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Observation of the redistribution of nanoscale water filled porosity in cement based materials during wetting

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A B S T R A C T

Spatially resolved GARField NMR has been used to follow the ingress of water into previously dried Portland cement concrete and mortar samples. It is shown that the amount of capillary water in the surface layers of different samples after 1 day of capillary absorption exceeds the amount found before drying but that over the subsequent 7 days the amount of capillary water decreases once more, even though the external source of water is maintained. The hydrate gel pore water was additionally tracked in the mortars. It shows complementary behaviour. The data is discussed in terms of C–S–H swelling.

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1. Introduction

This paper presents experimental data that shows that the initial ingress of water into previously dried cement based materials is accompanied by a subsequent re-arrangement of the nano-scale porosity within which that water resides. Such an observation is surprising, but lends support to earlier observations of a sharp decrease in the capillary absorption rate of water into dried cement based materials with time [1–5]. It also lends support to the idea of C–S–H shrinkage followed by swelling when water egresses and subsequently reinvades cement based materials [3].

The observations have been made through spatially resolved ^{1}H NMR T_2 relaxation time analyses of Portland cement mortars and concretes. The NMR signal intensity is directly proportional to the amount of ^{1}H and hence water in the sample. T_2 is the NMR signal lifetime. For water in the pore spaces of cementitious materials, it is well known that T_2 correlates linearly with the pore volume-to-surface ratio, that is with the pore size. Hence the T_2 distribution reflects the water filled pore size distribution [6]. In the case of never-dried, hydrated white Portland cement measured at ^{1}H frequency of 7.5 MHz, separate T_2 components (from long to short) are normally seen representing water in capillary pores (size > 0.1 μm, T_2 > 10 ms, resultant from chemical shrinkage), inter-hydrate spaces (circa 5–20 nm, 0.5–2 ms, containing original mix water still available for reaction), hydrate gel pores (2–5 nm, 200–500 μs) and hydrate inter-layer spaces (~1 nm, ~100 μs) [7]. These times are generally lower in grey cement due to

additional paramagnetic impurity relaxation. A further very short T_2 component for water in crystalline phases can also be seen in appropriate experiments. The desorption isotherm of white Portland cement was measured using the same method and showed that as the sample is equilibrated at ever lower relative humidity, so water is lost successively from larger pores down to small pores [8]. Gajewicz [9] continued this by measurement of the subsequent sorption branch of the isotherm and also a secondary desorption branch. Classic hysteresis is observed, mainly originating in the gel porosity. The spatial profile of the T_2 distribution in a cement paste exposed to, and equilibrated under, an RH gradient for more than 1 year has also been measured and from this the water relative permeability during primary desorption was measured [10].

The observations made in this work go beyond these earlier studies in that they examine the T_2 distribution as a function of spatial position within the sample *during* rewetting after first drying rather than for the equilibrated sample. The results vary slightly from one type of cementitious material to the next, but the underlying features are the same. Water initially invades the dried material. A concentration close to the original saturation, if not the original saturation, is rapidly achieved in the surface layers. However the fraction of water in the inter-hydrate and capillary porosity is significantly greater than before drying. As water continues to penetrate to deeper layers, the T_2 distribution within the surface layers changes so as to decrease the longest T_2 fraction representing the inter-hydrate and capillary pore water (hereafter in this work called the capillary water, since, due to molecular diffusion in the strong magnetic field gradient of GARField it is hard to differentiate the two) and to increase the shorter T_2 fraction representing gel pore water. The distribution returns close to that before drying. Notice that

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the capillary pore water decreases even though a constant supply of water is maintained at the sample surface.

Experiments were performed using two different NMR systems. The first is a portable surface GARField operating at ^{1}H frequency of 2.8 MHz [11]. This instrument is designed to profile into the surface of large samples and flat structures. It readily records signal to a depth of a few centimetres with millimetre resolution. It samples a large surface area of circa 225 cm^2 (i.e. 150 mm $\times$ 150 mm). Samples used with this system are typically large blocks of concrete. The second system is a laboratory GARField [12] operating at ^{1}H frequency of 23.4 MHz. This instrument can profile long cylindrical samples of 18 mm in diameter with a spatial resolution of a few microns, although in this study a much coarser resolution, 1 mm, was used. Samples were mortars and concretes cured both sealed and underwater for up to 6 months.

The new data should contribute to answering a number of evolving questions concerning pore–water interactions in cement based materials. As well as the observations of a dramatic slowdown in the rate of capillary absorption during sorption tests and the question of C–S–H swelling already mentioned, other topics of current discussion upon which the results may shed light are: what is the nature of the nanoscale damage caused to C–S–H by drying of cement and is it reversible? [13,14]; does the relative water permeability of cement show hysteresis resultant from a variable pore size distribution above and beyond the well known hysteresis with respect to relative humidity in a fixed pore size distribution? [15]; and does the depth of water penetration as measured by NMR correspond to other more traditional indicators? The last question in particular will be addressed in a future publication based on some of the current results.

2. Materials and methods

2.1. Materials

Concrete was designed with 0.5 water-to-cement (w/c) ratio by mass and 30% paste by volume with 1.5% air content using Portland cement. The aggregate fractions used were 0/2 mm sand (30% by volume) and 2/8 mm gravel (38%). Standard mortar (EN 196-1) with a water:cement:aggregate ratio of 0.5:1:3 by mass was mixed using Portland cement. Both the concrete and mortar were cast in 150 mm cubes. One day after mixing, the cubes were demoulded and either put under lime water (underwater curing) or sealed in a double layer of plastic sheet (sealed curing). Samples were cured at 20 °C for a minimum of 3 months. A limited number of concretes with $w/c = 0.8$ were also made.

After curing, 150 $\times$ 150 mm^2 concrete slabs were wet cut from the middle of the cubes with the cut faces parallel to the casting-surface face. The slab thicknesses were variably 40, 70 and 100 mm for surface GARField analysis. In the case of the mortars, 18 mm diameter cylinders of 150 mm length were wet cored from the 150 mm cubes for laboratory GARField analysis. All cores with the same curing condition were taken from the same cube. The paste skin that forms on the surface of the sample at casting was not removed from the end of the cylinders.

Concrete slabs were oven dried at 60 °C to constant mass in a standard oven. This typically required 1 month. The mortar cylinders were dried to constant mass under light vacuum to minimise carbonation at the same temperature in typically 2 weeks. At 60 °C, it is expected that the capillary and C–S–H gel pores are emptied, but that the C–S–H inter-layer water remains as evidenced by NMR [16]. The impact of drying, insomuch as drying may damage the structure and lead to micro-cracking, is discussed in Section 4.

After drying, the sides of the samples were sealed with PTFE tape. The PTFE wrapping was used to inhibit surface drying and encourage a one-dimensional water transport across the sample thickness (slabs) or length (cylinders). Other common sealants and tapes, e.g. epoxy coating or parafilm® could not be used as they contribute a significant ^{1}H background signal in 1 dimensional NMR profiles.

Dried samples were subsequently exposed to liquid tap water on one exposed side/end. In the case of concrete slabs for the surface GARField experiments, the slabs were stood on saturated foam in a pool of water in a large plastic container. In the case of the mortar cylinders, the samples were suspended such that the lower end dipped 1–2 mm into a shallow pool of water. The water levels were maintained constant by regularly replacing absorbed and/or evaporated water.

2.2. NMR measurements

Due to wet cutting, the pre-drying sample mass is of limited significance, especially for sealed cured material. Hence, the sample mass was measured after drying, and subsequently at 1, 2, 4 and 8 h, then 1, 2, 4, 7, 14, and, in a few cases, 28 days although data at 4 days was only recorded for mortar samples. Samples were taken out from the water, the surface in contact with water was dabbed dry with a paper towel and the mass was measured. For mass measurement, the samples were removed from water for a maximum of 30 s.

NMR data in the form of relaxation echo decay profiles were acquired after 1, 2, 4, 7, 14 and, in a few cases, 28 days of capillary absorption. NMR data was also acquired pre-drying for underwater cured samples. In the case of sealed curing, the wet cutting rendered this measurement meaningless. During the measurement, the samples were covered in plastic film to avoid further drying. The relaxation measurements were made using the Carl–Purcell–Meiboom–Gill (CPMG) pulse sequence [17]. Profiles were generated with the surface GARField using, for the most part, 1 mm motor steps. The maximum profile length is 30 mm, the first 5 mm of which is above the sample surface, within the Perspex® facing of the instrument. Data acquisition parameters were optimised for maximum signal-to-noise ratio. The pulse length varied by depth. At each depth, 12 echoes were recorded with an echo spacing of 130 µs and 4k averages. Spot measurements of T_2 with enhanced signal-to-noise ratio were made 3 mm into the wet surface. Data was acquired for 20 echoes with 16k averages. For the laboratory GARField measurements at 23.4 MHz, the pulse length was 6.5 µs, and the echo spacing was 64 µs. 64 echoes were recorded with 2k averages at each depth. The profile step was 1 mm in regions of interest, more for dry samples. The repetition delay was 0.25 s for both systems, taking about 8.5 min to record an echo train dataset for the laboratory GARField and about 1 h for the surface GARField with enhanced signal-to-noise ratio.

The surface GARField measurement was calibrated using saturated sandstone of the same lateral dimensions as the concrete samples, 150 $\times$ 150 mm^2. The sandstone was uniformly wet on this scale. A sandstone profile was acquired with the same parameters as the concrete (pulse length, pulse gap and motor step) though with double the number of averages. Also more echoes were recorded. The signal amplitude decreases with depth due to the decreasing sensitivity of the detector. The profile acquired from the sandstone was used to compensate for this effect. Further, the sandstone that had known water filled porosity was used to calibrate the porosity measurement. The laboratory GARField was calibrated using both a saturated sandstone core and a rubber reference sample, the latter used to correct for pulse duration artefacts [18].

2.3. NMR analysis

The sums of the intensities of echoes in CPMG trains recorded as a function of depth were used to generate profiles. The use of echo sum improves the signal to noise ratio of the profile, but at the cost of over emphasising the long T_2 components in the signal. In the case of concrete, where a single exponential decay fitting was used (see below), the profiles were calibrated against the sandstone taking into account the difference in relaxation time between sandstone and concrete. Hence a rough measure of filled porosity is possible.