Characterisation of intra- and inter- C-S-H gel pore water in white cement based on an analysis of NMR signal amplitudes as a function of water content.

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Abstract

¹H nuclear magnetic resonance (NMR) relaxation analysis of water in progressively dried white cement paste is used to estimate the width and relative specific area of intra C-S-H sheet pores and inter C-S-H particle gel pores. The measurement is based on the ratio of solid-echo to free-induction-decay signal amplitudes and the observation that as water is removed, so the surface fraction contributing to the solid echo increases. The intra- and inter- C-S-H pores are found to be 1.5 nm and 4.1 nm thick respectively. The total specific area and volume ratio is 2.4 and 0.88 respectively. The volume ratio of readily evaporable water within the pore types is 0.63. Hence, the sheet porosity is 47% of the total or 38% if based solely on evaporable water. The method is distinct from NMR analyses based on the relaxation time. There is good agreement between the measured widths by the two methods.

1 **1. Introduction**

2 An extended series of papers have progressively explored the dynamics of water
3 within the C-S-H gel that comprises the greater part of hydrated cement using low
4 frequency (bench-top) ^1H Nuclear Magnetic Resonance (NMR) [1,2]. In its most basic
5 form, the ^1H NMR free-induction-decay (FID) signal comprises a series of discrete
6 components with different T_2 (spin-spin) or T_1 (spin-lattice) relaxation times. The
7 more quantitative studies are those of Lasic et al [3,4], Miljkovic et al [5,6], Schreiner
8 et al [7], Greener et al [8], Halperin et al [9], Bohris et al [10] and MacTavish et al
9 [11]. In addition, in an important study, Plassais et al [12] correlated magic angle
10 spinning NMR spectroscopy results and relaxation analysis in C_3S in order to assign
11 spin lattice relaxation, T_1 , reservoirs to different pore / chemical environments.
12 Moreover, in recent experiments, 2D relaxation correlation and exchange methods
13 have been employed to estimate the exchange rate between pores of different size
14 [13,14,15].

15 Amongst the above, different studies have identified at least three T_2 relaxation
16 components, with a minority reporting as many as five. This apparent discrepancy is
17 in part a matter of definition. It is also in part a consequence of the experimental
18 apparatus or method employed: not all spectrometers or all measurement protocols
19 can detect all components. Notwithstanding these differences, it is valuable to
20 consider carefully the water reservoirs within the cement to which each belongs. The
21 most widely accepted assignment is as follows. The shortest lived component has a T_2
22 relaxation time of the order of $10\ \mu\text{s}$ and originates from chemically combined water
23 most obviously within micro-crystalline phases such as Portlandite (Calcium
24 hydroxide, $\text{Ca}(\text{OH})_2$ or, in cement chemistry notation CH). Longer lived signal

1 components are assigned to gel and capillary pore water. For pore water, the fast-
2 diffusion limit of relaxation in porous media is considered valid [16,17] in which case

$$3 \quad \frac{1}{T_2^{obs}} \approx \lambda_2 \frac{S}{V} + \frac{1}{T_2^{bulk}} \approx \lambda_2 \frac{S}{V} \quad (1)$$

4 where λ_2 is the pore-surface relaxivity and S and V are the pore surface area and
5 volume respectively. T_2^{obs} is the observed relaxation time and T_2^{bulk} is that for bulk
6 water. In cements and relaxation time order, the next two components have relaxation
7 times of the order of 80 - 120 μ s and 500 μ s to 2 ms respectively. Separately resolved,
8 these are usually assigned to “gel-pore” and “capillary-pore” water respectively. Any
9 longer component is assigned to water in cracks and to water adsorbed on the sample
10 surface. Assignment of water between the sheets of the calcium silicate hydrate (C-S-
11 H) gel is less clear. It is sometimes considered NMR similar to the chemically
12 combined water; sometimes it is considered like gel pore water. This mirrors a wider
13 debate in the cements literature as to the characteristics of gel water and the detailed
14 morphology of the microstructure of C-S-H.

15 The purpose of this paper is to carefully examine the amplitude of the solid and more
16 mobile T_2 relaxation time components in cement pastes with a view to confirming the
17 detailed assignment of relaxation components to cement microstructure.
18 Measurements are made as a function of sample moisture content during careful, and
19 ultimately destructive, drying starting with a few minutes heating at a few degrees
20 above ambient temperature and ending at temperatures of the order of 400°C for
21 several hours. The NMR measurement is accomplished by measuring the amplitude of
22 the shortest relaxation time fraction using a solid echo experiment [18] combined with
23 FID intensity analysis. The amplitude of each T_2 relaxation component is directly
24 proportional to the fraction of water, or, more strictly ^1H in a corresponding reservoir.

1 By this method we seek to more carefully assign especially the shortest relaxation
2 time components to water in different environments. While presence of inter-pore
3 water exchange may modify the relative amplitudes of the longer components
4 individually considered, it has minimal effect on the relative amplitude of the
5 chemically combined water signal and the aggregated mobile water signal as
6 measured here.

7 A by-product of the study has been realisation that the NMR intensity measurement
8 leads to an alternate assessment of the gel pore size based not on the absolute value of
9 the more mobile component T_2 through Equation (1), but rather on the amplitude of
10 the “solid” and “mobile” component as a function of moisture content. It is also
11 possible to calculate the ratio of the pore specific areas and volumes. The
12 measurements derive from the observation that, during the early stages of drying
13 during which easily evaporable water is lost, not only does the fraction of bound water
14 increase, but so does the absolute volume due to the increasing presence of a residual
15 adsorbed layer. The analysis also sheds some light on the means of drying of these
16 pores. The new methodology for measuring pore size has an advantage compared to
17 that based on the use of Equation (1) because it is calibration independent, meaning
18 that the surface relaxivity λ is not required to calibrate the experiment.

19 Current literature presents a series of potential models for the microstructure of
20 cement gel, reflecting the ongoing debate as to the morphology of C-S-H and related
21 phases. These models are based on the interpretation of data arising from different
22 spectroscopies and imaging methods including neutron and X-ray scattering, electron
23 microscopies and magnetic resonance. At issue is the scale of the heterogeneities
24 within the microstructure, the morphology of the C-S-H sheets and the extent to
25 which elements of C-S-H may, or may not, be viewed as discrete particles. Many of

1 these models have recently been reviewed by Jennings [19]. The results of this work
2 are discussed in the context of a model proposed by Feldman and Sereda [20] which is
3 the model towards which most prior NMR work by our group has been pointing. It is
4 possible, however, to see how the results, which offer insight into pore size, could be
5 re-interpreted in terms of other models. This is discussed further in section 6.i.

6 The key observation of this work will be that the apparent bound water fraction
7 changes in a non-intuitive manner as cement samples are dried and that this leads to a
8 new estimate of pore size. Indeed, two characteristic pore sizes are calculated. The
9 numerical results are generally in agreement with other estimates made by other
10 means. However, the exact values obtained may be questioned due to the manner of
11 sample drying which is in a vacuum oven up to 200 C and an ordinary oven beyond.
12 Carbonation and micro-structural damage both play a role. The likely impact of this,
13 and mitigating factors, is discussed in Section 6.ii. Neither micro-structural damage
14 nor carbonation invalidates the measurement of bound water fraction as measured by
15 NMR in as cured material that was the original driver of this work.

16 **2. Experimental**

17 *i. Materials*

18 White cement was obtained from the European NANOCCEM consortium materials
19 bank (Nanocem Cement “A”) developed as part of the Nanocem Marie Curie Project
20 [21]. It was used in all experiments. The composition is known to be 67.3% Alite,
21 23.3% Belite, 3.6% Aluminate and 4.3% Gypsum / Hemihydrate / Anhydrite with
22 other phases less than 1.5% total. Carefully measured amounts of the cement powder
23 were mixed in the water-to-cement ratio of 0.4 at room temperature according to the
24 NANOCCEM protocols: in summary mix for 3 minutes at 500 revs/min, pause for 2

minutes, then re-mix for 2 minutes at 2000 revs/min. The cement was cast in cylindrical moulds 8 mm in diameter and 20 mm deep. Once set, the samples were removed from the moulds and cured under a small quantity of saturated calcium hydroxide solution at room temperature. The curing time was variously 2, 4 or more weeks. After curing, and immediately prior to use, samples were dabbed dry, ground in a pestle and mortar to a coarse grain and placed in 10 mm diameter NMR tubes. Care was taken to ensure that the sample fitted well within the NMR sensor to avoid fringe effects. Measurements were made on progressively dried samples. A vacuum oven was available up to 200°C and an oven without vacuum beyond that to 450°C although the maximum temperature reported here is 380°C. Samples were weighed at every opportunity: before and after both measurements and periods of drying. All measurements were made at room temperature, not at the drying temperature. Reagent grade calcium hydroxide upon which parallel experiments were carried out was purchased from Sigma-Aldrich.

ii. *Methods*

¹H NMR data was acquired using a Resonance Instruments “Maran” bench top NMR spectrometer (Oxford Instruments, Whitney, Oxon UK) operating at 20 MHz. The solid-echo pulse sequence, $90_x \tau 90_y$ acquire, where $90_{x/y}$ is a 90° excitation pulse of relative phase x or y and τ is a short delay interval was employed. The precise timing diagram is shown in Fig. 1. Following the second pulse and a short instrument dead time ($\cong 10 \mu\text{s}$) the solid echo and free induction decay signal were detected. Dependent on signal level, up to 2048 averages of 1024 points per decay were acquired with a recycling time of 1s and at a sampling rate of 1 MHz respectively. Echoes were acquired for pulse gaps, τ , from 15 to 45 μs in 5 μs intervals. In all cases a small

1 residual NMR signal emanating from the empty NMR probe was subtracted from the
2 measured data and all acquisitions were normalised by the number of averages.

3 iii. *Data Analysis*

4 The signal from mobile hydrogen following the $90_x \tau 90_y$ pulse sequence is
5 unaffected by the second pulse and is therefore an exponential decay with apparent
6 origin at the time of the first pulse and relaxation time, T_2^* , that is determined by the
7 magnet inhomogeneity. In contrast, Powles and Strange [18] have shown that, for
8 rigid coupled spin $\frac{1}{2}$ (i.e. hydrogen) pairs such as in solid Ca(OH)_2 , the pulse
9 sequence refocuses magnetisation that would otherwise decay rapidly due to rigid
10 dipole-dipole interactions so that the signal from the solid comprises an echo of
11 approximately Gaussian shape centred on a time τ after the second pulse. Hence, the
12 composite signal can be approximated by, and fit to

$$13 \quad I(t, \tau) = I_m(\tau) \exp\left(-\frac{(t + \tau)}{T_2^*}\right) + I_s(\tau) \exp\left(-\left(\frac{t - \tau}{\sigma}\right)^2\right) \quad (2)$$

14 where I_m and I_s are the mobile and solid intensities respectively, σ is the Gaussian
15 width (approximate solid T_2) and t is time from the second pulse.

16 The echo refocusing is not total due to longer range interactions and residual motion.
17 Therefore, to obtain a true measure of the solid intensity it is necessary to back
18 extrapolate $I_s(\tau)$ to $\tau = 0$. This has been done using linear, exponential and Gaussian
19 fitting. Empirically, the exponential was found to fit the data best and it is these
20 results that are reported below. For completeness and to overcome residual errors,
21 $I_m(\tau)$ was also back extrapolated.

3. Theory

The much simplified model of cement microstructure adopted in this work follows closely that of Feldman and Serada [20]. This structure is suggested by Fig. 2e. We consider that cement gel is composed of tetrahedral silica layers interspersed by layers of water and calcium ions in a sheet like structure. For clarity, we refer to this water as intra-C-S-H sheet water. The C-S-H sheets are randomly stacked with water in inter-C-S-H gel pore spaces. While many authors would refer to water in both reservoirs as “gel water”, we maintain the above distinction throughout to avoid ambiguity. Water in both intra and inter C-S-H sites may be considered as being confined to planar pores. We include within this description other comparably structured phases such as AFm and Ettringite. In addition there are solid phases such as Portlandite.

Consider a planar pore as suggested by Fig. 2a. In this pore, the water molecules associated with the surface are in rapid exchange with those in the bulk of the pore. Hence they are characterised as mobile and the NMR signal has a long relaxation time. Fig. 2d shows the pore completely dried, with no water remaining. There will be no signal. Fig. 2c shows an intermediate stage of drying where all the readily evaporable water has been removed and the remaining water is adsorbed to the surface. It is relatively immobile and so has a short relaxation time. Fig. 2b(i) and 2b(ii) illustrate two alternate drying scenarios leading to Fig. 2c. In Fig. 2b(i), water is removed uniformly across the pore. The surface to volume ratio of the remaining water is increasing so that, from Eq. (1), T_2 is decreasing. However, the T_2 distribution remains unimodal. The scenario of Fig. 2b(ii) arises if capillary forces are significant. Here there is a clear demarcation of the T_2 distribution corresponding to a component with the original relaxation time but decreasing amplitude, and a second short relaxation time component with increasing amplitude.

1 Suppose that, for an as prepared sample, the total specific area of inter-C-S-H gel pore
 2 water measured in surface water molecules per unit volume of C-S-H is M and that a
 3 typical inter-C-S-H gel pore is $(p+2)$ water molecules thick. The model is
 4 insufficiently precise to warrant distinction between water molecules adsorbed to pore
 5 surfaces and surface hydroxyls. Then the signal intensity due to the inter-C-S-H gel
 6 pore water is proportional to $M(p+2)$. A similar argument can be composed for the
 7 intra-C-S-H sheet water save here we have a specific area of N surface molecules per
 8 unit volume and write the water layer thickness as $(q+q')$ molecules. We use q' rather
 9 than 2, since, as water is removed, residual water associated with the calcium ions
 10 may appear as bound. The signal intensity due to the intra-C-S-H sheet water is
 11 proportional to $N(q+q')$. Finally, we assume that the signal intensity due to the CH
 12 is proportional to Lr where L and r are an effective CH surface area per unit volume
 13 of C-S-H and an effective CH thickness respectively. Normalising to unity, the total
 14 initial signal intensity is

$$15 \quad M(p+2) + N(q+q') + Lr = 1 \quad (3)$$

16 The pore water is in fast exchange with the surface adsorbed water and appears as
 17 mobile. The CH water is bound and solid like. Thus, the initial intensities for the
 18 mobile (I_m) and solid (I_s) signal intensities back extrapolated to $\tau = 0$ are given by

$$19 \quad I_m = 1 - I_s = M \cdot (p+2) + N \cdot (q+q') = 1 - Lr. \quad (4)$$

20 Consider now that the pores are dried according to the schematic Figure 2b (ii).
 21 Evaporable water is removed from a fraction $(1-s)$ and $(1-s')$ of the specific area of the
 22 inter C-S-H gel and intra C-S-H sheet water leaving an upper and lower surface mono
 23 layer in the former case and a total q' molecules per unit area in the latter. Once the

1 evaporable water is removed, the remaining water that was in fast exchange is
 2 immobilised and joins the “solid” fraction. Hence, during drying

$$3 \quad I_m = M \cdot (p + 2) \cdot s + N \cdot (q + q') \cdot s' \quad (5)$$

4 and

$$5 \quad I_s = 2M \cdot (1 - s) + q'N \cdot (1 - s') + Lr \quad (6)$$

6 The normalised mass of water remaining during drying is:

$$7 \quad \rho = 1 - Mp \cdot (1 - s) - Nq \cdot (1 - s') \quad (7)$$

8 Experimental evidence to be presented suggests that the drying is characterised by
 9 three distinct stages. It is assumed that the first stage corresponds to removal of
 10 evaporable water from the inter-C-S-H gel pores only. Hence, during the first stage,
 11 $s' = 1$, leading from (5) and (7) to

$$12 \quad I_{m1} = a_1 \rho + b_1 \quad (8)$$

13 where I_{m1} is the stage 1 mobile intensity and

$$14 \quad a_1 = 1 + \frac{2}{p} \quad \text{and} \quad b_1 = M \cdot (p + 2) - \frac{2}{p} + N \cdot (q + q') - 1 \quad (9)$$

15 Eq. (8) characterises the mobile signal intensity as function of mass during early
 16 drying. The relationship is linear, with gradient a_1 and intercept b_1 . The second stage
 17 is assumed to correspond to removal of evaporable water from the intra-C-S-H sheets.
 18 During this stage, $s = 0$ and $s' < 1$ so that, using similar notation to above

$$19 \quad I_{m2} = a_2 \rho + b_2 \quad (10)$$

20 with

$$1 \quad a_2 = 1 + \frac{q'}{q} \text{ and } b_2 = Mp + \frac{q'}{q} \cdot (Mp - 1) + N \cdot (q + q') - 1. \quad (11)$$

2 The model parameters p , q and M and N can be calculated from Eqs. (9) and (11) as:

$$3 \quad p = \frac{2}{a_1 - 1} \quad (12)$$

$$4 \quad q = \frac{q'}{a_2 - 1} \quad (13)$$

$$5 \quad M = \frac{\frac{2}{p} - \frac{q'}{q} + b_1 - b_2}{2 - p \frac{q'}{q}} \quad (14)$$

$$6 \quad N = \frac{\frac{q'}{q} - Mp \cdot \left(1 + \frac{q'}{q}\right) + b_2 + 1}{q + q'} \quad (15)$$

7 The product Lr is available from the solid signal intensity before drying although
8 nothing can be said about the L and r separately, that is the shape of the CH crystals.

9 The final stage of the drying, that only occurs with more extreme heating, is removal
10 of the “solid” water. It is broken down into at least two processes. The first is removal
11 of surface adsorbed water both from intra C-S-H sheet and inter C-S-H gel pores. The
12 second is water lost due to breakdown of CH into C+H; that is Ca(OH)_2 into CaO and
13 water.

14 A further process that is not “drying”, but which materially affects the results, is
15 carbonation of the C-S-H and CH. Carbonation involves the ingress of CO_2 such that

17 and

2 The ingress of CO₂ causes an increase in net mass even though there is a loss of signal
3 due to loss of water.

4 **4. Results**

5 We consider first the inset to Fig. 3. This shows a solid echo signal measured from
6 dried and powdered reagent grade Ca(OH)₂. In this measurement, $\tau = 20 \mu s$. The echo
7 is seen to decay rapidly and to be followed by a small negative going oscillation
8 known as a Pake doublet. Pake doublets are a well known feature of systems
9 comprising rigid pairs of dipolar coupled spin $\frac{1}{2}$ nuclei such as hydrogen protons in
10 Ca(OH)₂ [22].

11 The main part of Fig. 3 shows an exemplar echo signal recorded from a cement paste
12 sample. The sample has been dried progressively at temperatures up to 120°C and at
13 this stage has attained a fractional mass compared to the start of 0.80 so that most of
14 the evaporable water has been lost. Moreover, the pulse gap τ is 40 μs which is
15 relatively long, so the solid echo is already significantly attenuated. Hence, the signal
16 to noise ratio of this measurement is relatively low at 15. It is therefore close to a
17 “worst case” data set from the viewpoint of data analysis. Nonetheless, the signal can
18 be well fit to an exponential decay and a Gaussian according to Eq.(1). The relaxation
19 time fit parameters are $\sigma = 18.3$ and $T_2^* = 71 \mu s$ for the bound and mobile components
20 respectively. The corresponding signal amplitudes are 5.85 and 9.00 respectively.

21 Fig. 4 shows the pulse gap dependence of the echo and decay fit amplitudes for the
22 cement sample at the same drying conditions as in Fig. 3. It is seen that the bound
23 signal amplitude is a strong function of the pulse gap whereas the mobile signal
24 amplitude is a much weaker function. Both amplitudes have been fit to single

1 component exponential decay curves as a function of the pulse gap and back
2 extrapolated to zero time in order to gain the best estimate of the bound and mobile
3 hydrogen fractions. In this example the amplitudes at zero time are 48.3 (bound) and
4 8.2 (mobile).

5 Fig. 5 shows the amplitude of the bound and liquid signals and their combined total as
6 a function of the sample mass. All signal amplitudes have been normalised to the
7 overall initial total (solid + mobile) amplitude and are therefore fractions. The sample
8 mass is shown in 3 ways. The primary axis shows the actual mass of the sample
9 relative to the initial mass. It is seen that the sample dries to 77% of the starting value
10 at the maximum temperature attained. The subsidiary second and third axes
11 immediately below, show the relative water fraction based on knowledge of the
12 sample composition at mixing, and of the curing and preparation conditions. They are
13 discussed below. The axis above the plot shows the maximum drying temperature
14 used to reach the corresponding sample masses. This is indicative only of the
15 temperature required since, to a limited extent, the same mass can be achieved by a
16 longer drying period at lower temperature or, conversely shorter period at higher
17 temperature than actually used.

18 This experiment has been repeated on several samples, albeit not always with as many
19 data points. The essential features to be discussed in the next section are highly
20 reproducible.

21 **5. Analysis**

22 *i. Initial observations*

23 The primary observation to be made from the inset to Fig. 3 is that we are
24 satisfactorily working in a regime where we can see the broadest line components as

1 evidenced by observation of the Pake doublet for $\text{Ca}(\text{OH})_2$. For cement, the echo is
2 clearly partitioned into two components reflecting the bound and more mobile water.
3 Interestingly, the same is true for as-received $\text{Ca}(\text{OH})_2$ which clearly holds a
4 significant fraction of adsorbed water on the crystallites. The inset is for dried
5 material. The mobile water signal in the cement is not differentiated into different
6 reservoirs with different T_2 values reflecting different pore size environments because
7 the experiment is magnet inhomogeneity (T_2^*) limited. As a result, any amplitude and
8 T_2 modification resultant from exchange between pores of different size is not
9 affecting the result.

10 The second observation (confirmed by an NMR Carr-Purcell-Meiboom-Gill [23]
11 analysis as used in our previous work) is the almost total lack of a very long T_2
12 component that might be attributed to large capillary pore water. When present, water
13 in large pores should manifest as a long T_2 component to the signal. This perhaps
14 surprising result is not new. Previous NMR data on similarly prepared samples of
15 white cement with a water to cement ratio of 0.4 prepared in our laboratory have also
16 exhibited almost no capillary pore water despite the samples being cured underwater
17 [13]. A similar observation has been made by others. For example, Halperin et al [9]
18 report pores of characteristic size of circa 3 and 12 nm, but nothing larger, in mature
19 pastes on the basis of NMR T_2 relaxometry. Larger pores (>100 nm) are only seen in
20 the first few hours of hydration.

21 The first conclusion to be drawn from Fig. 5 is that, initially, 27 % of the signal is in
22 the solid fraction and 73% in the mobile. It is suggested that, at this stage, the bound
23 fraction is made up exclusively from signal from the CH: the Portlandite. The cement
24 pores are fully saturated and the pore water hydrogens, if not the water molecules

1 themselves, are in rapid exchange with water and hydroxyls occupying the pore
2 surface. Hence all the C-S-H water appears as mobile.

3 As water is removed from the sample, so the total signal decreases. The decrease is
4 linear in two distinct regions with different gradients: first in the relative sample mass
5 range 1.0 to 0.8 and then with a strongly accelerated gradient below 0.8. More careful
6 inspection of the bound and mobile fractions in the range 1.0 to 0.8 mass fraction
7 suggests that the first part itself divides into two stages. Hence we refer to three stages
8 of drying: the first and second from 1.0 to 0.8 mass fraction and the third below 0.8.

9 Linear signal loss with mass is expected as each lost water molecule contributes equal
10 signal: hence the observation of accelerating signal loss below 0.8 mass fraction in
11 stage 3 is a surprise, discussed further below. For the present we confine discussion to
12 the behaviours between 1.0 and 0.8. In this range, it is reasonable to expect that
13 readily evaporable water is lost. One therefore expects the mobile fraction to decrease
14 in parallel with the total. In fact, it decreases more quickly while the bound fraction
15 increases.

16 This is better understood with reference to the second and third axes which show the
17 sample mass in terms of the calculated water content. Given that the water to cement
18 ratio is 0.4, unity water fraction on the second axis corresponds to an actual water
19 content of 28.6%: equally, 0 corresponds to a relative sample mass of 71.4%. Based
20 on the second axis, the gradient of the total water signal loss curve is 0.836. This is
21 close to, but not equal to, the expected value of 1.0. The reason is almost certainly due
22 to error in the water fraction calculation. The sample was prepared with a water to
23 cement ratio of 0.4, but was subsequently cured under a saturated calcium hydroxide
24 solution. Since the sample is small, any water ingress raised the water to cement ratio
25 of the final product. Equally, the cured sample was crushed in air before use and

likely dried slightly. In principle, both effects can be quantified gravimetrically. In practice, residual bulk sample surface water and sample losses on crushing make this difficult. Notwithstanding, a correction can be carried out within the analysis. However, looking forward to what follows, we note that applying this correction does not substantially affect the quantitative conclusions of the work. The correction adopted first is to change the effective water to cement ratio in order to force the gradient of the best fit line to the total signal loss relative to the calculated water fraction to be equal to 1.0 down to a sample mass fraction of 0.8. The effective water to cement ratio required to achieve this is found to be 0.52. This is the basis of the third axis presented in Fig. 5 and, unless otherwise explicitly stated, all further discussion refers to this axis.

ii. *Readily evaporable water, pore size and porosity analysis*

The mobile fraction decreases linearly between water fractions 1.0 and circa 0.75. We refer to this as the first stage of drying. Below 0.75, the mobile fraction starts to decrease at a slightly faster rate before plateauing out close to zero. This is the second stage. The bound fraction increases in sympathy with the mobile fraction decrease while mobile signal remains. Thereafter, it decreases sharply towards zero in the final third stage of drying as previously noted. There are therefore two clear stages of loss of evaporable water. We seek to employ the model embodied by Eqs. (3) to (15). To that end, we have fit the mobile water loss to a straight line function first in the range 1.0 to 0.74 (stage 1, axis 3) and then again in the range 0.69 to 0.57 (stage 2, axis 3). Fig. 5 shows the best fit lines. In stage 1, the gradient and intercept are 1.16 and -0.424 while in stage 2 they are 1.60 and -0.717. Direct application of the model, and assuming $q'=2$ representing a mono-layer of adsorbed hydrogen in the sheet pores

1 yields pore thicknesses of $(p+2) = 14.6$ water molecules and $(q+2) = 5.3$ water
 2 molecules for the two pore types respectively.

3 Given no NMR evidence for large capillary pores, we assume that the first pores to
 4 dry are the inter C-S-H gel pores and infer that these have a nominal width of 4.1 nm
 5 on the basis of 0.28 nm per water molecule [24]. Equally, we assume that the next
 6 (second) stage of drying involves water loss from the intra C-S-H sheet pores in
 7 which case these have a width of 1.5 nm. The larger of these two widths, which are
 8 calculated from the *amplitudes* of the NMR signal, is a little below, but generally in
 9 accord with, the estimated range of our previous results which were based on the
 10 NMR relaxation *times* [13,14]. The smaller is fractionally larger than that previously
 11 estimated. Both methods assume fast exchange of hydrogen between pore surface and
 12 bulk sites. The relaxation time method however, requires considerable reliance on
 13 careful calibration of the pore surface relaxivity: detailed model dependence that is
 14 not inherent to the new estimates. Moreover, the new analysis goes further than the
 15 previous analysis based on relaxation times in so much as the relative specific surface
 16 area of the two pore types can also be evaluated. The intercepts of the fit lines in Fig.
 17 5 can be used in conjunction with Eqs. (12-15) to yield $M = 0.027$ and $N = 0.065$ both
 18 in arbitrary signal intensity units. The ratio, N/M is the ratio of the specific area of
 19 intra C-S-H sheet to inter C-S-H gel pores respectively. This ratio is 2.4. As a guide, if
 20 it is assumed that gel pores arise from the arbitrary stacking of layers of a few sheets
 21 each, then they will likely have a comparable area. Hence one may conclude that the
 22 C-S-H layers are on average 2 to 3 sheets thick.

23 Also, one can calculate the ratio of the sheet to gel porosity as
 24 $N(q+2) : M(p+2) = 0.88$. This implies that the sheet porosity is 47 % of the total.

1 However, if the porosity is based on the easily evaporable water content only, then the
2 volume ratio is $Nq : Mp = 0.63$ so that the sheet porosity is 38 % of the total.

3 iii. *Alternate corrections to data*

4 These calculations have been based upon a calculated effective water to cement ratio
5 of 0.52. The alternate correction factor is to add a constant to the sample mass to
6 reflect water loss during crushing, again to force the gradient of the total signal loss to
7 unity. The necessary correction factor required is -29.9% of the water content at
8 $w/c = 0.4$. This is negative suggesting that the sample gained water from the air
9 during crushing. This is unrealistic. Notwithstanding, the fit parameters for this
10 correction yield $(p+2) = 14.6$ and $(q+2) = 5.3$. These are both unchanged reflecting the
11 pore thickness model invariance to these corrections. The pore specific areas are more
12 affected: $M = 0.011$ and $N = 0.084$ giving pore areal and volume (porosity) ratios of
13 7.6 and 2.8 respectively. A difficulty with this correction is that the predicted
14 Portlandite fraction becomes 39%.

15 A further enhancement to the fitting is to not only force the gradient of the total signal
16 loss to unity, but also require the Portlandite fraction to be the 28.8 based on XRD
17 analysis of samples made from the same material by similar methods [25]. This is
18 achieved for an effective water to cement ratio of 0.49 and a crushing water mass gain
19 of 6%. In this case $(p+2) = 14.6$ and $(q+2) = 5.3$ as before and $M = 0.024$ and
20 $N = 0.068$ so that the sheet to gel pore area and volume (porosity) ratios are 2.8 and
21 1.0 respectively in reasonable agreement with the earlier estimate based on a water to
22 cement ratio correction only.

23 iv. *The third stage of drying*

1 Finally we explore the third stage of drying. Here we find that, after a transition
2 around 180 °C, relative sample mass circa 0.8, we see a greatly accelerated loss of
3 total signal with mass. Unfortunately this coincides with our need to switch to a non-
4 vacuum oven at 200 °C. The graph is near linear with a gradient of 3.0 (axis 3). Since
5 signal is lost in direct proportion to water loss in the readily evaporable stages, the
6 only possibilities are that to a greater or lesser extent, hydrogen, but not oxygen is
7 being lost or that the sample is also gaining mass in parallel with drying. We look to
8 carbonation as a mechanism for the latter. Differential scanning calorimetry (DSC)
9 experiments performed on duplicate samples showed that carbonation is indeed
10 significant on our completely dried material, although it is not possible to exactly
11 quantify the extent from the DSC carried out. Given the molecular mass of water (18)
12 and carbon dioxide (44), we calculate that the observed total signal loss with mass is
13 achieved if, for every water molecule leaving the sample, 0.273 CO₂ are gained. Put
14 another way, we gain 1 CO₂ for every 3.66 waters lost. Up to a temperature where the
15 bound intensity re-attains the initial value, it is reasonable to assume that this is
16 carbonation of the C-S-H. This would be in accord with conventional understanding
17 where carbonation accelerates in partially dried C-S-H [26]. Such an analysis and
18 interpretation then suggests that there are circa 3 - 4 evaporable water molecules
19 associated with each Ca ion if complete carbonation is achieved. However, since this
20 is stage 3, the implication would be that $q' > 2$ in stage 2. The apparent discrepancy is
21 almost certainly an artefact of assuming discrete drying stages.

22 Beyond a temperature of 180 °C the experiment begins to enter a regime where
23 breakdown of the Portlandite into C and H is possible and where carbonation of the C
24 within Portlandite can become significant. Hence the total signal decreases below the
25 initial bound value.

6. Discussion

i. C-S-H micro-structure

Taylor [27a] reviews work and presents further data on the water content of cement, discussing this in the context of evaporable / non evaporable water (non-evaporable being defined as that remaining at circa 150 °C) and bound / unbound water (bound being defined as that remaining at circa 90 C or 11% RH). He presents exemplar calculations of mass balance and water content for different cement phases from which the bound and non evaporable water fractions are calculated, noting that “*many variants of the calculation are possible*” [27b]. Observing the difference between bound and non-evaporable water contents, the conclusion is reached that the Feldman-Sereda model [20] is compatible with “*the essential features*” of the Powers-Brownyard model [28] and that “*about a third of the gel porosity of the Powers Brownyard model is inter layer space*” [27c] - that is intra C-S-H sheet as defined in this work. Our results support these calculations and observations.

In a series of papers based on the results of small angle neutron and X-ray scattering, Jennings, Allen and co-workers [19,29,30] have proposed a hierarchical structure comprising highly concentrated, colloidal C-S-H nano-particles dispersed in water. The particles are made of sheet like solids interspersed with water layers as discussed here. The particles pack and flocculate into what they term “globule flocs” producing further gel pores with characteristic sizes 1-3 and 3-12 nm. The primary differences to the analysis presented here are that, first we consider a hierarchy of only two sizes and second that we consider that the inter-particle pores are predominantly planar. It is possible to modify our analysis for the case of spherical particles. If this is done, then, in order to obtain the same surface to volume ratio for the space between the particles, the radius of the particles should be 6.7 or 5.2 nm depending on whether cubic or

1 hexagonal packing is assumed. Considering the wide range of sizes proposed the
2 results presented in this paper are not incompatible.

3 In other work, Richardson [31] discusses a distinction between high density inner
4 product and low density outer product. The outer product is further dependent on the
5 C/S ratio, being either fibrillar or foil like. The proposed geometries are more
6 consistent with the suggestions of this work, although without considerably more data
7 on different cements, at different ages and at different C/S ratio, we cannot resolve the
8 finer distinctions of Richardson.

9 More recently, Pellenq et al [32] have carried out molecular dynamics simulations of
10 C-S-H starting from tobermorite–jennite like structures in which the C/S ratio has
11 been adjusted and the water content slowly relaxed to equilibrium. This results in a
12 sheet structure with a C-S-H density much closer to that measured by small angle
13 scattering, distorted layers around the silica regions and a modified sheet spacing
14 with additional adsorbed water. The spacing is not too far removed from the 1.5 nm
15 calculated in this work. The adsorbed water is found to be in ultra-high confining
16 environments. Pellenq et al, however, do not comment on the size of the larger pores
17 between C-S-H particles.

18 ii. *Carbonation and micro-structural damage*

19 Two potential criticisms of our work are first that the sample was dried by heating and
20 second that the experiments were not performed in a CO₂ free environment. The
21 former, especially drying at elevated temperature, almost certainly led to micro
22 structural damage. The latter led to carbonation. The reasons are both historical and
23 pragmatic. The initial aim was only to ascertain the bound water fraction in as cured
24 material as measured by NMR in order to compare this with expectation. For this

1 reason, neither subsequent damage by heating nor carbonation were an issue at the
2 outset. Only subsequently, was it realised that the data potentially contained new pore
3 size information and that the significance of this information was likely greater than
4 the initial result, but that carbonation and damage due to sample preparation were
5 therefore problematic.

6 We discuss the likely impact of carbonation on the results first. Up to a temperature of
7 200 C, the samples were dried in a vacuum oven and measured at room temperature in
8 small sealed tubes. This will have lessened opportunity for carbonation. That it is not
9 hugely significant is suggested by the fact that the gradient of total signal loss with
10 mass in Figure 5 is constant and, for the uncorrected relative mass axis, a little less
11 than one. Carbonation would have increased the gradient above one. Also, over such a
12 wide mass loss range, one might not expect the degree of carbonation to always be
13 proportional to the total mass loss (especially given the mode of drying in short
14 bursts) as would needs be the case for a linear decrease. Since all the pore size
15 information is calculated from well within this range of drying temperature, then we
16 believe that the pore sizes deduced are more reliable than simply indicative.

17 Above 200 C, a vacuum oven was not available. The signal loss gradient increases
18 dramatically due to carbonation as discussed. No pore size information is deduced
19 here. Rather, an estimate is made of the degree of carbonation in terms of the number
20 of added CO₂ for total lost water molecules. That carbonation has occurred is further
21 evidenced by the DSC experiments performed on the dried material.

22 We turn now to the impact of micro structural damage due to heating. Potentially this
23 is a more serious problem as it negates one of the primary advantages of NMR which
24 is usually regarded as both non-destructive and non-invasive. Not even drying by
25 other means will necessarily overcome this difficulty. However, careful consideration

1 of the effect that collapse of empty pores may have on our results suggests that the
2 impact may not be as serious as at first thought. The implicit assumption in Figure 2 is
3 that pores do not collapse on drying. Consider drying as assumed in Figure 2b(ii), and
4 additionally that an empty pore space collapses as water is removed. What remains
5 within the pore are the two surface layers of water. The solid-like NMR signal will be
6 unaffected. For this reason, a degree of credence can be applied to the pore size
7 analysis. This would not be the case for drying as suggested by Figure 2b(i), but then
8 we do not assume this mode of drying.

9 To conclude this section, we note that both carbonation and micro structural damage
10 may affect our data. However, the work to date has shown an important new way in
11 which we may probe the microstructure of cement. With the caveats outlined,
12 quantitative results have been obtained. It should be stressed that the total time
13 required to acquire all the data presented in Figure 5 is circa 6 weeks. This is for two
14 reasons: first that the samples are equilibrated at each and every stage; and second that
15 in order to resolve the changing gradients, a large number of water contents have been
16 measured. Drying at constant relative humidity using salts was not thought to offer
17 sufficiently refined drying to see the break in gradient, with only limited steps
18 available, while using a humidity controlled environmental chamber was too resource
19 intensive for initial work. Plans have been made to repeat the experiments using
20 controlled drying in controlled humidity, CO₂ free environment.

21 iii. *NMR methodology*

22 The method we have presented for pore size analysis of C-S-H in this work is distinct
23 from previous measurements using either relaxation time analysis or (potentially)
24 restricted NMR diffusometry. Most importantly, the new method is independent of
25 knowing the surface relaxivity. However, the problem has shifted to one of fitting,

1 and extrapolating to zero time, NMR signals. We have chosen an exponential form for
2 the mobile signal component (which is likely uncontroversial) and a Gaussian for the
3 solid component and have back extrapolated both their amplitudes to zero time using
4 simple exponentials. Authors such as Powles and Strange [33] and Boden and Levine
5 [34] have discussed the shape and echo time dependence of solid echoes for simple
6 spin systems such as in crystalline gypsum. Empirically, for a complex structure such
7 as cements the analysis is inapplicable and hence we have used the forms as
8 discussed. Alternate forms yielded less good fits to the data.

9 **7. Conclusion**

10 We have presented an analysis of the porosity in white cement pastes based upon
11 NMR signal amplitudes as a function of sample mass during controlled drying. The
12 analysis has been interpreted in terms of water loss from two reservoirs of nano-scale
13 planar pores that are suggested to be first the intra C-S-H sheet pores and second the
14 inter C-S-H gel pores. The best estimates for the sheet- and gel-pore thicknesses are
15 1.5 and 4.1 nm respectively. The ratio of the specific areas of the two pores types is
16 estimated to be 2.4. The total volume ratio of the pore types is 0.88 whereas the
17 volume ratio of readily evaporable water within them is 0.63, implying that the sheet
18 (sheet mobile water) porosity is 0.47 (0.38) of the total. The work has thrown light
19 from a new perspective on the question of pore widths and total volumes. Further
20 insight into the lateral extent of pores is forthcoming from double quantum filtered
21 measurements being reported elsewhere [35].

22

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References

- 1 P. J. McDonald, M. Mitchell, M. Mulheron, Cement products: characterisation
2 by NMR and MRI, Encyclopaedia of Materials: Science and Technology, Elsevier,
3 (2005) 1-9
4
- 5 2 J. –P. Korb, NMR and nuclear spin relaxation of cement and concrete
6 materials, Current Opinion in Colloid & Interface Science 14 (2009) 192–202
7
- 8 3 D. D. Lasic, J. M. Corbett, J. Jian, J. C. Mactavish, M. M. Pintar, R. Blinc, G.
9 Lahajnar, NMR Spin Grouping in Hydrating Cement at 200 Mhz, Cem. Concr. Res.,
10 18 (1988) 649-653.
11
- 12 4 D. D. Lasic, M. M. Pintar, R. Blinc, Are Proton NMR Observations
13 Supportive of the Osmotic Model of Cement Hydration, Philosophical Magazine
14 Letters, 58 (1988) 227-232.
15
- 16 5 L. Miljkovic, D. D. Lasic, J. C. Mactavish, M. M. Pintar, R. Blinc, G.
17 Lahajnar, NMR-Studies of Hydrating Cement - a Spin-Spin Relaxation Study of the
18 Early Hydration Stage, Cem. Concr. Res., 18 (1988) 951-956.
19
- 20 6 L. Miljkovic, J. C. Mactavish, J. Jian, M. M. Pintar, R. Blinc, G. Lahajnar,
21 NMR-Study of Sluggish Hydration of Superplasticized White Cement, Cem. Concr.
22 Res., (16) 1986. 864-870.
23

1 7 L. J. Schreiner, J.C. Mactavish, L. Miljković, M.M. Pintar, R. Blinc, G.
2 Lahajnar, D. Lasic, L.W. Reeves, NMR line shape-spin-lattice relaxation correlation
3 study of portland-cement hydration, J. Am Ceram. Soc. 68 (1985)10-16
4

5 8 J. Greener, H. Peemoeller, C.H. Choi, R. Holly, E.J. Reardon, C.M. Hansson,
6 M.M. Pintar, Monitoring of hydration of white cement paste with proton NMR, J.
7 Am Ceram. Soc. 83 (2000) 623-627.
8

9 9 W. P. Halperin, J. –Y. Jehng, Y. –Q. Song, Application of spin-spin relaxation
10 to measurement of surface area and pore size distributions in a hydrating cement
11 paste, Magn. Reson. Imag. 12 (1994) 169-173.
12

13 10 A. J. Bohris, U. Goerke, P. J. McDonald, M. Mulheron, B. Newling, B. Le
14 Page, A broad line NMR and MRI study of water and water transport in Portland
15 cement pastes. Magn Reson Imag, 16 (1998) 455-461.
16

17 11 J. C. MacTavish, L. Miljkovic, H. Peemoeller, J. M. Corbett, J. Jian, D. D.
18 Lasic, R. Blinc, G. Lahajnar, F. Milia, M. M. Pintar, Nuclear magnetic resonance
19 study of hydration of synthetic white cement: Continuous quantitative monitoring of
20 water and $\text{Ca}(\text{OH})_2$ during hydration. Advances in Cement Research, 8 (1996) 155-
21 161.
22

23 12 A. Plassais, M. P. Pomies, N. Lequeux, J. –P. Korb, D. Petit, F. Barberon, B.
24 Bresson, Microstructure evolution of hydrated cement pastes, Phys. Rev. E, 72 (2005)
25 041401.

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2
3
4
5
6
7
8
9
10
11
12
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14
15
16
17
18
19
20
21
22
23
24

13 P. J. McDonald, J. -P. Korb, J. Mitchell, L. Monteilhet, Surface relaxation and
chemical exchange in hydrating cement pastes: a two-dimensional NMR relaxation
study, Phys. Rev., E 72 (2005) 011409.

14 L. Monteilhet, J.-P. Korb, J. Mitchell, P. J. McDonald, A NMR T_2 -store- T_2
2-dimensional correlation relaxation study of cement pastes, Phys. Rev. E 74 (2006)
061404.

15 A.Valori, V. Rodin, P.J. McDonald, On the interpretation of ^1H 2D NMR
relaxation exchange spectra in cements: is there exchange between pores with two
characteristic sizes or Fe^{3+} concentrations? Cem. Concr. Res. (2010)
<http://dx.doi.org/10.1016/j.cemconres.2010.03.022>

16 K.R. Brownstein, C.E. Tarr, Importance of classical diffusion in NMR studies
of water in biological cells, Phys. Rev. A, 19 (1979) 2446-2453.

17 F. D'Orazio, S. Bhattacharja, W.P. Halperin, K. Eguchi, and T. Mizusaki,
Molecular diffusion and nuclear-magnetic-resonance relaxation of water in
unsaturated porous silica glass, Phys. Rev. B 42 (1990) 9810-9818.

18 J. G. Powles, J. H. Strange, Zero time resolution nuclear magnetic resonance
transients in solids, Proceedings of the Physical Society of London, 82 (1963) 6-15.

1 19 H. M. Jennings, Refinements to colloid model of C-S-H in cement: CM-II.
2 Cem. Concr. Res., 38 (2008) 275-289.
3

4 20 R. F. Feldman, P. J. Sereda, A new model for hydrated portland cement and its
5 practical implications, Engineering Journal, 53 (1970) 53-59.
6

7 21 www.nanocem.org; European Commission contract MRTN-CT-2005-019283,
8 Nanocem.
9

10 22 G. E. Pake, Nuclear resonance absorption in hydrated crystals: fine structure
11 of the proton line, J. Chem. Phys. 16 (1948) 327-336
12

13 23 S. Meiboom, D. Gill. Modified spin-echo method for measuring
14 nuclear relaxation times. Rev. Sci. Instrum. 29 (1958) 688–691.
15

16 24 J. Israelachvili, Intermolecular and Surface Forces, 2nd ed. Academic Press,
17 London, 1992.
18

19 25 V. Kocaba, Personal communication, 2009
20

21 26 L. J. Parrot, A review of carbonation in reinforced concrete: Cement and
22 Concrete Association, 1987.
23

24 27 H. F. W. Taylor, Cement chemistry, 2nd ed.: Thomas Telford Publishing,
25 London, 1997. (a) Section 7.3.3; (b) Section 7.4.4; (c) Section 8.2.4.

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5
6
7
8
9
10
11
12
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14
15
16
17
18
19
20
21
22
23
24
25

28 T.C. Powers, T.L. Brownyard, Studies of the physical properties of hardened Portland cement paste, Bull. 22, Res. Lab. of Portland Cement Association, Skokie, IL, U.S.A., reprinted from J. Am. Concr. Inst. (Proc.), vol. 43 (1947). pp. 101– 132, 249– 336, 469– 505, 549– 602, 669– 712, 845–880, 933–992.

29 H. M. Jennings, A model for the microstructure of calcium silicate hydrate in cement paste. Cem. Concr. Res., 30 (2000) 101-116.

30 A. J. Allen, J. J. Thomas, H. M. Jennings, Composition and density of nanoscale calcium-silicate-hydrate in cement, Nature Materials, 6 (2007) 311-316.

31 I. G. Richardson, The calcium silicate hydrates, Cem. Concr. Res., 38 (2008) 137-158

32 R. J. –M. Pellenq, A. Kushimac, R. Shahsavarib, K. J. Van Vlietd, M. J. Buehlerb, Y. Sidney, F. -J. Ulmb, A realistic molecular model of cement hydrates. PNAS, 106 (2009) 16102-16107.

33 J. G. Powles, J. H. Strange, Zero time resolution nuclear magnetic resonance transients in solids Proc. Phys. Soc. 82 (1963) 6-15.

34 N. Boden, Y. K. Levine, R. T. Squires, NMR dipolar echoes in solids containing spin ½ pairs, Chem. Phys. Letts. 28 (1974) 523-525.

- 1 35 A. Valori, Characterisation of cementitious materials by ^1H NMR, PhD
- 2 Thesis, University of Surrey, available at:
- 3 http://www.nanocem.org/fileadmin/nanocem_files/documents/MC-
- 4 RTN/Projects/Project_4/thesis_valori_final.pdf

Figure captions:

Fig. 1. The solid echo pulse sequence timing diagram.

Fig. 2. (a) A planar pore full of mobile water (circles). (b) Two possible ways of emptying a pore showing mobile and immobile (crosses) water. In (b(ii)) definitions of p (and q), and s (and s') are shown. (c) A pore with surface adsorbed water only. (d) An empty pore. (e) An illustrative schematic defining intra C-S-H sheet and inter C-S-H gel pore water (after reference [20])

Fig. 3. An exemplar solid echo signal ($\tau = 40 \mu\text{s}$) recorded from white cement paste after drying to 0.80 the initial mass. Inset: a similar echo ($\tau = 20 \mu\text{s}$) from dried $\text{Ca}(\text{OH})_2$. The dotted lines show the Gaussian and free induction decay signals fit to the data. The Gaussian is centred on $t = \tau$; the decay is extrapolated back to $t = -\tau$ (not shown). A solid line, almost totally overlain by data points, is the combined fit.

Fig. 4. The τ dependence of the solid echo (circles) and mobile (triangles) signal intensity for white cement paste after drying to 0.80 the initial mass. The solid lines are exponential decay fits to the data.

Fig. 5. The total NMR signal (squares), solid (circles) and mobile (triangles) signal fractions as a function of the actual relative mass of the sample (top axis); of the relative mass of water assuming a water to cement ratio of 0.4 (middle axis); and of the relative mass of water assuming a water to cement ratio of 0.52 (bottom axis). The indicative drying temperature is shown above the plot. The solid lines are least squares fits to the data discussed in the text.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5