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

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4 N Fischer^{a,b}, R. Haerdtl^a, P. J. McDonald^{c,*}

5
6 ^a HeidelbergCement Technology Center, Oberklamweg 6, 69181 Leimen,
7 Germany

8 ^b Micro and NanoMaterials and Technologies Industrial Doctorate Centre,
9 University of Surrey, Guildford, Surrey, GU2 7XH, United Kingdom

10 ^c Department of Physics, University of Surrey, Guildford, Surrey, GU2 7XH,
11 United Kingdom

12 *Corresponding author: p.mcdonald@surrey.ac.uk

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16
17 **Abstract**

18 Spatially resolved GARField NMR has been used to follow the ingress of water
19 into previously dried Portland cement concrete and mortar samples. It is shown
20 that the amount of capillary water in the surface layers of different samples after
21 1 day of capillary absorption exceeds the amount found before drying but that
22 over the subsequent 7 days the amount of capillary water decreases once more,
23 even though the external source of water is maintained. The hydrate gel pore
24 water was additionally tracked in the mortars. It shows complementary
25 behaviour. The data is discussed in terms of C-S-H swelling.

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 ^1H NMR T_2 relaxation time analyses of Portland cement mortars and concretes. The NMR signal intensity is directly proportional to the amount of ^1H 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 ^1H frequency of 7.5 MHz, separate T_2 components (from long to short) are normally seen representing water in capillary pores (size $> 0.1\ \mu\text{m}$, $T_2 > 10\ \text{ms}$, 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 ($\sim 1\ \text{nm}$, $\sim 100\ \mu\text{s}$) [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 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 ^1H frequency 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 cm² (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 ^1H frequency 23.4 MHz. This instrument can profile long cylindrical samples of diameter 18 mm 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 × 150 mm² 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 empty, 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 ¹H 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 hours, 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 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 μ s 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 23.4MHz, the pulse length was 6.5 μ s, and the echo spacing was 64 μ s. 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 minutes to record an echo train dataset for the laboratory GARField and about 1 hour 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 mm². 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.

The first few echoes of a CPMG recorded in a strong field gradient such as GARField are subject to systematic amplitude modulation [19]. In case of the Surface GARField with concrete samples, the first echo was never used and the second echo was also disregarded for T_2 analysis. In the case of the laboratory GARField and mortar samples, the echo amplitudes were corrected using a rubber reference. The average of 11 depth resolved slices was used for exponential fitting in order to improve the signal to noise ratio.

GARField data is generally of lower signal to noise ratio than that acquired for bulk samples using homogeneous magnets. Therefore inverse Laplace transformation cannot be used to discover the T_2 distribution. In the case of concrete samples measured using the surface GARField, the data was fit to a single exponential decay representing capillary pore water. The first two echoes that are affected by pulse artefact and that contain a contribution from gel pore water were disregarded. In the case of mortar samples, the data was fitted with 2 components at fixed relaxation times, 250 μs and 1250 μs plus a baseline. These values were chosen based on prior experience and literature reports and on multiple different fitting analyses. The 250 μs component is characteristic of gel porosity in Portland (grey) cement; that at 1250 μs of inter-hydrate water. The baseline represents a small contribution from long components due to water in the larger capillaries and original air voids notwithstanding signal attenuation due to molecular self diffusion in the strong magnetic field gradient of GARField [20]. Shorter components due to, e.g. hydrate inter-layer water are not seen from Portland cement in GARField (although they may be seen in white cement). A further discussion of the fit parameter choices is found in section 3.2.

3 Results and analysis

3.1 Concrete samples

The top left element of Figure 1 shows the profile through the surface 15 mm of one face of a concrete cube of side length 150 mm cured underwater

for 3 months before drying. The first 5 mm of the profile is recorded above the sample within the magnet Perspex® facing. The profile was acquired with 2 mm steps using the surface GARField magnet and a CPMG echo train as described in the methods section. The profile shown represents the sum of echoes 2-10. The first echo is disregarded since it is subject to considerable experimental artefact. Echoes beyond the 10th are disregarded because the signal to noise ratio decreases below unity.

Fig. 1 echo sum profiles of underwater cured concrete before and after drying and at different times of capillary absorption. The sample surface is at 0 mm along the depth axis. Representative error bars, that increase in size with depth, are shown for the 1 day data at 4, 9 and 14 mm depth of which the first is comparably sized to the data point. (a) as-cured, (b) dried, (c) 1 day, (d) 2 days, (e) 7 days and (f) 14 days capillary absorption

The top right element of Figure 1 shows the profile into the top 15 mm of a block dried at 60 °C for 4 weeks. The profile was acquired with 1 mm steps. No significant signal is observed. Missing data points are negative within the noise level. The block face is now exposed to liquid water in a capillary uptake experiment and the resultant profiles at different capillary absorption times are shown in the subsequent figure elements. Specifically, the profile is shown after

1, 2, 7 and 14 days of capillary absorption. Three observations can be made. The first is that water penetrates beyond the top 15 mm in 1 day. In fact, measurements from both sides of other slabs not shown suggest that water typically penetrates fully across 40 mm thick slabs in 1 day, but not 70 mm slabs. The second observation is that the echo sum intensity is greater after 1 day of capillary absorption than it is in the never-dried sample. The third observation is that after the first day of capillary absorption, the echo sum intensity decreases back down towards the pre-drying level across the top 15 mm. The essential feature of a maximum in the echo sum data after about 1 day of capillary absorption has been observed in all of 20 concrete samples studied: 10 plain OPC concretes and a further 10 made with added slag or silica fume that are not explicitly reported here, but are detailed in [21].

The data in Figure 1c show an estimate of the measurement errors. Error bars are drawn at 4, 9 and 14 mm depth and represent errors in the mean derived from 5 repeats of this particular measurement. Notice that the absolute error increases with depth, due to the decreased instrument sensitivity.

All further concrete sample results described in this report are higher signal to noise ratio spot measurements of relaxation times recorded from 3 mm below the surface of cut faces. The results span 10 samples: 4 sealed cured, 0.5 w/c ratio concretes, 3 sealed cured 0.8 w/c ratio concretes and 3 underwater cured 0.5 w/c ratio concretes. They all show essentially the same results, but are displayed in these separate groupings.

Figure 2 is the T_2 echo decay for a 0.8 w/c sealed cured concrete recorded before drying, and after 1, 2, 7, 14 and 28 days exposure to water. The signal maximum is at 1 day capillary absorption, thereafter the signal intensity decreases until 28 days. Echoes 3-20 were fit to a single T_2 decay representing the capillary water in the sample. The first echo was disregarded due to artefact, the second as it contains a significant element of gel-pore water. The standard error in the mean of the fitting of one sample (measured on a sealed cured 0.5 w/c sample) measured 5 times was about 1.2 % for the intensity and about 2.5 % for the T_2 relaxation time. Across three different samples made from the same original mix, the standard error for both intensity and T_2 was about 3 %.

Hence we estimate a total error of circa 4 % for intensity and 6 % for T_2 . The standard error was calculated for all groupings and gave similar results. The figure shows that there is no signal for the dry sample.

Fig 2. Echo decay data and associated single component exponential fits of sealed cured 0.8 w/c ratio concrete measured 3 mm from the wet surface at different times of capillary absorption, (a) dried, (b) 1 day, (c) 2 days, (d) 7 days, (e) 14 days and (f) 28 days.

The collated fitting analysis results for the three sample groupings are shown in Figure 3, relative to the 1 day capillary absorption data. In every case, during re-wetting, the surface capillary water signal intensity decreases. The calculated T_2 behaves similarly. It too decreases during rewetting.

Fig 4. shows the gravimetric water uptake for $w/c = 0.5$ sealed cured concrete slabs of 40, 70 and 100 mm thickness. Water uptake slows down significantly after 1 day of capillary absorption in all sample sizes. Water uptake obviously slows down when the waterfront reaches the top of the sample, as is the case for the 40 mm thick sample. However, the 70 and 100 mm thick samples were measured at the top by NMR where they showed no signal after 1 day.

290

291 Fig 3. Normalised signal intensity (left bars) and T_2 (right) at 3 mm depth
 292 as a function of capillary absorption time for, from top, $w/c = 0.5$ underwater
 293 cured and $w/c = 0.5$ and 0.8 sealed cured concrete. Data are mean results within
 294 each group. Error bars show the error in the mean.

295

296 Fig 4. Gravimetric water uptake of $0.5 w/c$ sealed cure concretes for 40
 297 (circle), 70 (square) and 100 mm (triangle) thick slabs.

298

299 **3.2 Mortar samples** 300

301 In order to better quantify all the evaporable water in the samples, including the
302 gel pore water, further measurements were made on the mortar cylinders
303 exposed to water from one end using the laboratory GARField. It is possible to
304 use a shorter echo time (about half compared to the Surface GARField) and
305 hence record signal from smaller pores with shorter relaxation times.

306 Figure 5 shows the echo sum profile of water across the top 30 mm of a
307 sample cured underwater for 6 months (circles). A generally uniform water
308 distribution is observed. Also shown in Figure 5 is the profile of the same sample
309 after oven drying at 60°C for 14 days (crosses). All the readily evaporable water
310 is removed as evidenced by the almost total absence of signal. Water in
311 crystalline solids and in hydrate inter-layer spaces is not expected to be
312 observed in the mortar for the echo time used. During drying, the sample lost
313 6.15 g of water, equivalent to 16% of the overall sample volume. This volume of
314 water is consistent with the idea that gel and capillary pore water is lost, but that
315 inter-layer and water in crystalline solids remains. Based on Muller *et al.*, the gel
316 and larger porosity in cement paste with 0.48 w/c , is about 40 % by volume [7].
317 The w/c of the mortar was 0.5, very close to the 0.48 in paste especially as some
318 water is usually adsorbed on the fine aggregate surface. The paste content of
319 standard mortar is about 42 % by volume, therefore the gel and large porosity in
320 mortar is about 17 % comparable to the 16 % observed.

321 Finally, the figure shows the water profile after 24 hours of re-wetting by
322 contact with liquid water from the sample end in a capillary absorption
323 configuration (open squares). As evidenced by the NMR, water has completely
324 invaded this part of the sample once more. It shows a near uniform
325 concentration greater than that before drying. During this time the sample mass
326 increases by only 2.13 g presumably because the sample is not wetted along the
327 full 150 mm length. As an aside, the mass of the sample takes more than one
328 month to stabilise and we never observed it back to the original value. This may
329 be because a dynamic equilibrium profile is established with an evaporation

front partway along the sample length or because pore-blocking prevents water penetration along the full sample length.

Fig 5. Echo-sum profile of an underwater cured mortar sample as prepared (circles), after drying (crosses) and after 1 day of capillary absorption (open squares).

The characteristic behaviour exemplified in Figure 5 was observed in most mortar samples cured both sealed and underwater. However, in a few samples, the water uptake did not pass through the full 30 mm in one day, but rather slowed dramatically, perhaps due to pore-blocking. These samples have not been included in the report of this work but are reported elsewhere, [21]. In other samples cured with silica fume in the mix, the uptake was slower from the start and did not traverse 30 mm in the first day, perhaps due to a finer porosity. These too are presented elsewhere [21].

As with the concrete, the echo sum trace does not properly reflect the water content by mass because the T_2 decay time is pore size dependent. Moreover, it is not easily calibrated because the decay is multi-exponential. T_2 analysis overcomes this problem. The top left element of Figure 6 shows the average echo train decay in the top 11 slices (0-10 mm) of the sample before drying together with a fit to the data assuming two T_2 components with T_2 relaxation times of 250 and 1250 μ s and a baseline. The log scale makes clear the multi-exponential character of the decay. Similar analyses of the dried sample and of the re-wetted sample after 1, 2, 4 and 7 days of rewetting are shown in the

other figure elements. Notice that the scale of the dried sample is different to all the rest. There is almost no signal compared to the other traces except in the first few echoes.

Fig 6. Average echo decays recorded from the top 10 mm of an underwater cured mortar sample before drying, dried and at different times of capillary absorption. The data is fit to a two-component exponential decay function plus baseline offset. (a) as-cured, (b) dried and after (c) 1 day, (d) 2 days, (e) 7 days and (f) 14 days of capillary absorption.

Figure 7 shows total average signal intensity from 5 to 15 mm of the mortar relative to that of 1 day of capillary absorption (considered 100%) as a function of drying and re-wetting. It also shows the breakdown of the signal into the short and long components of the fit. The baseline is typically 2 % of the total, and is never more than 4 %, for mortar samples. As the baseline could be associated with a long T_2 decay, it has been added into the long component fit.

Fig 7. Water content normalised to the total for 1 day of capillary absorption for underwater cured (top) and sealed cured (bottom) samples, showing total (black bars), short (grey) and long (white) components by time.

Consider first the underwater cured sample. Quite noticeably, save for the dried sample (where the intensity is close to zero) the total intensity decreases slightly from pre-drying, and through one day and beyond of capillary absorption. What is also noticeable is that the total signal in the longer components after 4 days rewetting is very similar to the pre drying value, whereas at 1 day it is substantially greater. The fraction in the shorter component behaves in the opposite way. It has a minimum at 1 day of capillary absorption. Hence, while the total signal before drying and after 1 day of rewetting are very similar, the distribution across the long and short components is very different. The long component corresponding to larger pore spaces is over represented after 1 day rewetting. After 4 days rewetting the distribution has returned to that before drying.

In the case of the sealed cured sample, the same redistribution is still there. However, now, after 1 day of rewetting, the increase in the short component exceeds the decrease in the long component leading to an increasing total. The experiment has been repeated for 5 different mortars: 2 cured underwater and 3 cured sealed. These repeats have been used as the basis of the

error bars in Figure 7. However, multi-sample variability is likely a more important contribution to the error bar size than single sample measurement uncertainty across a time course.

The absolute signal intensities in the long and short components depend critically on the choice of T_2 values used in the analysis. Hence the analysis has been repeated for different fixed pairs of T_2 values including 250 μs and 1500 μs , and for variable T_2 within the 150-450 and 1000-3000 μs ranges: although the absolute signal fractions clearly change, the story of a decreasing amount of large filled pore spaces and an increasing ratio of filled small pore spaces to large pore spaces during capillary absorption remains the same.

It may be considered that the water has not fully penetrated the top 30 mm of the sample notwithstanding the evidence of Figure 5. Hence the analysis has been repeated for just the surface 5 layers. The story is the same.

4 Discussion

The key result seen across every sample investigated is that after initial uptake of water into a previously dried sample during a capillary absorption experiment, the amount of capillary water near the exposed surface first increases, and then decreases, with time. Where it has been possible to measure the saturation level in the as cured material (i.e. in underwater cured samples), the initial uptake after drying is to a level greater than before drying. The fall-back is to an amount near to the as-cured material. This observation is counter intuitive. It suggests that water first enters capillary pores then desorbs once more. In the case of mortar samples, the gel pore water is also seen. This increases throughout the capillary uptake. In the case of the mortars, the combined gel pore and capillary total is available. While the capillary water reaches a maximum after 1 day and then decreases as stated, there is a marked difference between the underwater and sealed cured samples. In the former case, the total gel plus capillary pore water decreases after the initial capillary absorption; in the latter case it increases monotonically.

One possibility is that there is delayed hydration taking place during the capillary absorption. The effect would be compounded if drying caused micro-

cracks that exposed unhydrated material to water during capillary absorption. That such cracking is possible by drying at 60 °C has been shown by [14]. Delayed hydration has been suggested as a mechanism for anomalous diffusion in capillary absorption experiments of cementitious materials in the long-time regime, greater than a few days [1, 22]. Further hydration would create additional gel porosity at the expense of capillary porosity. However, the timescale of capillary absorption in that work is different to ours. The first and most dramatic change in the NMR dataset is seen after only 1 day of capillary absorption. Also, the effect has been observed in systems cured underwater for several months that have already attained a high degree of hydration. In case of 0.5 w/c underwater cured concrete, the degree of hydration was measured after drying on a reference sample and also after re-wetting for 28 days. Analysis by XRD showed no change. The degree of hydration was $90\pm1\%$ both before and after rewetting. Hence, we discount delayed hydration, and in particular delayed hydration resulting from exposure of anhydrous material by micro-cracking, as the cause of the effect.

A second possibility concerns ettringite. In cement paste, ettringite decomposes during drying [23]. XRD showed an increased amount of ettringite after 28 days of capillary absorption compared to the reference dried paste of the concrete sample. An idea is that ettringite progressively fills the capillary pore space during rewetting. However, the amount of other hydrate phases slightly decreases and the overall volume of hydrates does not change significantly. Also, without macroscopic volume change data, it cannot be assumed that change of the volume of solid phases necessarily leads to the same change in the pore space. The results of mortar samples do not show a decrease in the overall evaporable water amount and therefore a reduced pore volume. Hence this proposal is also discounted.

A third possibility is that ingressing water first invades large pores and then the smaller pores fill with water taken indirectly from the large pores [2]. Such an argument could account for the more slowly increasing filled gel pore signal in the mortars. However, it is unreasonable to expect that, in presence of a continued source of water, the gel pores fill at the expense of water in the large

pores which can be continuously maintained full by the external source. Hence, this too is discounted as an explanation.

A yet further explanation relates to trapped air in the pores after rewetting¹. The suggestion is that upon initial rewetting, trapped air is compressed in small pores by capillary forces. Only more slowly can this air diffuse out into the larger pore network so leading to a movement of water from large to small pores. The difficulty with this idea is that it fails to explain why the large pore volume revealed in underwater cured samples is initially greater after rewetting than before drying. In underwater cured concrete, one would expect these pores to be saturated before drying representing a maximum possible water level. The idea also fails to explain why large pores initially fill but subsequently empty given the continued presence of a water source. Why would water push in against the air, only later to be pushed back out?

Therefore, the only reasonable explanation that we can see is C-S-H gel swelling [3]. Gel porosity may partially collapse during sample drying in favour of creating larger capillary sized pore spaces. As long ago as 1980 Parrott *et al* [24] suggested on the basis of nitrogen sorption that small pores close as a result of capillary tension forces during loss of capillary water on first drying in alite pastes. The changes were largely recoverable, but there was some irrecoverable loss of porosity. A more recent and more comprehensive study by Maruyama *et al* [23] also suggests closure of the gel porosity and an increase of capillary porosity on drying. Our results show that when the sample is rewet, the newly created larger spaces fill but, with time, the network returns to nearer the original pattern of space filling. Some of the change is reversible. This is consistent with both Parrott *et al* and Maruyama *et al*. The timescale of the swelling during capillary absorption is about 1 day. Further work using the laboratory GARField is required to decide whether the large pore space increase arises due to expansion of large capillary pores (that is pores created by chemical shrinkage of the original mix, that may or may not be water filled due to additional water arriving after mixing) or to expansion of smaller interhydrate

¹ We thank an anonymous referee for making this suggestion.

pores (that contain water that has not yet been involved in reactions and which are an intimate part of the gel).

We have no immediate explanation of the difference in the behaviour of the total signal intensity beyond one day of capillary absorption between underwater and sealed cured mortar samples. One possibility is that the different curing methods affect the internal stresses of the paste and how the large porosity is created during hydration [25]. The macroscopic shrinkage of the sealed cured mortar is significantly bigger than for the underwater cured mortar. The pore network of the underwater cured sample may be more refined, and so filling of the gel network from the capillary network may be a slower process. If this is the case, then potentially insufficient gel pores fill in the first day for us to observe an overall maximum in the signal intensity. Without knowing the capillary and gel water content of samples cured both ways before drying (that we cannot measure in one case with the current set-up) it is not possible to fully resolve this difficulty. Also, delayed hydration may be more significant, and hence a more important secondary effect, in the sealed cured sample compared to the underwater cured sample.

As a final comment, we note that we have carried out further experiments on concretes made with blended cements containing silica fume or slag. These concretes show substantially the same behaviour, [21]. We also note that the effects we see are measured near the sample surface rather quickly after re-wetting. The measurements do not integrate across the whole sample, as does a bulk NMR or gravimetric measurement. It is possible that earlier work using NMR relaxometry failed to observe these changes, as it did not combine spatial resolution with adequate relaxation time resolution. That is a general, sample wide, increase in both small and large pore water content during rewetting masked any redistribution occurring locally. The benefit of using spatially resolved measurements in this work is thus clear. While we have necessarily confined ourselves to measurements in the first ten millimetre or so of the sample, we have no evidence to suggest that the effect is confined to the surface layers. It most likely occurs in deeper layers also, as water ingresses that far. However, as water invades more slowly at depth (due to the square root of time

dependence of capillary absorption), it is possible that invasion and swelling go hand-in-hand and are less differentiated. In future work we will look further at the spatial dependence and also the second drying/wetting cycle.

5 Conclusions

NMR measurements using GARField NMR spectrometers have shown that the amount of inter-hydrate and capillary water in surface layers of concrete and mortar samples first increases and then, from about 1 day, decreases during capillary absorption experiments. In the case of underwater cured concretes, the amount of capillary water increases substantially above the amount in the as prepared sample before returning close to the original. As there is a constant supply of water, the results suggest a redistribution of porosity in favour of smaller gel pores not visible by the surface GARField system. Further measurements on mortars that include gel water show that in case of underwater cured samples additional large porosity is created during drying at the expense of gel water and that after 4 days of capillary absorption the large to small pore water volume ratio is restored close to the original, never dried value. The data has been interpreted as evidence for C-S-H swelling in the dried material upon water ingress.

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