The densification of C-S-H measured by ¹H NMR relaxometry.

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ABSTRACT:

The nano-scale morphology of, and pore water interactions in, calcium-silicate-hydrate (C-S-H), the active component of cement, remain uncertain. ¹H nuclear magnetic resonance (NMR) can fully characterise the nano-porosity of C-S-H in as-prepared material without the need for damaging sample drying. We use NMR to follow the density of C-S-H in sealed cured pastes as a function of degree of hydration (α) and water to cement ratio. We show clear evidence for C-S-H densification. The C-S-H "solid" density, exclusive of gel pore water, slightly decreases from $\rho_x = 2.73$ g/cm³ at $\alpha \approx 0.4$ to 2.65 g/cm³ at $\alpha \approx 0.9$ due to an increase in the number of layers in the nanocrystalline aggregates. In the same range, the C-S-H "bulk" density, including gel water, increases from around 1.8 to 2.1 g/cm³. The increase corresponds to a transition from growth of low density product containing gel pores to higher density product devoid of gel pores. We update Powers' classical model from 1947. In contrast to the single "hydrate" of Powers', NMR differentiates between C-S-H and calcium hydroxide and separates out the inter-layer water within the C-S-H. It shows a clear non-linearity in the growth of the different fractions with α .

KEYWORDS: porosity, density, hydrates, chemical composition, white cement

INTRODUCTION:

Calcium silicate hydrate (C-S-H) is a highly disordered nano-scale material comprised of layers of calcium and oxygen, with SiO₂ tetrahedra attached and interspersed by water and further Ca ions. It is formed in a dissolution-precipitation reaction involving mixtures of tricalcium silicate (Alite) and dicalcium silicate (Belite) with water. Due to the importance of C-S-H as the binder phase of Portland cement it has been widely studied over many decades. Current interest in C-S-H is fuelled by the substantial contribution of cement production to global CO₂ production (currently $5-8\%^1$) and the requirement to reduce this by the incorporation of supplementary cementitious materials without impacting long term mechanical performance or durability of concrete.

Notwithstanding extensive effort, the morphology, density and composition of C-S-H continue to be the subject of active debate in the literature^{2,3,4,5}. The primary reasons are twofold. First, the structures formed are highly dependent on the chemical mixtures and reaction conditions and they may evolve over long periods of time. Second, until very recently, there has not been an experimental method available that is able to adequately characterise as-prepared C-S-H without removing the water: a procedure that damages the very nano-scale structures that are of interest.

In 1947, Powers and Brownyard published seminal work⁶ that is still widely used and cited. They reported the composition of hydrated cements based on careful study of the water adsorption and desorption isotherms. In the case of white Portland cement, the principle hydration components are solid calcium hydroxide and nano-crystalline C-S-H gel. These products are interspersed by un-reacted cement grains, capillary pores filled with water and void space. Grudemo⁷ was one of the first to propose that the C-S-H gel

comprised "solid" regions of layers including some 'chemically combined' water with small water filled pores between these regions now widely known as gel pores. Subsequent work identified two broad types of C-S-H in cement pastes, a more and a less dense phase⁸. These are sometimes attributed to C-S-H that forms in spaces within and between the confines of the original anhydrous cement particles referred to as inner and outer product respectively⁹. Richardson¹⁰ identified different morphologies of C-S-H by TEM: a fine-scale homogeneous morphology for the inner product and two distinct morphologies for outer product, a fibrillar-like structure and a foil-like structure that appear to correlate with the C/S^{*} ratio. The foil-like structure preferentially forms below a C/S ratio of about 1.5.

Growth mechanisms are likely to play a crucial role in determining the evolved structure. Several authors have proposed mechanisms of C-S-H nucleation and growth from existing surfaces with a quasi-continuous network of C-S-H layers extending from one nanocrystalline region to another interspersed by gel pores¹¹. Other authors propose nucleation of colloidal particles of C-S-H within the pore solution leading to a morphology arising from coalesced or flocculated particles⁴. In either case, different authors distinguish various types of water filled spaces including nanometre thick layers of water between the calcium silicate sheets and slightly larger gel pores between the nano-crystalline regions. In the colloidal model of Jennings⁴, the nano-crystalline regions are referred to as globules and comprise calcium silicate layers with water between.

^{*} A note on notation. In cement chemistry, C=CaO, S=SiO₂, H=H₂O, A=Al₂O₃ and CH=Ca(OH)₂. The atomic elements without oxides are expressed in a conventional manner. In this work, where it is ambiguous, atomic hydrogen is notated *Hyd*. The abbreviation *AMU* denotes atomic mass units, *n* is molar content and *f* is mass fraction of anhydrous powder.

Additionally, there are intra-globular pores within nano-crystallites formed by heterogeneities in the sheet packing, small globular pores between the nano-crystalline particles and large globular pores between particle flocs all within the size range <1 to 12 nm.

Measurements of the density of C-S-H depend upon method and sample preparation. Results of different studies and calculations have been reviewed by Jennings⁴ in the context of the colloidal model and vary between 1.8 and 2.8 g/cm³. Much of this variability arises from the fraction of the gel pore water and other nanoscale confined or bound water that is, or is not, inferred to be included in the measurement. It also depends on whether or not the sample has been dried, a process that potentially damages the delicate nano-structure. A recent and widely cited result¹² is the density obtained by small angle neutron scattering (SANS) for C-S-H in Portland cement hydrated for 28 days at 20°C. This measurement is made in saturated material but is specifically for the solid nanocrystalline C-S-H excluding the gel pore water: $\rho = 2.604$ g/cm³.

In a recent paper¹³, we showed how a simple bench-top ¹H NMR experiment can be used to measure the density of the C-S-H layers and inter-layer water exclusive of the gel water and how the water fractions in each of the primary components of the paste may be quantified. The measurement was performed on a 28 day old paste cured underwater. We also reported the first pore-type resolved desorption isotherm for cement paste. It is the purpose of this paper to exploit this new capability to follow the density of C-S-H throughout the hydration of cement pastes cured under sealed conditions at different water to cement ratios and to show how this leads naturally to clear evidence for densification during growth. The results shed light on the possible ways in which the C-

S-H can grow. In a subsequent paper we will extend the adsorption isotherm study to show one and a half complete cycles of the desorption-adsorption isotherm and thus shed light on the manner in which pores first empty and then re-fill with water.

THEORY:

• C-S-H density and composition

The interpretation of ¹H NMR relaxation data in cements as presented in¹³ and further discussed in the results section is based on the observation that the NMR signal can be resolved into 5 discrete populations of water. The first is a fast relaxing component with a ¹H nuclear spin-spin relaxation time T_2 of the order of 10 µs. It is assigned to ¹H chemically combined in the solid crystalline phases calcium hydroxide and ettringite. Two further components have relaxation times of the order 80-120 µs and 300-500 µs. These are attributed to water in C-S-H inter-layers and to gel pore water respectively. The fourth and fifth components are assigned to water in nano-scale inter-hydrate spaces and to water in larger capillary pores and micro-cracks. A key test that proper account has been taken of all the water in the sample was provided in our earlier paper where we showed that the total NMR signal loss with drying is linear and consistent with the known water to cement ratio¹³.

This assignment is generally in accord with earlier observations of similar materials made with comparable equipment by Holly *et al*¹⁴. However, we note that some other prior studies have lacked the temporal resolution to see the fastest relaxing components, in particular the CH and ettringite while others have either failed to separately resolve the

C-S-H layer and gel pore water. Moreover, some earlier studies have lacked quantification of signal amplitudes and hence water mass in different environments due to the difficulty of measuring the intensity fraction of chemically combined ¹H. We have overcome this last difficulty by use of a quadrature echo pulse sequence method^{15,16}.

With this assignment, mass and volume balance equations can be written for the paste per gram of anhydrous powder:

$$1 + \frac{w}{c} = (1 - \alpha) + \frac{w}{c} \left[\beta I_{solid} + \gamma I_{CSH} + \delta \left(I_{gel} + I_{cap}\right)\right]$$
 Eq. (1)

$$\frac{1}{\rho_{uc}} + \frac{w}{c\rho_{w}} = \frac{(1-\alpha)}{\rho_{uc}}$$

$$+ \frac{w}{c} \left[\frac{\beta I_{solid}}{\rho_{solid}} + \frac{\gamma I_{CSH}}{\rho_{CSH}} + \frac{\delta (I_{gel} + I_{cap} + I_{void})}{\rho_{w}} \right]$$
Eq. (2)

The subscripts *uc*, *w*, *solid*, *CSH*, *gel*, *cap* and *void* refer to unreacted cement, water, chemically combined water, C-S-H, gel pore water, capillary pore water and chemical shrinkage respectively. In Equation (1), the left hand side is the sum of the original anhydrous powder and the mix water mass. The right hand side is the sum of the masses of the different products, written in terms of their respective water contents and signals, *I*, as detailed below. Equation (2) reworks Equation (1) for volume by dividing by the product densities, ρ , and adding a term for the chemical shrinkage volume (voidage). The measured water signal intensities, *I*, are expressed as a fraction of total signal intensity

arising from the original water of mixing which for a sealed paste, is $I_{solid} + I_{CSH} + I_{gel} + I_{cap} = 1$. The signal fraction, I_{void} , takes the total above unity. It corresponds to water occupying the chemical shrinkage volume. In underwater cured samples, I_{void} is measured by NMR as explained elsewhere¹³. For sealed cured samples, as here, I_{void} is calculated from a separate (not NMR) measurement of the chemical shrinkage volume.

The parameter α is the degree of hydration, defined as the mass fraction of anhydrous powder consumed in the reactions. The parameters β , γ and δ are the inverse mass-fractions of water in the solid, C-S-H and pore fluid respectively. The solid signal is assumed to comprise two parts, CH and ettringite: $I_{solid} = I_{CH} + I_{ett}$. The molecular mass of CH, i.e. Ca(OH)₂, is 74 while that of water is 18. Hence, $\beta_{CH} = 74/18$. The fraction of the total water consumed in the CH is I_{CH} so that the mass of CH per gram anhydrous cement is $w\beta_{CH}I_{CH}/c$. Similarly, $\beta_{ett} = 1255/576$ and the mass of ettringite is $w\beta_{ett}I_{ett}/c$. It follows that the total mass and volume of the solid products (CH and ettringite) per gram of anhydrous powder are given by $W/c \beta I_{solid} = W/c (\beta_{CH}I_{CH} + \beta_{ett}I_{ett}/\rho_{ett})$ respectively. We treat the pore fluid as water, so that $\delta = 1$. We take $\rho_{uc,CH,ett,w} = 3.15, 2.24, 1.77$ and 1 g/cm³ respectively. Once I_{ett} is known, I_{CH} may be calculated from I_{solid} and known constants, as may β and ρ_{solid} .

The unknowns are therefore α , I_{ett} , ρ_{CSH} and γ . A measurement of α , the degree of hydration can be made independently, using, for instance, XRD. I_{ett} can be calculated from the mass fraction of ettringite also measured independently, using, for instance,

XRD. Hence we have two equations that enable the C-S-H density, ρ_{CSH} , and inverse mass fraction of water, γ , to be found.

The C-S-H composition is expressed as $Ca_z.(Si_y,Al_{(1-y)})O_{(z+1/2y+3/2)}.(H_2O)_x$. The parameters *x*, *y* and *z* may be determined from three further equations. First, γ is related to the number of water molecules *x* as

$$x = \frac{56z + 9y + 51}{18(\gamma - 1)}$$
 Eq. (3)

where $y = n_{Si}^{CSH} / (n_{Si}^{CSH} + n_{Al}^{CSH})$ and $n_{Si,Al}^{CSH}$ are the molar content of Si and Al in the C-S-H. The numerical constants derive from the atomic masses of Ca, Si, Al, O and H.

Second, a conservation equation can be written for the overall Ca/(Si+Al) ratio. If α' is defined as the mass of reacted (C₃S + C₂S) divided by the mass of the anhydrous powder, and ignoring minor reactive components other than C₃A, then

$$\frac{3\left(\frac{0.9\alpha'}{C_3 S^{AMU}}\right) + 2\left(\frac{0.1\alpha'}{C_2 S^{AMU}}\right) + 1.5n_{Al}^{CSH}}{\left(\frac{0.9\alpha'}{C_3 S^{AMU}}\right) + \left(\frac{0.1\alpha'}{C_2 S^{AMU}}\right) + n_{Al}^{CSH}}$$
Eq. (4)
$$= \frac{\frac{I_{CH}n_{Hyd}}{2} + \frac{I_{CSH}n_{Hyd}z}{2x} + 1.5n_{Al}^{CSH}}{\frac{I_{CSH}n_{Hyd}y}{2x} + n_{Al}^{CSH}}$$

The first term of the numerator of the left hand side of this expression expresses the fact that there are 3 moles of Ca per mole of C_3S ; $1/C_3S^{AMU}$ moles per gram of C_3S ; and that subject to the assumptions detailed below $0.9\alpha'$ grams C_3S consumed in reactions per gram of anhydrous cement. Similar arguments for Ca from C_2S and for Si from C_3S and

 C_2S lead to the second term of the numerator and the first two of the denominator respectively. Ca and Al derived from C₃A lead to the final term in the numerator and denominator respectively. On the right hand side, $n_{Hyd} = (2/18)(w/c)$ is the molar content of hydrogen in the paste per gram anhydrous powder. The moles of Ca and Si in the CH and C-S-H are written in terms of the signal fractions and n_{Hyd} . The Ca and Al contributions to the C-S-H from the C₃A are the same as on the left hand side. Equation (4) is an elaborated version of equation (4) in our earlier paper¹³. The further assumptions leading to equation (4) as now stated are as follows. First, it is known that in the hydration reaction, C_3S is consumed much more quickly than C_2S^{17} . Hence, we assume a consumption ratio of 9:1 in favour of C_3S until it is been used up. This implies that equation (4) is valid in the range $0 < \alpha' \leq f_{C3S}/0.9$ where f_{C3S} is the fraction of C₃S in the anhydrous powder (assuming $f_{C3S}/9 < f_{C2S}$, the C₂S fraction). Equation (4) may be re-cast for $f_{C3S}/0.9 < \alpha' \le 1$ by replacing α' in the first two terms in both the denominator and numerator of equation (4) by $f_{C3S}/0.9$ and adding an additional term to the numerator of $2(\alpha' - f_{C3S}/0.9)/C_2S^{AMU}$ and of half this value to the denominator. Second, X-ray analysis of samples at different ages, to be described in the next section, shows that ettringite all forms early, at most within the first 3 days. Since our analysis mainly focuses on data acquired after three days, we make the simplifying assumption that the ettringite forms at the start of the process. Third, we assume that the aluminium from the C₃A remaining after ettringite formation is included in the C-S-H from the start. The factors determining the extent of aluminium uptake into the C-S-H are not well understood¹⁸. This hypothesis implies there is a negligible amount of alumina in the pore solution, which is in accord with thermodynamics and experimental results¹⁹. It follows

that $n_{Al}^{CSH} = 2(f_{C3A} - f_{C3A}^{Ett})/C_3 A^{AMU}$ where f_{C3A} and f_{C3A}^{ett} are the mass fractions of C₃A in the anhydrous powder and the C₃A mass fraction used to form ettringite respectively.

Finally, given the above assumptions concerning the formation of ettringite, the Si to (Si+Al) ratio, *y*, can be expressed as

$$y = \frac{n_{Si}^{CSH}}{n_{Si}^{CSH} + n_{Al}^{CSH}} = 1 - \frac{4x(f_{C3A} - f_{C3A}^{Ett})}{I_{CSH}n_{Hyd}C_3A^{AMU}}$$
Eq. (5)

The alternate C-S-H composition including gel water, $Ca_z \cdot (Si_y, Al_{(1-y)})O_{(z+1/2y+3/2)} \cdot (H_2O)_x$ has

$$x' = x(I_{CSH} + I_{gel})/I_{CSH}$$
Eq. (6)

In summary, therefore we find the inverse water content, γ , from Equation (1), the NMR intensities and an XRD measurement of the degree of hydration and ettringite content. We go on to find the C-S-H density from Equation (2) knowing additionally the chemical shrinkage. Finally, using Equations (3), (4) and (5) and the anhydrous powder composition, we find the 3 C-S-H composition parameters, *x*, *y* and *z*. Of these, *x* gives the water content and *z* the Ca/(Si+Al) ratio of the C-S-H.

As a final observation, we note that there will always be a (small) experimental discrepancy between the solid content measured by NMR and by, e.g. XRD. This means that there are two means by which the NMR CH content may be determined. One is to subtract the XRD ettringite mass, converted to water fraction from the NMR solid signal. The other is to apportion the NMR solid signal between CH and ettringite in the same

ratio as measured by XRD, converted to water fraction. We use the former for two reasons. First, beyond the early stages of hydration that are not considered in this study, the ettringite content is constant (see below) whereas the CH content is increasing. Thus, in principle, a measurement is only required at one time point. Second, the ettringite content is relatively difficult to measure, so an average content from multiple samples may be used. We have tested the alternate method. For our results it leads to changes in the measured parameters at the 1% level. The biggest discrepancy is for z, where the difference is about 3%.

• Cement pore size distribution

It is well accepted in the NMR literature that the size of pores may be inferred from NMR relaxation times using the fast diffusion model of relaxation. According to this model²⁰, first applied to cement by Halperin *et al*²¹, the surface to volume ratio of a filled pore is given by

$$\frac{1}{T_{1,2}} \sim \frac{\varepsilon S}{V} \frac{1}{T_{1,2}^{surf}}$$
 Eq. (7)

where $T_{1,2}$ are the measured spin-lattice and spin-spin relaxation times, $T_{1,2}^{surf}$ are the corresponding values for surface adsorbed molecules, *S* and *V* are the pore surface area and volume respectively and ε is the thickness of the adsorbed layer. The key unknown here is the surface relaxivity, $\varepsilon/T_{1,2}^{surf}$. In cements, the primary ¹H relaxation mechanism is interaction with surface Fe³⁺ paramagnetic impurities. Korb and co-workers^{22,23} have shown how the relaxivity may be calculated given the surface density of paramagnetic Fe³⁺ impurities within the pore and other parameters such as the distance of closest

approach of a water molecule to an impurity and the thickness of an adsorbed water layer. In our previous paper¹³, we made an empirical measurement of the surface relaxivity based on the asymptotic value of the relaxation time as the pore water is removed down to monolayer surface coverage (75 µs at an NMR frequency of 20 MHz) combined with the diameter of a water molecule, 0.28 nm. This gave 3.73×10^{-3} nm/µs, an indicative value we use here since the NMR frequency is different. In subsequent calculations we assume planar pores of area *A* so that, ignoring edge effects, S = 2A, V = Ad and hence S/V = 2/d where *d* is the pore width or "*size*".

EXPERIMENTAL METHODS:

White cement paste was obtained from Aalborg Portland. The composition of the anhydrous powder is: 66.9 % C₃S; 20.0 % C₂S; 3.5 % C₃A; and 4.4 % calcium sulfates with all other phases less than 1 %. Typically 80 g of anhydrous powder was mixed in the desired water to cement, w/c, for 2 minutes at 1600 rpm. Aliquots about 0.35 cm³ were deposited directly into NMR tubes and tightly sealed with parafilm®. A glass rod was included to reduce the free air volume. Samples were stored in a temperature controlled room at 20 °C during hydration. Samples were periodically measured as prepared, in a temperature controlled NMR probe. Considerable care was taken to ensure the reproducibility of the results across multiple repeat samples and repeat measurements.

¹H NMR measurements were made on a Bruker Minispec NMR spectrometer operating at 7.5 MHz. The 90° pulse length was 2.9 μ s. Both quadrature (solid) echo¹⁵ and Carr-Purcell-Meiboom-Gill CPMG²⁴ (spin) echo measurements were made. The quadrature

echo signals were recorded as a function of pulse gap in the range $\tau = 15 - 45 \,\mu s$. They were deconvoluted into a Gaussian and an exponential decay part. The exponential fraction was attributed to mobile water. The Gaussian had a very short time constant, of the order of 10 µs, and was assigned to water in crystalline solid phases. Its amplitude was back extrapolated to zero pulse gap using Gaussian fitting to elucidate the solid fraction. The mobile part of the signal was separately resolved into different T_2 components using the CPMG sequence. Typically 128 echoes were recorded, logarithmically spaced from 50 µs to 68 ms. The repetition time was progressively decreased from 1000 ms to 500 ms and the number of averages increased from 512 to 1024 echo trains as the relaxation times and signal-to-noise ratio decreased from initially high values to lower values in mature pastes. The signal-to-noise ratio was typically 1500:1. A minimum of 3 repeat samples were measured in every case. To find the T_2 components from the echo decays, the inverse Laplace Transform algorithm developed by Venkataramanan²⁵ was applied to the CPMG echo intensity decay. The regularisation parameter was optimised as described in Reference [25] and a value of 1.5×10^{-4} used. While the widths of the T_2 components depend upon the regularisation parameter, the integrated "peak" intensities as reported and used in this work are robust to its variation.

In sealed cured samples, the w/c ratio is known from mixing. The key unknown is the chemical shrinkage. This was measured by the conventional method of following the height of a column of water in a capillary above a sample during hydration.

Further experiments to ascertain and confirm the cement composition were carried out using X-ray diffraction with Rietveld analysis (XRD) and thermo-gravimetric analysis (TGA) for samples cured for 10 and 28 days. At 10 days the hydration was stopped by

isopropoanol exchange in one set of samples and freeze-drying in another, duplicate, set. At 28 days, only isopropanol exchange was used. XRD measurements were made with a Panalatical X'Pert Pro MPD diffractometer in a θ - θ configuration using a CuK α source (wavelength 1.54 Å) with a fixed divergence slit of 0.5°. Samples were scanned on a rotating stage between 7 and 70° (2 θ) using a X'Celerator detector with a step size of 0.0167° (2 θ) and a time step of 77.5s. TGA measurements were made with a Mettler Toledor (Switzerland) TGA/SDTA 851 analyser operating between 30 and 950°C at 10°C/min. under N₂ gas flow to prevent carbonation.

RESULTS:

Figure 1 shows the T_2 distribution map for sealed cured cement pastes after 10 days of hydration with initial *w/c* ratios of 0.32, 0.40 and 0.48. Taking the *w/c* = 0.40 data as an example, the map shows five principle components: 22.6 % at 10 µs; 25.7 % at 100 µs; 46.7 % at 340 µs; 4.9 % at 845 µs; and <0.5 % at 12 ms. The first three of these components are assigned to CH plus ettringite, to inter-layer water within the C-S-H and to C-S-H gel pore water respectively. The last two components are attributed to water in inter-hydrate spaces and to large capillary pores. They can be combined and defined as the "free" water within the paste.

In support of this assignment, we show that the water in CH and ettringite fully accounts for the shortest T_2 component and hence that no inter-layer water or residual hydroxyl group signal of C-S-H is within it so that, the next shortest T_2 component must be attributable to the inter-layer water in C-S-H.

The ettringite mass fraction in each of the pastes was measured by XRD after 3, 6 and 10 days. It did not change appreciably during this time as might be expected since calcium sulfates have all reacted by one day²⁶ and the small C₃A content does not allow a significant precipitation of AFm at later ages. As the precision of XRD for such low amounts of ettringite is not good, the average of all measurements, 0.066 grams of ettringite per gram anhydrous cement, was taken as the value for all samples as shown in Table 1. The CH fraction measured using XRD and TGA at 10 and 28 days is also shown in Table 1. From the solid phase mass fractions, and known molecular compositions²⁷, it is possible to evaluate the fraction of water consumed. This is directly comparable to the normalised NMR signal attributed to the solid. Table 1 shows that the combined water in the CH and ettringite as determined by XRD / TGA is within 1% of that determined by NMR in all the samples. This degree of agreement is better than we might have expected given the inherent uncertainties in each of the methodologies. Notwithstanding, the trend is clear and we judge that there are no immobile hydrogens within the C-S-H. The degree to which the inter-layer is protonated by OH groups remains a matter of contention and indeed such OH groups as exist in the inter-layer may be associated with relatively (rotationally?) mobile Ca ions^{3,28}. In further support of the assignment, we also note our earlier result¹³ that, upon sample drying, the NMR signal decreases linearly and yields a w/c ratio entirely consistent with the paste composition. This result verifies that we are "seeing" all the water by NMR.

NMR data has been acquired for samples as a function of hydration time. As an example, Figure 2 shows the amplitude of the NMR response assigned to crystalline

solids (CH and ettringite), C-S-H inter-layer water, gel pore water and free water for the w/c = 0.4 paste.

The free water signal decreases rapidly during the first 2 days to just over 10% of the initial value, after which it decreases much more slowly. It is of negligible amplitude at circa 28 days. During the first two days, the signals attributed to crystalline solids, to C-S-H layers and to gel pores all increase. The volume ratio of inter-layer water and gel water is approximately constant, 1:2. After two days the gel pore water signal stops increasing and stabilises at a constant value before eventually decreasing beyond 62 days. On the other hand, the water in the crystalline solids (CH and ettringite) and C-S-H interlayer water continue to grow throughout the entire experimental period (300 days). Hence, after two days, the volume ratio of inter-layer water to gel water monotonically increases.

The corresponding T_2 relaxation times of the inter-layer, gel and free water fractions are shown in Figure 3. Initially, while the signal is dominated by the single T_2 component corresponding to free water in the mix, the T_2 is long. However, it falls rapidly, along with the T_2 signal for the gel pores, approaching asymptotic values of about 1000 and 300 µs respectively as early as 0.5 days. As might be expected, the values for the C-S-H inter-layer, are fairly constant from the beginning of the measurement time at 100 µs.

Figure 4 shows the chemical shrinkage volume as measured by the conventional capillary height method for different w/c ratios and sample age. A linear best fit to the data yields a chemical shrinkage of 0.075 \pm 0.003 cm³g⁻¹ of reacted anhydrous powder. We use this as our measure of the signal voidage in equations (1) to (5). In our previous work¹³ NMR measurements were made on underwater cured material. In that case, the

voidage was determined directly from the increase in the w/c ratio of the paste measured by NMR and was very comparable to the voidage measured here by chemical shrinkage. An attempt to use NMR for sealed cured samples, by measuring the increase in signal intensity for re-wetted samples consistently under-estimated the voidage by circa 50 %.

ANALYSIS AND DISCUSSION:

• Porosity and *T*₂ analysis

The relaxation times reported above may be interpreted in terms of pore sizes according to the fast diffusion model of relaxation^{20,21,23,29}. Since the relaxation times rapidly approach constant values, it is concluded that the pores rapidly approach constant size. Application of equation (7) with surface relaxivity 0.00373 nm/µs gives averages of 0.85 nm (C-S-H inter-layer spacing), 2.5 nm (gel pores) and 8.0 nm (inter-hydrate pores). These values are fractionally smaller than previously reported (0.94, 3.1 and 10 nm), probably because the surface relaxivity is frequency dependent (earlier measurements were made at 20 MHz). We note that the inter-layer spacing is a little larger than might be expected based on the mineral analogue of C-S-H, tobermorite 14³⁰. However, in such small spaces, the concept of mobile pore-water above an adsorbed layer that underpins the model starts to break down.

A key feature of the NMR data is that the total gel porosity and gel pore size reach a plateau after about 1 to 2 days whereas the volume of hydrates continues to grow. We speculate that this marks a transition from the growth of "less dense" to "more dense" product. At the same time the size of the pores containing free water stabilises at around 8-10 nm and we assign this reservoir to inter-hydrate pores. This category of pores does not seem to be an intrinsic part of the C-S-H hydrate, because the total porosity in this

category decreases with the degree of hydration, rather than increasing, reaching zero at about 2 months hydration. Since the gel porosity does not decrease from circa 2 to 60 days hydration, we infer that the C-S-H is growing in the inter-hydrate spaces, using the inter-hydrate pore water during this time. Since the inter-hydrate pores do not decrease much in size below about 8-10 nm, it is as if the inter-hydrate spaces are either present, or filled with C-S-H. We do not see evidence for a half-way house. Only when all of this space is consumed, beyond 2 months, is there any evidence that the C-S-H grows within the gel pore space with a small decrease in the gel pore size.

The signal intensities can be recalibrated as volume of water per unit volume of paste. Given the pore sizes, the specific surface area of the C-S-H inter-layer spaces and of the gel pores may be calculated. They are 171 and 111 m²cm⁻³ respectively for the w/c = 0.4 paste at 28 days. Given the specific surface area and sizes of the inter-layer and gel pores we conclude that the number of locally stacked layers comprising a region of C-S-H can only be 2 or 3 at 28 days hydration.

• Density of C-S-H over time (w/c = 0.40)

The data presented in the foregoing sections allows us to calculate the C-S-H density and composition according to equations 1 to 5. The results can be presented either exclusive (called "C-S-H solid density") or inclusive (called "C-S-H bulk density") of the gel water. We present both, as together they reveal interesting observations about the underlying C-S-H morphology. Figure 5 (solid circles) shows the solid C-S-H density in the w/c = 0.4 paste as a function of degree of hydration. To help interpret the data, Figure 6 shows a schematic of the C-S-H as envisaged. The solid C-S-H density, exclusive of the gel pores, ρ_x , is largely independent of degree of hydration, decreasing only very slightly from $\rho_x = 2.73 \pm 0.01$ g/cm³ at 1 day ($\alpha =$ 0.4) to $\rho_x = 2.69 \pm 0.01$ g/cm³ at 2 months ($\alpha = 0.8$) and on to $\rho_x = 2.65 \pm 0.01$ g/cm³ at 10 months ($\alpha = 0.9$). Perversely, the decrease arises due to "densification" of the C-S-H. The NMR C-S-H "solid" density includes the Ca-O layers with SiO₂ tetrahedra and the inter-layer water of the C-S-H but specifically excludes the water and any hydroxyls on the outermost C-S-H surfaces. These outer hydrogens are in rapid exchange with gel water and consequently have a longer relaxation time (circa 300 µs). As C-S-H densifies, the local number of aggregated layers increases. Hence, the ratio of calcium silicate layers (*s*) to inter-layers of water (*s*-1) asymptotically decreases to 1, Figure 6. As the calcium silicate layer is more dense than water, the average density falls.

The "bulk" C-S-H density, including the gel water, $\rho_{x'}$, (open circles), behaves in opposite manner. It increases, and markedly so, during hydration. After 1 day, ($\alpha = 0.4$), the total volume of gel water first reaches a plateau but the hydrates continue to grow by consuming the inter-hydrate water. The bulk C-S-H density necessarily increases. Later, when the inter-hydrate water is fully consumed 2 months, ($\alpha = 0.8$), hydrates grow at the expense of gel water. The density rise continues and the values for the mature pastes agree very well with the densities calculated by other methods. The reader is referred to reference [4] for a review of the relevant literature. We speculate that the C-S-H growing in the very early stages, in parallel with gel pores, corresponds to the low density C-S-H and that which grows thereafter, devoid of corresponding new gel porosity, corresponds to the high density C-S-H that other authors have detected by, for instance, nanoindentation measurements³¹.

Corrections to the density for C-S-H surface water

As explained, the solid C-S-H density excludes the adsorbed layer of water on the outer surface of agglomerates of C-S-H layers. If we take tobermorite 14 Angstrom as a C-S-H analogue, then the layer repeat distance is 1.4 nm. If there are three layers as the NMR results suggest, then the NMR thickness is $3 \times 1.4 - 2 \times 0.28 = 3.64$ nm. If a monolayer coverage of water molecules is added on the outer surface of the C-S-H agglomerate, the NMR density ρ_x is decreases to $\rho_x^m = (3.64\rho_x + 0.56)/4.2$. For example, for $\rho_x = 2.70$ g/cm³, the density reduces to 2.47 g/cm³.

• Density as a function of w/c

Figure 7 shows the calculated densities as a function of w/c at 28 days hydration time. Since the solid C-S-H density probes only the locally stacked C-S-H layers, in the w/c ratio range studied ρ_x is constant as expected. The slight increase in ρ_x for w/c = 0.48 may be explained by a lower ratio of layers to inter-layer spaces, s/(s-1). Likewise, at 28 days of hydration the bulk density, $\rho_{x'}$, decreases with increasing water content as expected. There is simply more water available for gel pores.

Chemical composition

We first focus on the Ca/(Si+Al) ratio, *z*, of the C-S-H. The results are shown as a function of degree of hydration for the w/c = 0.4 paste in Figure 8a. Overall, *z* decreases

with increasing degree of hydration. At 300 days, the Ca/(Si+Al) ratio of the C-S-H is 1.70 ± 0.02 , which is in good agreement with previous studies³². We note that here is a clear difference in the calculated Ca/(Si+Al) ratio between the C-S-H that forms during the first few days ($\alpha < 0.63$, $z \approx 1.84$) and the C-S-H that forms later ($\alpha > 0.63$, $z \approx 1.70$). A transition in the rate of increase of gel porosity at around 2-3 days was previously identified with a transition from growth of low to high density C-S-H. It is conceivable that the Ca/(Si+Al) ratio may be different in to the two types of product, as suggested by, for instance Taylor *et al*³².

The water content of C-S-H without and with the gel water included, x and x' are shown in Figures 8b for the w/c = 0.4 paste as a function of degree of hydration. The value x for the water content excluding gel water follows the inverse trend of ρ_x . The slight increase in x beyond 2 days, ($\alpha \approx 0.6$), is attributed to densification. As the average number of locally aggregated C-S-H sheets, s, increases, there are fractionally more interlayers containing water compared to solid sheets, (s-1)/s, Figure 6, and hence more water molecules, x, per Si or Al atom. The average value of x between 7 and 300 days is 1.80 ± 0.03 . On the other hand, the value of x', that includes the gel water, decreases as the paste densifies. These results are entirely consistent with the changes in the densities.

Figure 9a presents the dependence of Ca/(Si+Al) ratio on the w/c ratio after 28 days of hydration. The higher the water-to-cement ratio, the less calcium ions are incorporated into the C-S-H nanostructure. Figure 9b shows the associated x and x' as a function of w/c. Again, the trends of water bound in the C-S-H microstructure, x and x', follow the inverse behaviour of ρ_x and $\rho_{x'}$.

Finally, we note that the parameter $y = n_{Si}^{CSH} / (n_{Si}^{CSH} + n_{Al}^{CSH})$ ranges from 0.94 at 2 days hydration to 0.96 in the mature paste reflecting the fact that the Al is incorporated early in the process.

• Implications for Powers and Brownyard composition model⁶

Figure 10 (a-c) brings all our data together and shows revised composition diagrams of cement with w/c = 0.32, 0.40 and 0.48 as a function of degree of hydration, in a manner akin to the well known results of Powers and Brownyard. The phase compositions are presented both in terms of mass and volume fractions. Two factors are immediately apparent. The first is that Powers and Brownyard did not distinguish between C-S-H and CH. Nor did they separate out inter-layer water within the C-S-H layers. The NMR experiments clearly differentiate all these components. The second is that there is a clear non-linearity in the growth of the different fractions with degree of hydration. In particular, NMR data shows that the development of gel porosity from $\alpha = 0$ to $\alpha = 1$ is nonlinear, contrary to the Powers and Brownyard proposal. We see that the gel porosity of C-S-H develops mainly at early age when the volume of capillary water still remains significant. The gel water volume then plateaus and does not increase after, $\alpha = 0.33$ for w/c = 0.32, $\alpha = 0.56$ for w/c = 0.40 and $\alpha = 0.79$ for w/c = 0.48. This limitation of the gel pore volume can be interpreted by the transition between the formation of low and high density C-S-H, as already discussed in the previous sections. That the transition is dependent on the initial w/c ratio is related to the mean distance between anhydrous cement particles. A "space filling" model has previously been applied with success by Bishnoi and Scrivener³³ to model hydration kinetics. Notwithstanding the mismatch in

the gel/capillary water volumes at early age between NMR and the Powers and Brownyard model, we note that the latter produces good result at later ages / larger degrees of hydration and therefore that it remains a powerful tool to predict long term paste composition.

• Implications for Jennings colloidal model, CM-II⁴

As well as the inter-layer water, Jennings suggests 3 nanoscale pore sizes associated with C-S-H: intra-globular pores associated with stacking heterogeneities of the calcium silicate layers, (circa 1 nm), small globule pores between particles (circa 1-3 nm) and large globule pores between particle flocs (3-12 nm). We find just two: the inter-layer spaces between the calcium silicate sheets and the gel pores of comparable size to the small globule pores. The large globule pores reported by Jennings are comparable in size to what we call the inter-hydrate spaces (10 nm). However, we do not believe that the inter-hydrate pores that NMR sees are integral to the C-S-H since they always decrease in volume as C-S-H grows. What is interesting, however, is that NMR suggests that C-S-H aggregates of layers are approximately 3 layers thick. Based on the analogue tobermorite 14, this leads to a stack thickness of 4.2 nm, close to the CM-II globule size.

Care must be taken when comparing the density and water fraction of C-S-H according to different models. NMR "solid" density probes locally stacked C-S-H layers excluding any water molecule adsorbed on the outer surface of the agglomerates. SANS measurements¹² upon which much of CM-II is built, also exclude water on particle surfaces and give the result $\rho = 2.604$ g/cm³. NMR gives a slightly larger average value of $\rho_x = 2.71$ g/cm³ between 7 and 300 days hydration. If the surface water correction is applied, ρ_x drops to 2.47 g/cm³, and identical to the value reported by Jennings, $\rho = 2.47$ g/cm³, for a saturated globule with a monolayer of water at 11% RH. The water content of "solid" C-S-H determined by SANS is in good agreement with the average NMR result between 7 and 300 days, x = 1.8. It is difficult to make meaningful comparisons of the water content inclusive of gel water as it constantly decreases while C-S-H densifies.

• Implications for Feldman and Sereda model¹¹

The primary difference between the picture of C-S-H morphology emergent from NMR and that proposed by Feldman and Sereda is that the latter propose C-S-H with mainly inter-layer water and physically adsorbed water but no larger intrinsic reservoirs. The Feldman and Sereda model additionally proposes small nanometer pores that arise from irregularities in the C-S-H layer stacking. The picture of C-S-H coming from NMR relaxometry displays two distinct categories of pores: inter-layer spaces of about 1 nm and gel pore spaces in the order of 3 nm. The remaining nanometre pores are interhydrate in character.

CONCLUSION:

¹H relaxation NMR measurements have enabled a remarkably complete and selfconsistent picture of C-S-H morphology to be established as a function of hydration degree and water to cement ratio of cement paste. The experiments show that initially (during the first few days) C-S-H grows as a loose packed assembly of nanocrystalline regions in which the calcium silicate layers are well stacked with inter-layer water, interspersed with fine "gel" pores, of characteristic and relatively constant size, 3-5 nm.

During this period, the amount and size of large capillary pores decrease rapidly. Once the size reaches around 10 nm, the number of "gel" pores in the C-S-H no longer increases, even though CH and C-S-H with inter-layer water continue to form. The transition to the formation of this dense C-S-H (without gel pores) leads to an overall increase in the "bulk" density of the C-S-H with time from around 1.8 g/cm³ at one day to around 2.1 g/cm³ at one year. Throughout the hydration process the density of the solid nanocrystalline C-S-H remains fairly constant, decreasing slightly from around 2.73 g/cm³ at one day to 2.65 g/cm³ at one year, due to an increase in the number of layers in the nanocrystalline regions.

From this new data, we have updated Powers-Brownyard's classic model of 1947 and identified non-linear growth of the gel porosity. This has largely all come from a single technique: ¹H NMR relaxometry, supported by an XRD measurement of the degree of hydration and ettringite mass fraction. The quick and easy experiments have been performed on fully hydrated material without destructive drying using widely available equipment. We suggest that this opens the door to the rapid characterisation of novel, potentially improved, cements.

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Tables

	age	mass fraction [g /g anhydrous]						fraction of water			NMR
w/c		СН					ett.	consumed			signals
		isopropanol exchange		freeze drying		average	XRD	СН	ett.	CH + Ett	solids
		XRD	TGA	XRD	TGA		u i orugo			Lu.	
0.32	10	0.207	0.200	0.212	0.209	0.207	0.066	0.157	0.095	0.252	0.248
	28	0.217	0.218			0.218	0.066	0.165	0.095	0.260	0.258
0.40	10	0.260	0.231	0.255	0.238	0.246	0.066	0.150	0.076	0.225	0.226
	28	0.266	0.286			0.276	0.066	0.168	0.076	0.243	0.241
0.48	10	0.305	0.311	0.296	0.294	0.302	0.066	0.153	0.063	0.216	0.207
	28	0.313	0.323			0.318	0.066	0.161	0.063	0.224	0.230

Table 1. CH and ettringite mass fractions measured by XRD and TGA and calculated and

 measured NMR signals.

Figure Captions

Figure 1. T_2 distribution map of different pastes at 10 days hydration. The water-tocement ratios, from bottom to top, are w/c = 0.32, 0.40 and 0.48.

Figure 2. Evolution of NMR signal amplitude of different water populations with hydration time (w/c = 0.40). Diamonds are solids such as CH, squares are inter-layer water, triangles are gel pore water and solid rounds are free water, becoming inter hydrate water.

Figure 3. Evolution of T_2 relaxation time of the different water populations throughout the hydration (w/c = 0.40). Squares are inter-layer water, triangles are gel pore water and solid rounds are free water, becoming inter hydrate water.

Figure 4. Voidage volume measured by following the height of a column of water in a capillary above a sample during hydration. The solid line is a linear least squares fit to the data.

Figure 5. C-S-H density as a function of the degree of hydration (w/c = 0.40). Solid symbols are the "C-S-H solid density", exclusive of the gel water; empty symbols are for "C-S-H bulk density", inclusive of the gel water.

Figure 6. A schematic of the calcium silicate layers (solid lines), inter-layer water (squares) and gel pore water (circles). The solid density includes only the calcium silicate layers and the inter-layer water. As it excludes water on the outer surfaces of locally aggregated layers, it is clearly a function of the average number of aggregated layers, *s*. The bulk density includes both types of water.

Figure 7. C-S-H density as a function of w/c at 28 days of hydration. Solid rounds are for solid C-S-H and open rounds are for bulk C-S-H, including the gel water.

Figure 8. a: The ratio Ca/(Si+Al) and b: the water in the C-S-H, excluding (*x*, solid rounds) and including (*x'*, open rounds) gel water as a function of degree of hydration for a w/c = 0.40 paste.

Figure 9. a: The ratio Ca/(Si+Al) and b: the water in the C-S-H, excluding (x, solid rounds) and including (x', open rounds) gel water as a function of w/c ratio.

Figure 10. Mass and volume composition of cement paste for (a) w/c = 0.32, (b) w/c = 0.40 and (c) w/c = 0.48. In each figure, from top, the shaded regions correspond to free water, gel pore water, C-S-H, ettringite, CH and unreacted cement. These results are calculated from the NMR signal intensities of samples measured as prepared throughout hydration (equations 1 to 5) and are presented as a function of degree of hydration.





Figure 1.



Figure 2.



Figure 3.



Figure 4.



Figure 5.



Figure 6.



Figure 7.



Figure 8.



Figure 9.



Figure 10.

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