanisms are particularly efficient at the liquid/surface interfaces[3,4]. Based on the fast exchange model[3,4], it is assumed that water molecules are able to probe fully the pore microstructure during the time scale of an NMR pulse sequence. In this condition, NMR measurements give relaxation time averages based on the volume fraction of water molecules at the solid interfaces and in the bulk liquid following: $T_2^{obs} = \dfrac{V}{\rho S}$ where T_2^{obs} refers to the spin-spin relaxation times, V (Volume) and S (Surface) refer to the pore space accessible to ^{1}H water molecules and ρ refers to surface relaxivity. Any changes in blend composition will affect ρ and consequently the values of the relaxation times. If two populations of pores (capillary and C-S-H gel for example) filled with water coexist in a cementitious material then, bi-modal distribution of relaxation times is, at least, expected showing two marked main components. Here, T_2^{cap} (longest component) and T_2^{gel} (shortest component) are determined experimentally from the bi-exponential decays used to model the CPMG signal.

Results
Variations in water volume content as a function of ageing for a selection of cement blend systems are shown in Figure 1. For all samples, a sharp decrease in the amount of capillary water is detected during the first week as shown in Figure 1.a. Over time, further decrease is detected in samples B2 and B3 initially prepared using respectively a w:s of 0.32 and 0.37. At the same time, the amount of capillary water detected in B1 (high BFS content) reaches a plateau at about 13 vol.%. Either a lower amount of water is required for the hydration of blends prepared using a high substitution level of BFS or a lower degree of hydration is reached in this system. In contrast, in the case of B4, content in capillary water reaches a plateau at about only 4 vol.%, the water having reacted more quickly. As the curing temperature is higher, an increased amount of water was probably consumed by the OPC hydration reaction.
The amount of water trapped between layers of C-S-H gel is shown in Figure 1.b as a function of ageing. The amount of gel water is found to increase sharply over the first week for all samples. Similar variations are observed for all the samples over time, also, a greater amount of gel water is detected in sample B4 at all times. A weak decrease of gel water is observed after 14 days for all samples. This may indicate that some amount of gel water is consumed by the cement hydration reaction. Using the values of capillary and gel water contained in samples B1, B2, B3 and B4, the "hydrated" porosity after 90 days can be estimated at respectively 38, 29.7, 32.2 and 32.8 vol.%.
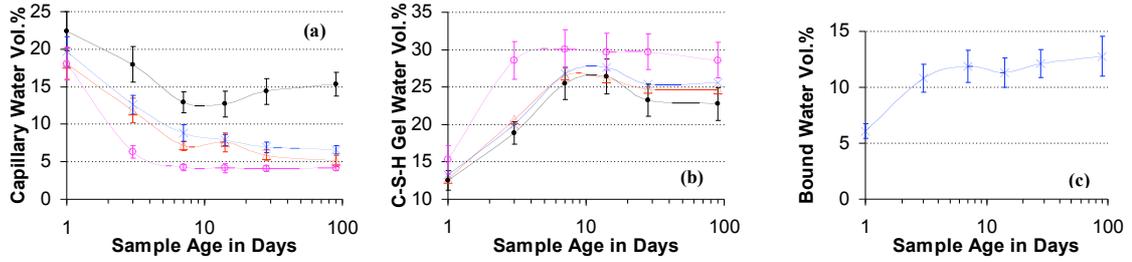
Figure 1: (a) capillary water, (b) C-S-H gel water and (c) chemically bound water volume content in cement blends B1 (●), B2 (Δ), B3 (reference, ×) and B4 (○) as a function ageing; lines are guide to the eyes.

Finally, the variation in the amount of chemically bound water (hydrates) as a function of ageing is shown in Figure 1.c for sample B3 only as this trend is quite similar for all samples. It varies from about 6 vol.% after 1 day to about 13 vol.% after 90 days.

$T_2{}^{cap}$ and $T_2{}^{gel}$ are shown respectively in Figure 2.a and Figure 2.b. Their values are respectively in the range between about 3.7 to 0.6 ms and 0.6 to 0.2 ms. Samples can be separated in three categories based on the behaviour of their relaxation times over time.

First type of behaviour as exhibited by B2 and B3, shows both T_2 components decreasing progressively over time. This decrease is directly attributed to a decrease in pore space (volume to surface ratio) for both capillary and gel pores. Average capillary pore size in B3 has decreased by a factor of about 3.5 (2.58 ms /0.74 ms) between days 1 and 90 while gel pore size has decreased by 2.7 (0.55 ms /0.20 ms). At the same time in B2, these pore sizes have decreased respectively by 3.9 and 3.1.

Second type of behaviour as exhibited by B4, shows relaxation times almost unaffected by ageing. Both capillary and gel components stay constant after 3 days at respectively about 2 ms and 0.31 ms. Therefore, the microstructure may be assumed to be unchanging beyond 3 days. It has been reported that at high curing temperatures, the increase in the kinetics of the hydration mechanisms produces matrices of higher final porosity and lower ultimate degree of hydration[5,6]. These reports support our results for B4.

While the relaxation times are constant after 3 days, a small decrease of $T_2{}^{gel}$ is observed between the first and third day in Figure 2.b. It decreases by a factor of about 1.6 as does the gel pore size. This may be explained by the fact that samples are kept at room temperature during the first 24 hours after mixing (samples rotated horizontally on roller mixer to avoid water bleeding for about 12 hours, analysed in the benchtop NMR) and only then cured at 60°C.
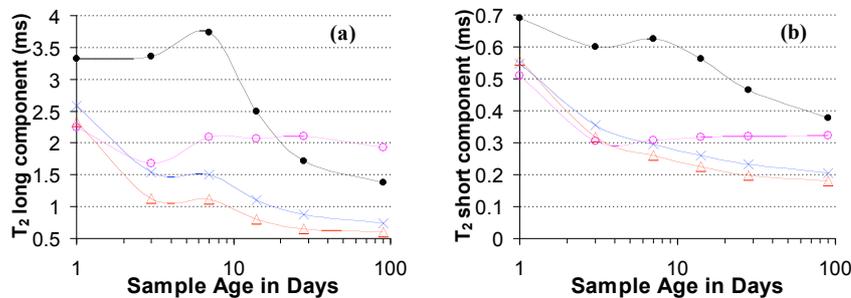

Figure 2: (a) $T_2{}^{cap}$ (long component) and (b) $T_2{}^{gel}$ (short component) in cement blends B1 (●), B2 (Δ), B3 (reference, ×) and B4 (○) as a function of ageing; lines are guide to the eyes.

Finally, one can compare the relaxation times obtained for B4 with the ones obtained for B2 and B3 in order to estimate differences in mean pore sizes in these blends. These samples share the same cement matrix composition and therefore ρ should be identical in all cases.

Hence, after 90 days, capillary pore size in B4 is 2.6 times greater than in B3 while the gel pore size is only 1.6 times greater. Storage at high temperature may affect the development of larger capillary pores more strongly than smaller gel pores suggesting a denser gel structure.

Finally, a third type of behaviour is characterised by B1. B1 having a different matrix composition, only relaxation time trends as a function of ageing can be compared between samples. B1 trend is intermediate to that observed for the other samples. Firstly, the relaxation times are almost constant over the first week, then, decrease continuously up to 90 days. The capillary component decreases at a greater rate than for B2 and B3 (by a factor of 2.7 instead of 2). If this trend persists in the longer term, B1 matrix could be expected to have a lower permeability than either B2 or B3.

Conclusion

Capillary water content decreases gradually over time while the amounts of gel water and chemically bound water increase. Gel water is the main constituent after 3 days but some of it may start to be consumed due to hydrate formation from 14 days onwards.

High temperature curing (B4) significantly increase the initial rate of cement hydration as indicated by both the low capillary water content and high C-S-H gel water content measured after only 3 days at about 6 and 28 vol.% respectively. It affects the development of the cement matrix microstructure. Indeed, both capillary and C-S-H gel pores appear unchanged over the first 90 days while in the reference blend, they decrease respectively by 3.5 and 2.7.

Variations in both water contents and average pore sizes as a function of ageing is very similar for blends prepared using different initial w:s (i.e. 0.32 and 0.37). Also, for samples prepared using a lower initial w:s, both water content and pore sizes remain smaller at all times.

In the high BFS:OPC blend (B1), an increased content of capillary water is detected over the 90 day period. This system shows increased hydrated porosity compared to the reference blend B3. Also, after a week, decrease in average capillary pore size is greater in B1 than in B3. Lower average pore size and, therefore, lower permeability could be expected on the longer term for high BFS:OPC cement matrices.

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