Use of bench-top NMR to measure the density, composition and desorption isotherm of C-S-H in cement paste.

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Abstract

\textsuperscript{1}H nuclear magnetic resonance (NMR), supported by a measurement of the degree of hydration using X-ray diffraction, has been used to fully characterise the nano-scale porosity and composition of calcium-silicate-hydrate (C-S-H), the active component of cement. The resultant “solid” density and composition are $\rho = 2.68$ g/cm$^3$; (Ca)$_{1.53}$ \((Si_{0.96}Al_{0.04})O_{3.51}$(H$_2$O)$_{1.92}$ for an underwater cured, never-dried cement paste with an initial mix water-to-cement ratio of 0.4 after 28 days of hydration. In addition, the first pore-type resolved desorption isotherm of cement that shows the location of water as a function of relative humidity has been measured. Critical to our results is verification of the assignment of the different NMR spin-spin relaxation time components. These have been corroborated with conventional analyses. The new methodology is key to enabling design of cement pastes with lower environmental impact.
Keywords:
Calcium silicate hydrate;
Density;
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Pore size distribution;
Desorption isotherm.

1. Introduction

Cement production currently accounts for 5-8% of global CO$_2$ emissions [1]. One route to reducing this impact is to introduce new supplementary cementitious materials. However, for this to become routine, it is necessary to fully characterise calcium-silicate-hydrate (C-S-H), the active phase of cement, and then to have means to assess changes made to it by the new materials. The problem is that C-S-H is a highly heterogeneous, nano-porous and delicate material comprising disordered sheets of Ca and oxygen atoms and silicate tetrahedra separated by sheets of water. Regions of stacked sheets are reported to be separated by nano-sized gel pores and larger capillary pores. However, beyond this basic picture, there remains considerable uncertainty [2,3,4,5,6].

Literature reports various densities for C-S-H dependent on the measurement methodology and sample preparation. A review by Jennings [7] reported values from 1.83 to 2.85 g/cm$^3$. At the lower end, both C-S-H and gel water are encompassed so the measurement says little about morphology. At the higher end, the gel water is not
included. However, to make the measurement, the gel water must generally be removed. This disturbs the structure and hence the result. Attempts to measure the “solid” C-S-H density in the presence of water have hitherto required small angle neutron scattering (SANS) [2]. However, SANS is complex and not widely available.

NMR of cement directly probes water in different environments [8,9,10,11] but to date there has been disagreement on the assignment of signals so limiting the interpretation of results. We provide clarification by cross-referencing NMR results to thermogravimetric (TGA), X-ray diffraction (XRD) and thermodynamic modelling analyses of the same samples. We show how widely available bench-top nuclear magnetic resonance (NMR) relaxometry in combination with XRD may be used to measure the density (both “solid” and inclusive of gel water), composition and morphology of C-S-H of never-dried cement pastes, thereby meeting the need for a routine characterisation technique. The C-S-H density and composition follow from solution of mass, volume and oxide content balance equations written in terms of the NMR signal intensities; the degree of hydration; the chemical shrinkage volume; and the anhydrous cement composition. XRD is used to measure the degree of hydration. It is also used here to measure the ettringite fraction so as to allow an improved estimate of the C-S-H density and composition. The chemical shrinkage is determined from the difference in water-to-cement (w/c) ratio of an under-water cured paste, compared to that of the mix. The paste w/c ratio is calculated from the NMR signal intensity of partially dried material after measurement of the “never-dried” parameters.

The NMR analysis is extended to a full study of hydrated samples subsequently equilibrated to constant relative humidity. These measurements enable the first pore size resolved desorption isotherm to be measured. Pore sizes, and in particular gel pore
sizes, are independently inferred both from the spin-spin relaxation times in accordance with the well known fast diffusion model of relaxation and from the rate of signal amplitude loss with drying.

Taken together, the experiments suggest a picture of C-S-H morphology that, while incorporating aspects of widely promulgated models (due to Feldman and Sereda (FS) [12] and to Jennings (CM-II) [7]) nonetheless differs from both.

2. Experimental

2.1. Methods

Hydrogen NMR was performed at 20 MHz. The chemically combined, or “solid”, water fraction was measured by quadrature echo (QE) with pulse gaps, \( \tau \) between 12 and 45 \( \mu \text{s} \) [13]. QE signals were decomposed into Gaussian (solid) and exponential (more mobile) water parts. The solid component was back extrapolated to \( \tau = 0 \) to yield the solid fraction free from relaxation artefact. The solid fraction was confirmed by TGA operating between 30 and 950 °C at 10 °C/min. under \( \text{N}_2 \) gas flow and by XRD in a \( \theta-\theta \) configuration between \( 2\theta = 7 \) and 70° using a \( \text{CuK}_{\alpha} \) source. NMR Carr-Purcell-Meiboom-Gill (CPMG) decays were recorded to separate the mobile water into different components [14]. Decays comprised 128 echoes logarithmically spaced from 50 \( \mu \text{s} \) to 70 ms and were Laplace inverted using the algorithm developed by Venkataramanan et al [15].

2.2. Materials
Low C\textsubscript{3}A\textsuperscript{1} white cement (67 % C\textsubscript{3}S; 20 % C\textsubscript{2}S; 3.5 % C\textsubscript{3}A with other phases all as minor components as measured by XRD with Reitveld analysis) was mixed with water in a \( w/c \) mass ratio 0.4 for 3 minutes at 500 rpm, rested for 2 minutes and further mixed for 2 minutes at 2000 rpm. Aliquots, \( \approx 0.35 \text{ cm}^3 \), were inserted into moulds and covered with a small quantity of saturated CH solution (less than 10% sample volume) for underwater curing, all at 20 °C. For the desorption isotherm measurements, underwater cured samples were broken into millimetre sized pieces after 28 days and equilibrated at constant relative humidity (RH) to constant mass in a moisture sorption analyser using N\textsubscript{2} gas. At every significant stage, samples were weighed with a microbalance.

3. Results

Critical to our analysis is verification that the NMR measurement senses all the water in the sample. Figure 1 (inset) shows the total NMR intensity at 20 MHz as a function of sample mass during controlled drying of an underwater cured cement paste. The plot is linear. The intercept with the mass axis implies an effective \( w/c = 0.463 \). The increase reflects that the sample is cured underwater and proves that there is no “hidden” water as discussed below in the analysis section.

Next we demonstrate that the QE solid fraction of the signal (24.3%) arises predominantly from CH and ettringite, and in particular does not contain any component of C-S-H. TGA, XRD and calculation using the thermodynamic model

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\textsuperscript{1} Cement chemistry notation is used throughout this paper to refer to the compositional oxides. In addition, we refer to atomic elements in conventional manner. Hence: C=CaO; S=SiO\textsubscript{2}; H=H\textsubscript{2}O; A=Al\textsubscript{2}O\textsubscript{3} and so CH=Ca(OH)\textsubscript{2}. To avoid confusion within the text, where it is ambiguous, atomic hydrogen is notated \textit{Hyd}. The abbreviation \textit{AMU} denotes atomic mass units; \( n \) is molar content and \( f \) is mass fraction of anhydrous powder.
GEMS \[16\] give the mass fraction of CH in the paste as 22.5±1%, 23.7% and 24% respectively. The average, 23.4 ± 0.6 %, is equivalent to, $m_{CH} = 0.34 \pm 0.01g/g$

anhydrous cement. XRD gives the mass fraction of ettringite in the paste as 5.7 ± 1.0 %, equivalent to $m_{et} = 0.083\pm 0.015 \text{ g/g}$ of anhydrous cement. Hence, the fraction of water combined into the solid phases is

$$[(0.34\times18^{AMU}/74^{AMU}) + (0.083\times576^{AMU}/1255^{AMU})]/0.463 = 26 \pm 2\%$$

in reasonable agreement with the NMR value, 24.3%.

The CPMG experiment subdivides the mobile water fraction into components with $T_2$ of 126 ± 5 µs (25.5%), 420 ± 20 µs (44.1%), 1.4 ± 0.4 ms and 12 ± 2 ms (6.1% taken together). We assign the component with $T_2 = 126 \mu s$ to water (and surface hydrogen contacting water) in interlayer spaces of the C-S-H since the immobile water associated with solid is already fully accounted for by CH and ettringite; with $T_2 = 420 \mu s$ to water in C-S-H gel pores; and with $T_2 = 1.4 \text{ ms}$ and $T_2 = 12 \text{ ms}$ to water in inter-hydrate spaces, capillary pores and cracks, hereafter abbreviated simply to capillary water. This assignment is similar to that proposed by Holly et al \[11\].

The main part of Figure 1 shows the amplitude of these 4 components as a function of relative humidity. As such, it is the pore-size resolved desorption isotherm. The total signal loss closely resembles the first-drying weight-loss isotherm as reviewed by Jennings \[7\]. The capillary pore water dries above 90% RH. The gel pore water decreases from 50% of the total to practically zero between 100 and 25% RH. In the same range, the interlayer water apparently increases. This is because water associated with surface sites in a full gel pore rapidly exchanges with the pore fluid and therefore has the same $T_2$. However, as the pore empties, so surface water is left as a less mobile
monolayer that, in NMR terms, more resembles interlayer water with shorter $T_2$. Below 25% RH, water is rapidly lost from the C-S-H interlayer spaces with a noticeable acceleration around 10% RH. At low RH there is an increase in the solid signal. Similar to the gel, as interlayer water is lost, so hydrogen in, for example, residual silanol groups appears solid-like.

4. Analysis

To measure the C-S-H density, we need to know the change in volume of the paste during hydration. Chemical shrinkage, due to the lower specific volume of the hydration products compared to the solid reactants and water, creates porosity that is expected to be of the order of 7 – 10 \% the total volume [17]. In small underwater cured samples as here, water is drawn into the chemical shrinkage volume and so the extra porosity is calculated from the increase in the $w/c$ ratio of the hydrated paste compared to the mix.

The macroscopic volume change, a small swelling in underwater cured material, is negligible in comparison and is ignored. The $w/c$ ratio of the paste, $w/c = 0.463$, is calculated from the intercept with the mass axis of the NMR signal during controlled drying (inset to Figure 1).

Simultaneous equations for mass and volume conservation expressed per gram anhydrous cement are:

$$1 + \frac{w_{\text{mix}}}{c} = (1 - \alpha) + \frac{w_{\text{mix}}}{c} \left[ \beta I_{\text{solid}} + \gamma I_{\text{CSH}} + \delta(I_{\text{gel}} + I_{\text{cap}}) \right]$$ \hspace{1cm} (1)

$$\frac{1}{\rho_{\text{uc}}} + \frac{w_{\text{mix}}}{c \rho_{\text{w}}} = (1 - \alpha) + \frac{w_{\text{mix}}}{c} \left[ \frac{\beta I_{\text{solid}}}{\rho_{\text{solid}}} + \frac{\gamma I_{\text{CSH}}}{\rho_{\text{CSH}}} + \frac{\delta(I_{\text{gel}} + I_{\text{cap}} + I_{\text{void}})}{\rho_{\text{w}}} \right]$$ \hspace{1cm} (2)
Here, $\rho$ is density and $I$ are signal fractions normalised to the total signal before chemical shrinkage (i.e. the creation of filled voids) so that $I_{\text{void}} = \left( w_{\text{paste}} - w_{\text{mix}} \right) / w_{\text{mix}}$ and $I_{\text{solid}} + I_{\text{CSH}} + I_{\text{gel}} + I_{\text{cap}} = 1$. The subscript $uc$ refers to unreacted cement; others are clear from the text. The parameters $\alpha, \beta, \gamma$ and $\delta$ are the degree of hydration and the reciprocal water mass fractions of the solid, C-S-H and pore fluid respectively.

The solid signal is assumed to comprise two parts, CH and ettringite, so that

$$I_{\text{solid}} = I_{\text{CH}} + I_{\text{Et}}; \quad \beta I_{\text{solid}} = \beta_{\text{CH}} I_{\text{CH}} + \beta_{\text{Et}} I_{\text{Et}} \quad \text{and}$$

$$\beta I_{\text{solid}} / \rho_{\text{solid}} = \beta_{\text{CH}} I_{\text{CH}} / \rho_{\text{CH}} + \beta_{\text{Et}} I_{\text{Et}} / \rho_{\text{Et}} .$$

The constants $\rho_{uc,\text{CH,Et}}, \alpha = 3.15, 2.24, 1.77$ and 1 g/cm$^3$ respectively, $\beta_{\text{CH}} = 74/18$, $\beta_{\text{Et}} = 1255/576$ and $\delta = 1$. We take the mass of ettringite per gram anhydrous from XRD, calculate the associated water content,

$$I_{\text{Et}} = m_{\text{Et}} / (0.4 \beta_{\text{Et}}) \quad \text{and subtract this from } I_{\text{solid}} \text{ to get } I_{\text{CH}} .$$

An alternate method of dividing $I_{\text{solid}}$ between $I_{\text{CH}}$ and $I_{\text{Et}}$ is to use the mass ratio of ettringite and CH determined by XRD. It leads to slightly different results because of the discrepancy between the total solid fractions determined by XRD and NMR. We do not favour this alternate route. The reason is that, whilst the ettringite content is hard to determine accurately, it is essentially constant after the early stages of hydration. Hence, using the former method of signal split, the average ettringite content of multiple samples measured at one, relatively early, time point may be used to increase accuracy in temporal studies of sealed cured samples reported elsewhere [18].

This leaves $\alpha$, $\rho_{\text{CSH}}$ and $\gamma$ unknown. A measurement of $\alpha$, the degree of hydration, was made using XRD so enabling the C-S-H density and water fraction to be found.

Assuming $\text{Ca}_2(\text{Si}_y\text{Al}_{1-y})\text{O}(2y/3+3/2)(\text{H}_2\text{O})_x$, the water fraction $x$ is related to $\gamma$ as
\[ x = \frac{(56z + 9y + 51)}{(18(y - 1))} \]  

(3)

where \( y = \frac{n_S}{n_S + n_A} \) and \( n_{SL,Al} \) are the molar content of Si and Al in the C-S-H. The numerical constants derive from the atomic masses of C, S and H. The alternate C-S-H composition including gel water, Ca\(_x\)(Si\(_y\),Al\(_{1-y}\))O\(_{(2+y/2+3/2)}\)(H\(_2\)O)\(_{x'\prime} \), has

\[
x' = x(I_{\text{CSH}} + I_{\text{gel}})/I_{\text{CSH}}.
\]

A further conservation equation is written for the overall Ca/(Si+Al) ratio before and after reaction:

\[
3\left( \frac{f_{C3S}}{C_3S^{AMU}} \right) + 2\left( \frac{\alpha - f_{C3S}}{C_2S^{AMU}} \right) + 3\left( \frac{f_{C3A} - f_{\text{Et}}^{\text{En}}}{C_3A^{AMU}} \right) = \frac{I_{\text{CH}}n_{\text{Hyd}}z}{2x} + \frac{I_{\text{CSH}}n_{\text{Hyd}}y}{2x} + 3\left( \frac{f_{C3A} - f_{\text{Et}}^{\text{En}}}{C_3A^{AMU}} \right)
\]

(4)

Here, the first term of the numerator gives the number of moles of reacted Ca in the CH and C-S-H per gram of anhydrous cement that are derived from C\(_3\)S. The other terms give the moles of reacted Ca from C\(_2\)S and C\(_3\)A respectively. The denominator is similarly constructed for reacted Si and Al. On the right hand side, the corresponding molar contents of Ca, Si and Al are written in terms of the NMR signal fractions, the C-S-H composition parameters and \( n_{\text{Hyd}} = 2w_{\text{Hyd}} / H^{AMU} = 0.044 \), the molar content of hydrogen in the paste mix. The derivation of Equation (4) assumes that, for the degree of hydration considered (\( \alpha = 0.77 \)), all the C\(_3\)S of the anhydrous cement (\( f_{C3S} = 67\% \)) is consumed in the reaction before the more slowly reacting C\(_2\)S (\( f_{C2S} = 20\% \)).

Additionally, it is assumed that the C\(_3\)A not required for ettringite formation is incorporated within the C-S-H. It was shown above that the mass of ettringite is 0.083 g/g anhydrous cement. To produce this amount consumes \( f_{C3A}^{\text{Et}} = 1.79 \% \) of the
anhydrous cement in the form of C₃A and 0.0383 g of water. Hence the remaining C₃A
is \( f_{C3,A} - f_{et}^{C3,A} = 1.72\% \).

Finally, the equality \( y = \frac{n_{Si}}{n_{Si} + n_{Al}} = 1 - \frac{n_{Al}}{n_{Si} + n_{Al}} \), leads, after substitution of the two
terms in the denominator on the right hand side of Equation (4) to

\[
y = 1 - \frac{4x(f_{C3,A} - f_{et}^{C3,A})}{I_{CSH} n_{Hyd} C3A AMU}
\]  

(5)

The intensities, \( I \), of the solid, C-S-H interlayer, gel, capillary and void water NMR
signals at 100% RH defined as above are 0.281, 0.295, 0.510, -0.086 and 0.157
respectively, the negative sign implying that some water drawn into the sample has been
used for hydration products. The solid signal splits into that from CH and ettringite as
0.185 and 0.096 respectively. The degree of hydration is \( \alpha = 0.77 \) (from XRD). Solving
equations 1 to 5, the resultant C-S-H density is 2.68 g/cm³, with composition

\[
Ca_{z=1.53}(Si_{y=0.96}Al_{(1-y)=0.04}) O_{(z+y)/2+3/2}=3.51.(H_2O)_{x=1.92}
\]

The calculated density and composition are for the calcium-oxygen layers and silicate of C-S-H with the interlayer
space fully saturated. They are for “never-dried” material. This is because, even though
a sample was dried to determine the actual, as opposed to mix, water-to-cement ratio,
and hence chemical shrinkage, all the NMR signal intensities needed to calculate the
density and composition were recorded before the drying procedure.

C-S-H is often considered to form in agglomerates of sheets. The NMR derived “solid”
C-S-H density excludes water (and any OH groups) on the surfaces of the agglomerates
since surface water is in rapid exchange with the gel pore fluid (longer \( T_2 \)). This may
explain both a \( W/C \) and an \( \alpha \) dependence of the density that is reported elsewhere [18],
since the agglomerate size and hence apparent density may depend on both parameters. If gel water is included in the composition, the “bulk” density and water content are

\[ \rho_{\text{CSH}}' = 1.89 \text{ g/cm}^3 \quad \text{and} \quad x' = 5.25 \] respectively.

We note that taking the alternate means of dividing the solid signal between ettringite and CH changes the derived parameters typically by <1%. The biggest impact is upon \( z \) which changes by about 3%.

Pore sizes may be measured by NMR using either the fast exchange model of relaxation [19] or the change in signal amplitudes with drying [20]. We have used both methods. In the case of the fast exchange model we combine a water monolayer thickness of 0.28 nm and the interlayer water \( T_2 \) at low RH, 75\( \mu \)s (20 MHz), for the fast-exchange surface-relaxivity and thereby calculate 3.1 nm for the gel pores and 0.94 nm for the interlayer spacing. Sample drying yields 3.4 nm and 1.6 nm respectively. This last result is larger than expected, almost certainly because the underlying assumptions of the drying model break down in such a small space. Given the pore widths, the specific surface area (SSA) can be evaluated. From fast exchange, it is 91 m\(^2\)/cm\(^3\) of paste for gel pores and 175 m\(^2\)/cm\(^3\) for interlayer spaces in accord with earlier undifferentiated estimates [8,9].

5. Discussion

A feature of the data is that we see much less (about \( \frac{3}{4} \) to \( \frac{2}{3} \)) capillary porosity than expected from the Powers and Brownyard model [20,21]. In further work [18], we show that the primary capillary pore reservoir quickly diminishes in total volume throughout hydration and that the characteristic pore size asymptotically decreases to circa 10 nm.
We propose that this reservoir corresponds to inter-hydrate water and that it is not intrinsic to the C-S-H.

The lack of capillary porosity is significant as it strongly affects mechanical and transport properties of cement. It impacts the way in which the C-S-H gel fills space and hence the design of hydration models that seek to describe cement morphology numerically. Also, it implies that the finer gel pores must play a correspondingly greater role in controlling the rate of ingress of dissolved, aggressive ions such as chlorides and sulphates.

Figure 2 is a pictorial representation of C-S-H morphology and water placement consistent with our results. It depicts a continuous network of C-S-H layers and gel pores. The picture is similar to the widely reproduced figure of the FS model [12]. The principle difference is that FS viewed it as a picture of C-S-H only with interlayer spaces and pores due to local disorder in C-S-H stacking; together accounting for most of the C-S-H water as defined by Powers and Brownyard [21] at full saturation.

The alternate model, CM-II [7], describes C-S-H as colloidal globules, the globules being made up of particles each comprising a few C-S-H sheets. Particle sizes are 2-5 nm from SANS. As well as the interlayer spaces, CM-II proposes intra-globular pores within particles due to stacking faults (circa 1 nm), “small” pores between particles (circa 1 – 3 nm) and “large” pores between globule flocs (circa 3-12 nm). As evidenced by growth during the early stages of hydration, NMR shows evidence of only 2 nano-scale pore types intrinsic to the C-S-H, interlayer spaces and gel pores. In particular, there is no evidence for intra-globular pores. This is discussed more fully elsewhere [18].
Assuming that the lateral extent of C-S-H sheets and gel pores are similar, then, by comparing their respective SSA the sheet stacks can only be about two to three sheets thick. Based on the mineral analogue tobermorite-14 [3], the thickness is 2.8 - 4.2 nm. Interestingly, this is in accord with the particle size of CM-II.

With density and water fraction, one has to be careful to compare like-with-like. Most results are either for fully saturated gel (C-S-H plus gel water) in which case \( x' = 5 \) \((\rho = 1.8 \text{ g/cm}^3)\) is typical, or for dried material in which case \( x = 1.3 - 1.5 \) \((\rho = 2.2 - 2.6 \text{ g/cm}^3)\) [7]. SANS gives \( \rho = 2.604 \text{ g/cm}^3 \) and \( x = 1.8 \) for a fully saturated globule of CM-II [2], excluding water adsorbed on the outer particle surfaces. The NMR density also excludes water on the outer surface of locally aggregated C-S-H sheets since this water is in fast exchange with the gel pore water.

If, based on the pore size and SSA reported above, we assume that C-S-H typically comprises 3 sheets of repeat thickness 1.4 nm (based on tobermorite-14) including 2 external monolayers of water, compared to 3 sheets without the external monolayer, then the additional volume is \( \Delta V = 2 \times 0.28 \times 10^{-9} \text{ m}^3 / \text{ m}^2 \) of sheet on an original volume of \( V = (3 \times 1.4 - 2 \times 0.28) \times 10^{-9} \text{ m}^3 / \text{ m}^2 \). If this volume is filled with water, then the density of the C-S-H is reduced from 2.68 to 2.46 g/cm\(^3\). This is now very close to the value of, \( \rho = 2.47 \text{ g/cm}^3 \) reported by Jennings for a saturated globule with a monolayer of water at 11% RH. The water content result \( x' = 5.25 \), applicable when all the gel water is included in the calculation, is close to 5 as arises in CM-II with saturated LGP. Thus, throughout, the NMR structural parameters are in reasonable agreement with those of CM-II derived primarily from SANS, even though the NMR and SANS results are not interpreted in terms of the same morphological model. Finally we note that our
value of Ca/(Si+Al) (1.53 at \( w/c = 0.463 \)) is consistent with the results of Rayment and Majumdar [22], who found average inner and outer product values of Ca/(Si+Al+S+Fe) ranging from 1.70 at \( w/c = 0.3 \) to an average of 1.48 at \( w/c = 0.6 \), and also the results of Q. Li as reported in [24] who found values of 1.56 and 1.73 after 7 days hydration for inner and outer product respectively in cement similar to that used in this study.

6. Conclusion

To conclude, we have measured the density, Ca/(Si+Al) ratio and water fraction of C-S-H pertaining to never-dried white cement using widely available NMR equipment supported by XRD. Controlled sample drying and NMR were used to determine a pore size resolved desorption isotherm and the chemical shrinkage. The quick and easily performed experiments create means to characterise rapidly many novel, potentially improved, cements.

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References


Figure Captions

Figure 1:
Inset: The total normalised NMR signal against relative sample mass in progressively dried white cement paste. Main: The total signal plotted against relative humidity (circles) and de-composed into chemically combined water (diamonds), and water in C-S-H interlayer spaces (squares), gel pores (triangles) and capillary pores (inverted triangles): the pore-specific desorption-isotherm. Notice that, as gel pores empty, so residual water on the C-S-H surface appears interlayer space-like. Hence this signal increases.

Figure 2.
A schematic of C-S-H morphology at 100, ≈ 25, and ≈ 3 % RH. Solid lines are sheets of Ca ions and SiO$_2$ tetrahedra. Circles are water molecules in gel pores with intermediate $T_2 \approx 420 \mu$s. Squares are molecules in interlayer spaces and, at lower RH, residual gel pore surface molecules with $T_2 \approx 126 \mu$s. Diamonds are immobile molecules that appear solid like at the lowest RH values, with $T_2 \approx 10 \mu$s. Bottom right shows only those water molecules that, at 100 % RH, are included in the density measurement. Note that where locally there are, e.g. 3 sheets, then there are 2 interlayers and where there are 2 sheets there is 1 interlayer. The apparent density therefore varies with the number of sheets. Additional Ca ions associated with the water between the sheets are not shown.