Influence of curing temperature on cement paste microstructure measured by ^1H NMR Relaxometry

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ABSTRACT

^1H nuclear magnetic resonance (NMR) relaxometry, supported by X-Ray diffraction and thermogravimetric analysis, has been used to characterise microstructure of white cement pastes underwater cured at temperatures in the range 10 °C to 60 °C. As the temperature increases, so the C-S-H, capillary pore water and interhydrate pore water content all increase; the ettringite and gel pore water content decrease; and the Portlandite content stays constant. A non-linear increase in the C-S-H ‘solid’ and ‘bulk’ densities, that exclude and include gel pore water respectively, has been observed with the increase of temperature. This is accompanied by a decrease in C-S-H water content but no change in the Ca/(Si + Al) ratio. The increase in the C-S-H ‘solid’ density has been attributed to a decrease in the number of locally stacked C-S-H layers. The increase in the C-S-H ‘bulk’ density is additionally attributed to the decrease in the gel porosity.

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1. Introduction

The density of hydrates in cement paste, and specifically the density of C-S-H is a parameter of interest to those seeking to understand the hydration and microstructure of cement paste gel. A key factor affecting hydration is temperature and in particular the temperature dependence of the C-S-H density is of interest; meaning the temperature at which C-S-H is formed as distinct from the temperature it is subsequently exposed to and/or measured at. In previous work we have shown that ^1H NMR relaxation analysis of cement paste coupled with an independent measure of the degree of hydration is an excellent, non-destructive and non-invasive method to measure the density of, and hence to observe the densification of, C-S-H at room temperature as a function of hydration time and water to cement ratio for pure white cement pastes [1] and white cement pastes with added silica fume [2]. One advantage of the NMR method is that it can separately measure the densities of both the “solid C-S-H” (comprised of stacks of C-S-H layers but excluding gel porosity) and the “bulk C-S-H” (comprising C-S-H layers and gel porosity). In this study we extend the work to include measurements of pure white cement as a function of curing temperature in the range 10 to 60 °C.

Although NMR method has been used to measure changes in C-S-H for samples cured at room temperature and afterwards measured at elevated temperature [3], there are relatively few reports in literature of the curing temperature dependence of C-S-H density. Prominent is the work of some of us that reports bulk density measurements in the range 5 to 60 °C based on a multi-technique (but not including ^1H NMR) analysis that included SEM image analysis

and XRD measurements [4]. A surprisingly large apparent increase in density of 25% was inferred across this temperature range. More recently Bahafid *et al.* [5] measured the bulk density of the C-S-H using X-ray diffraction, thermogravimetric analysis and mercury intrusion porosimetry in the range 7 to 90 °C. The results were significantly different to Gallucci *et al.* [4]. There have been no reports of the temperature dependence of the solid C-S-H density.

The bulk of the work reported here was actually carried out during the time 2011–2013 by one of us (AMG-J), in parallel with some of our earlier studies, as part of her PhD thesis work. It is reported in part in her (unpublished) thesis [6]. However, the results were not reported more widely at that time because of the difficulty of reconciling them with the SEM study just described [4]. We now believe that these results may have been affected by the drawbacks of image and XRD data analysis in that earlier study which leads us to have much greater confidence in the validity of these new ^1H NMR results. The results presented here are much more in accord with these of Bahafid *et al.* [5]. We return to these points in the discussion.

2. Material and methods

2.1. Cement pastes

White Portland cement obtained from Aalborg Portland was used in this study. The mineralogical composition of the anhydrous powder is 64.0% C_3S , 19.5% C_2S , 3.3% C_3A , 3.3% $\text{C}\$\cdot 2\text{H}$, 2.1% $\text{C}\$\cdot 0.5\text{H}$ and 1.8% CH – a similar material to that we have used in earlier work (different batch). This cement is characterised by almost total lack of ferric impurities (Fe_2O_3 content 0.3%) making it especially suited to NMR analysis.

All cement pastes were prepared at the water to cement ratio (w_{mix}/c) 0.4 by mass. Distilled water was added to 80 g of anhydrous powder. Pastes were mixed for 3 min at 500 rpm,

rested for 2 min and then further mixed for 2 min at 2000 rpm. Immediately after mixing, aliquots of paste of circa 0.4 cm^3 were inserted into 10 mm outside diameter NMR tubes using a plastic pipette. Further fractions were put into larger containers for parallel X-ray diffraction and thermogravimetric analysis. A few drops of saturated calcium hydroxide (CH) solution were added on the top of pastes for “underwater” curing. The NMR tubes and larger containers were tightly closed using parafilm[®].

Samples were variously stored at six curing temperatures: 10, 20, 30, 40, 50 and 60 °C during hydration in, as appropriate, a fridge, the temperature controlled laboratory or a temperature controlled hot water bath. The temperature stability was: $10 \pm 1 \text{ °C}$ in the fridge; $20 \pm 0.5 \text{ °C}$ in the laboratory; and $30/40/50/60 \pm 0.2 \text{ °C}$ in water baths.

NMR measurements were performed periodically from 2 h to 90 days in a temperature-controlled NMR probe (at the same temperature as curing). Prior to the NMR measurements, the CH solution was removed using a pipette and the tube walls and sample surface were touch-dried with tissue paper. The weight of samples was recorded. This weight allowed the amount of water absorbed into the sample to compensate the chemical shrinkage to be calculated. To avoid evaporation of the sample water during the time of measurement, a solid glass rods was inserted into the NMR tube which was sealed with parafilm[®]. After measurements the solution was back-added at the top of samples.

2.2. NMR measurements

¹H NMR was carried out at the University of Surrey. Measurements were performed at 20 MHz using a permanent bench-top NMR magnet equipped with a Kea² (Magritek, New Zealand) NMR spectrometer. Quadrature “solid” [7] and Carr-Purcell-Meiboom-Gill [8] [9] echo trains were recorded. The duration of 90° and 180° excitation pulses were the same: 5 μs; the intensity of the 180° pulses was twice that of the 90°.

The quadrature echo (QE) experiment resolves the ^1H into two fractions: that in crystalline ‘solid’ phases such as Portlandite (*CH*) and ettringite (*Ett*) and more mobile water in pores including intrahydrate layer spacings. QE signals were recorded as a function of pulse gap (τ) measured between the centres of the two 90° pulses. Eight QE experiments were carried out with pulse gaps ranging from 12 to 54 μs . Data was acquired with repetition time² (τ_{rd}) of 1 s and number of averages of 32. Echo decays were acquired with a dwell time of 1 μs and analysed in the time range below 200 μs to minimise the influence of magnet inhomogeneity on mobile water signal. A small residual NMR signal emanating from the empty NMR tube/probe was measured and subtracted from the data. Analysis of QE signals was performed as previously described [10,11]. In brief, the decay is fit to a Gaussian echo with a narrow width (short time constant) of 10-20 and an exponential decay with long time constant. The former is due to ^1H in crystalline phases, the latter mobile water. The actual solid and mobile ^1H fractions are gained by back-extrapolation of the Gaussian and exponential amplitudes measured at different pulse gap, τ , to zero pulse gap using Gaussian and linear fittings respectively. Their sum is a measure of all the hydrogen within sample. The Carr-Purcell-Meiboom-Gill (CPMG) experiment further resolves the mobile water into fractions in different pore types (sizes) based on their different spin-spin relaxation times, T_2 . Typically, 420 logarithmically spaced CPMG echoes with 32 data points per echo were recorded from 60 μs out to 0.8 s (or even 2.8 s for very young samples). The number of averages was increased from 128 to 320 as the hydration progressed and the signal to noise ratio decreased. Again, residual empty cavity signals were subtracted.

There are multiple ways to analyse CPMG decay data including inverse Laplace transformation (ILT) and direct constrained and unconstrained exponential fitting. We have previously used the ILT developed by Venkataramanan *et al.* [12]. However, in this work, we

² Repetition time is treated as the time from the start of one sequence to the start of the next one.

choose to use a constrained exponential stripping method. This is due to the fact that the signal to noise ratio (S/N) of the data at higher temperature is of the order of 100 whereas ILT typically requires $S/N > 400$. On the other hand, exponential stripping requires knowledge of the expected number of relaxation components. This was taken as 4 based on our previous (ILT) work [1]: interlayer; gel pore; interhydrate pore and capillary pore. In stripping analysis, the longest relaxation component is fit to the tail of the CPMG decay starting at a cut-off time significantly greater than the relaxation time of the next shortest component but, ideally, also shorter than that of the component being fit. This fitting (which may include a baseline offset) is subtracted from the original data. The tail of residual data is then fitted to the next longest relaxation component (without baseline offset) in similar manner. The procedure is repeated iteratively until the shortest component has been fit. The analysis began with the oldest samples at room temperature where we had good knowledge of what to expect based on earlier results and so could make sensible choices for the “cut-off” times. The discovered relaxation times were used to refine the cut-off times for the next data set to be fit, progressively working up or down in temperature and towards younger age.

2.3. Thermogravimetric analysis

The Portlandite (m_{CH}) content was measured using TGA at University of Surrey on ‘as-prepared’ samples at 90 days of hydration and on isopropanol exchanged samples at EPFL at 28 days.

A TA Instruments SDT-Q600 Thermo Gravimetric Analyser was used at University of Surrey and a Mettler Toledo TGA/SDTA 851 analyser at EPFL. University of Surrey measurements were made on millimetre-sized pieces of paste taken from crushed larger samples while EPFL measurements were made on isopropanol exchanged (7 days isopropanol immersion) and dried (7 days in a desiccator) powdered samples. During

measurement, samples were heated to 1000 °C at Surrey University and to 950 °C at EPFL at 10 °C/min under the N₂ gas flow to prevent carbonation.

2.4. X-ray diffraction

X-ray diffraction (XRD) with Rietveld analysis was used to measure the degree of hydration (α) as well as the ettringite (m_{Et}) and Portlandite (m_{CH}) content of the cement pastes.

Measurements were carried out at EPFL using a Panalatical X'Pert Pro MPD diffractometer with a CuK α source (wavelength 1.54 Å) with a fixed divergence slit of 0.5°. An X'Celerator detector was used to scan the samples between $2\theta = 7$ to 70°. The rotation step size was 0.0167° (2θ) and the time step was 77.5 s. Degree of hydration at 28 and 90 days and Portlandite content at 28 days were measured on isopropanol exchanged powdered samples. Ettringite content was measured at 50 days on larger “as prepared” cut paste slices to prevent underestimation of its content. The ettringite measurement procedure was as follow: the fresh paste was cut with a diamond saw using water as a lubricant; the cut slice was then polished by hand on a sand paper using water; it was next washed with water to remove any impurities; and all surfaces were dried with a tissue paper. The slice was then immediately placed into the XRD machine and measurement started within 5 min after cutting the sample. The ettringite content calculation by Rietveld analysis were done including mixing water and water that was drawn into a sample due to chemical shrinkage (defined as described in next section) but no correction was made for any water loss during measurements.

2.5. Chemical shrinkage

The chemical shrinkage volume is given by the volume of water that is drawn into a sample to fill the shrinkage voids. It may be expressed as the difference between the actual w/c ratio of a saturated paste and the w/c at the time of mixing: $w_{paste}/c - w_{mix}/c$. The shrinkage correlates with the increase in the weight with hydration time of small underwater-cured

paste samples. It also correlates with the increase in NMR signal with hydration time of small underwater-cured paste samples.

2.6. Calculation of C-S-H density and composition

The C-S-H density and composition at various temperatures and hydration times may be evaluated from knowledge of the detailed breakdown of the water in different environments within the cement (NMR data), the degree of hydration, content of crystalline phases and the chemical shrinkage. The necessary mass, volume and oxides balance equations are developed in our earlier work [1,13], especially Eqs 1 to 5. They are reproduce here for ease of reading:

$$1 + \frac{w_{mix}}{c} = (1 - \alpha) + \frac{w_{mix}}{c} [\beta I_{sol} + \gamma I_{CSH} + \delta(I_{gel} + I_{cap})] \quad (1)$$

$$\frac{1}{\rho_{uc}} + \frac{w_{mix}}{c\rho_w} = \frac{(1 - \alpha)}{\rho_{uc}} + \frac{w_{mix}}{c} \left[\frac{\beta I_{sol}}{\rho_{sol}} + \frac{\gamma I_{CSH}}{\rho_{CSH}} + \frac{\delta(I_{gel} + I_{cap})}{\rho_w} \right] \quad (2)$$

$$x = (56z + 9y + 51)/[18(\gamma - 1)] \quad (3)$$

$$\frac{3 \left(\frac{f_{C3S}}{C_3 S^{AMU}} \right) + 2 \left(\frac{\alpha' - f_{C3S}}{C_2 S^{AMU}} \right) + 3 \left(\frac{f_{C3A} - f_{C3A}^{Ett}}{C_2 A^{AMU}} \right)}{\frac{f_{C3S}}{C_3 S^{AMU}} + \frac{\alpha' - f_{C3S}}{C_2 S^{AMU}} + 2 \left(\frac{f_{C3A} - f_{C3A}^{Ett}}{C_2 A^{AMU}} \right)} \quad (4)$$

$$= \frac{\frac{I_{CH} n_{Hyd}}{2} + \frac{I_{CSH} n_{Hyd} z}{2x} + 3 \left(\frac{f_{C3A} - f_{C3A}^{Ett}}{C_2 A^{AMU}} \right)}{\frac{I_{CSH} n_{Hyd} y}{2x} + 2 \left(\frac{f_{C3A} - f_{C3A}^{Ett}}{C_2 A^{AMU}} \right)}$$

$$y = 1 - \frac{4x(f_{C3A} - f_{C3A}^{Ett})}{I_{CSH} n_{Hyd} C_3 A^{AMU}} \quad (5)$$

where, ρ is density; I are signal fractions normalised to the total signal before chemical shrinkage; I_{void} is signal fraction due to water in chemical shrinkage voids; uc , w , sol , CH , Ett , CSH , gel , cap and $void$ refer to unreacted cement, water, chemically combined water, Portlandite, ettringite, C-S-H, gel pore water and capillary pore water respectively; α is the degree of hydration; β , γ and δ are the reciprocal water mass fractions of the solid, C-S-H and pore fluid respectively; $y = n_{Si}/(n_{Si} + n_{Al})$ and $n_{Si,Al}$ are the molar content of Si and Al in the C-

S-H; z is a molar content of Ca in C-S-H; x is a molar content of water in ‘solid’ C-S-H; f_{C3S} , f_{C2S} and f_{C3A} are a fraction of the C_3S , C_2S and C_3A in the anhydrous cement respectively; f_{C3A}^{Ett} is a fraction of C_3A consumed for ettringite formation; α' is the mass of reacted ($C_3S + C_2S$) divided by the mass of the anhydrous powder excluding minor reactive components other than C_3A ; $n_{H_{yd}}$ is the molar content of hydrogen in the paste; AMU refers to atomic mass units.

The NMR data allows separate calculation of the C-S-H ‘solid’ (ρ_{CSH}) and ‘bulk’ (ρ'_{CSH}) density. As shown in Fig. 1, the former includes the calcium and silicon backbones of the structure and the water within interlayer spaces. It especially excludes water, as well as any hydroxyl groups, on the surfaces of C-S-H agglomerates as this surface water (hydrogens) is in rapid exchange with the bulk gel pore water and has longer T_2 relaxation time. The ‘bulk’ C-S-H includes the gel pore water – Fig. 1.

Fig. 1. A scheme of water location for C-S-H ‘solid’ and ‘bulk’ density calculation. The C-S-H ‘solid’ density includes only water molecules in interlayer spaces (red squares), while for C-S-H ‘bulk’ density water in interlayer and gel pores (green triangles) is considered. Solid lines represents the calcium silicate layers [13].

To avoid confusion, we make the following observations. First, the 1H NMR signals are expressed as fractions, I , of the total 1H signal at the time of mixing. In consequence, $I_{sol} +$

$I_{CSH} + I_{gel} + I_{cap} = 1$. For small underwater cured samples, the total signal increases with degree of hydration, in line with the increase in chemical shrinkage volume and additional water is being drawn into the sample to fill that extra volume. The signal fraction due to water in chemical shrinkage voids is defined by the fractional increase in water mass/volume as the sample hydrates so that $I_{void} = (w_{paste} - w_{mix})/w_{mix} = I_{total} - 1$ and is included in the volume balance equation. A consequence of hydration using water drawn into shrinkage voids is that the capillary water fraction can appear to be negative.

Second, the solid intensity originates from Portlandite and ettringite so that $I_{sol} = I_{CH} + I_{Et}$. The water intensities within these two phases can be separately calculated knowing their mass fractions. In our previous work we suggested two different methods to determine this split: either $I_{CH} = m_{CH}/(w_{mix} \cdot \beta_{CH})$ with $I_{Et} = I_{sol} - I_{CH}$; or $I_{Et} = m_{Et}/(w_{mix} \cdot \beta_{Et})$ with $I_{CH} = I_{sol} - I_{Et}$ where β_{CH} and β_{Et} are the reciprocals water mass fractions in crystalline phases based on the atomic masses, $\beta_{CH} = 74/18$, $\beta_{Et} = 1255/576$. In the absence of experimental error they yield exactly the same result. However, in practice they do not. The former set of equations was applied in this analysis. Third, we make an assumption that entire alite (C_3S) is consumed first during hydration prior to slowly hydrating belite (C_2S). That has been done as the degrees of hydration achieved by studied pastes were very high and the measured alite contents were very low. Therefore consideration of actual alite and belite contents was not necessary and would introduce unnecessary level of complication to our calculation.

3. Results

3.1. Evolution of water signals

Fig. 2 shows the evolution of different 1H NMR signal fractions during hydration of white cement pastes cured underwater at different temperatures. The signal fractions are relative to the total NMR signal (water mass) at the time of mixing. Five fractions are identified, derived

from: water chemically combined in crystalline phases, I_{sol} ; water in C-S-H interlayer spaces, I_{CSH} ; water in C-S-H gel pores, I_{gel} ; and from water in interhydrate and capillary pores that are here combined and treated together as ‘free’ water, I_{cap} .

Fig. 2a presents the evolution of NMR signal fraction associated with the chemically combined water within crystalline phases. No correction has been made for possible fast exchange between protons of Portlandite and ettringite surface hydroxide groups and pore bulk water. As presented in previous publication [1,13] the solid ^1H fraction measured by QE accounts accurately for the hydrogens content within crystalline phases: Portlandite and ettringite as measured by XRD and TGA methods. The chemically combined water fraction increases with hydration time as expected. It develops earlier and increases faster in the early stages of hydration as the curing temperature is increased so that, as expected, there is more crystalline phase in samples cured at higher temperature. However, there is a distinct slowing down in growth of crystalline phase when the associated water fraction is about 20-25% and this slowdown is more accentuated at higher temperature. In consequence, beyond about 4-6 days of hydration, the trend reverses. The growth rate and the volume of crystalline phase is greater at lower temperature.

Consistent with the growth in crystalline phases, the signal fractions attributed to C-S-H interlayer and gel pore water, Figs. 2b and c respectively, appear earlier and develop more rapidly as the curing temperature is increased. Again there is a slowdown, so that, at later ages, the fractions of gel and interlayer water for samples cured at lower temperature exceed those for the higher temperatures. The “crossover” occurs for C-S-H interlayer water between 1 and 30 days of hydration and for C-S-H gel water between 0.5 and 3 days depending on the curing temperatures. It is also observed that the plateau in gel pore formation happens earlier at higher temperature. We note that the gel pore water signal seems to decrease and then increase again with the hydration time especially at higher curing temperatures. It may be

caused by a systematic analysis issue related to separation of the gel and interhydrate pore water or by the influence of the increase belite reaction at higher temperature, however we cannot fully explain it. The difference in C-S-H water fraction at 90 days of hydration is relatively small in absolute terms, about ~5%, across all the samples studied. However, it is quite significant in relative terms, closer to 20% difference for interlayer water and 10% for gel pore water. The ratio of C-S-H gel pore to interlayer space water fraction decreases faster for paste cured at elevated temperature. For mature pastes, this ratio reaches a value of about 2 at every temperature: it is ~1.9 at 10 °C and ~2.2 at 60 °C.

Fig. 2d presents the evolution of ‘free’ water fraction. During the initial stages of hydration, ‘free’ water is consumed faster at higher temperature. However, in more hydrated samples, there is more ‘free’ water left at elevated temperature compared to lower temperature.

Fig. 3 offers another way to interpret the influence of temperature on the microstructure of cement paste. Fig. 3 plots the time at which a given fraction of the mixing water is consumed against temperature. It is seen that the hydration time for which the initial mixing water is consumed by 50% and 80% decreases with increasing curing temperature from 10 to 60 °C. However, in striking contrast, the time at which 90% of mix water is consumed increases with increasing temperature. Indeed, this condition is not even reached in 90 days at 60 °C. One interpretation of the data is that a coarser porosity remains at higher temperature that is subsequently much harder to fill with hydration products. A coarser porosity at higher temperatures has been previously reported in literature based mainly on SEM observation [4,14–16] but also MIP results [15].

Together, Figs. 2 and 3 demonstrate not only the acceleration of hydration reactions at early age by elevated temperature but also a change in the way water is bound into hydrates at later ages.

The actual NMR signal fractions measured at 28 and 90 days of hydration as used in the C-S-H density calculation are presented in Table 1 of the supplementary materials.

Fig. 2. Evolution of different water populations (a: chemically combined water; b: C-S-H interlayer water; c: gel pore water; and d: 'free' water) as a function of hydration time for white cement pastes mixed at w_{mix}/c ratio 0.4 and cured underwater at different temperature.

Blue inverted triangles represents curing at 10 °C; black circles: 20 °C; cyan diamonds: 30

°C; red squares: 40 °C; orange left-triangles: 50 °C; and green triangles: 60 °C. Lines are guides for eyes.

Fig. 3. Consumption of ‘free’ water for white cement pastes mixed at w_{mix}/c ratio 0.4 and cured underwater at different temperature. The hydration time of sample at which the initial fraction of ‘free’ water is consumed by 50% is shown as blue squares, by 80% as red circles and by 90% as green triangles.

Fig. 4 shows how the associated T_2 relaxation times of the interlayer, gel and the principal component of the “free” (interhydrate) water fractions vary with hydration time at different curing temperatures. The T_2 relaxation time of ‘free’ water decreases with time and asymptotes to a value of about 1.5 ms for all curing temperatures. It just does this more quickly at higher temperature. The time at which the asymptote value is achieved is about the same as the time at which the plateau in gel pore formation starts. Corresponding pore sizes may be calculated according to the fast diffusion model of relaxation [17]. Using a surface relaxivity equal to $3.7 \cdot 10^{-3}$ nm/ μ s as discussed in our previous work [6,13], yields an

interhydrate pore size of about 11 ± 2 nm. The exception to all of this is the T_2 relaxation time for samples cured at 10°C . This shows an apparent increase after about one month of curing. This may be an artefact of the data fitting, ultimately linked to the very small size of this signal fraction.

Similar to the capillary water, the T_2 of gel pore water also decreases initially more quickly as the hydration process is accelerated at higher temperature. However, after about a week, the trend reverses. The pastes cured at higher temperatures are characterised by the longer T_2 . For instance, it is $360\ \mu\text{s}$ at 60°C compared to $240\ \mu\text{s}$ at 10°C after 90 days hydration. This indicates that the typical gel pore size may be larger in samples cured at higher temperature: 2.7 ± 0.2 nm at 60°C compared to 1.8 ± 0.2 nm at 10°C using the previous calibration factors.

The T_2 of water within C-S-H interlayer spaces stays almost the same at all temperatures after 3 days of hydration, $90\text{-}100\ \mu\text{s}$, resulting in the C-S-H interlayer spacing of $0.67\text{-}0.75 \pm 0.04$ nm. We note that the obtained values for interlayer and gel pores at 20°C are smaller than previously reported [13]. This may be due to the different cement composition, but may equally be due to a systematic bias in the stripped exponential data fitting methodology compared to ILT.

One further aspect to consider in reflecting on these results is the temperature dependence of the T_2 relaxation time. That this has minor impact in the current study is evidenced by experiments to evaluate the activation energy of ^1H NMR relaxation in cement paste [6] where samples are prepared and cured at a given temperature but measured at various temperatures. The differences in the T_1 relaxation time of interlayer and gel pore water at 28 days of hydration measured at 10°C and at 60°C were 50 and $60\ \mu\text{s}$, respectively. The ratio of T_1 to T_2 for cement pastes typically equals 4 [18]. Hence, the expected differences in T_2 relaxation time for interlayer and gel pore water for any given sample *measured* at 10 and 60

°C are expected to be about 12.5 and 15 μ s, respectively. This is smaller than the changes found here for the gel pore water for samples *cured* at 10 and 60 °C.

Fig. 4. The evolution of T_2 relaxation times of ‘free’ – interhydrate water (upper graph), gel pore water (middle graph) and C–S–H interlayer space water (lower graph) within white cement pastes mixed at w_{mix}/c ratio 0.4 and cured underwater at different temperature. Blue inverted triangles: 10 °C; black circles: 20 °C; cyan diamonds: 30 °C; red squares: 40 °C; orange left-triangles: 50 °C; and green triangles: 60 °C. Lines are guides for eyes.

3.2. Crystalline phases – Portlandite and ettringite

The XRD patterns showed presence of Portlandite (CH) and ettringite (Ett) and absence of monosulfoaluminate phases at all curing temperatures studied. TGA confirmed the presence of Portlandite. The average of XRD and TGA Portlandite content at 28 days of hydration, the TGA Portlandite content at 90 days as well as the XRD ettringite content at 50 days as a function of temperature are shown in Fig. 5. The contents separately measured by XRD and TGA methods are presented in Table 2 of the supplementary materials. For all 28 days old samples hydration was stopped by isopropanol exchange in contrast to the measurement performed on not altered samples at 90 days of hydration. Despite the fact that it has been reported in literature that the alcohol exchange, including isopropanol, may alter the Portlandite and calcite determination by TGA method [19], we report a good consistency between the TGA and XRD measurements performed at 28 days.

Additionally the contents of Portlandite and ettringite expressed as equivalent water fraction are presented in Table 2 of the supplementary materials. The combined water fraction within CH and ettringite determined by TGA and XRD is within 2.5% of the assigned NMR solid signal fraction across the full temperature range.

Fig. 5. The ettringite content measured by XRD (green triangles) at 50 days, the average of XRD and TGA measured Portlandite content at 28 days (blue circle) and Portlandite content measured by TGA at 90 days (red squares) of white cement pastes cured at different temperatures. The plot shows all measured data. At intermediate temperatures, where measurements are not available, the content was determined by linear extrapolation.

The results show that the content of CH does not vary substantially across the curing temperature range studied. The average values are $m_{CH} = 0.271 \pm 0.005$ g/g of anhydrous cement at 28 days of hydration and 0.308 ± 0.005 g/g of anhydrous cement at 90 days. The same observation was seen by Gallucci *et al.* [4] and by Kjellsen *et al.* [4,16]. On the other hand, the content of ettringite decreases significantly at higher temperature. A lower ettringite content at elevated temperatures was also found by Lothenbach *et al* [14] and Gallucci *et al* [4] and it can be explained by the relative changes in solubility of ettringite and monosulfate phases with temperature.

3.3. Degree of hydration

The degree of hydration (α) as measured by XRD is shown in Fig. 6. The difference of degree of hydration between lowest and highest applied temperatures is $\Delta\alpha = 0.11$ and 0.08 at 28 and 90 days of cement hydration, respectively. The actual data required for calculation of the C-S-H density is presented in Table 3 of the supplementary materials. It is noted the samples are small, contain 64% of alite, no ferrite and are cured underwater – facilitating hydration.

Additionally, the increase of the degree of hydration with temperature indicates that the degree of hydration of belite changes strongly with temperature. As mention before, the analysis applied in this study assumes that all alite reacts first and therefore the remaining hydration is due to belite, in such a way the temperature dependence of belite is included into calculation.

Fig. 6. Degree of hydration as a function of the curing temperature of white cement pastes mixed at w_{mix}/c ratio 0.4 and cured underwater 28 (blue circle) and 90 days (red squares). The plot shows all measured data. At intermediate temperatures, where measurements are not available, the degree of hydration was determined by linear extrapolation.

3.4. Chemical shrinkage

Fig. 7 shows the increase of chemical shrinkage volume (V_{sh}) during hydration at different temperatures. As the curing temperature increases, so the chemical shrinkage starts at earlier hydration times and initially proceeds more quickly, suggesting faster hydration at higher temperature. The acceleration of the hydration process at higher temperatures has been previously reported based on the measurements of chemical shrinkage [20], degree of hydration [4,14], TGA [14] and strength development [14,21].

The development of chemical shrinkage volume slows down considerably at later times and appears to asymptote towards a constant value. This constant value is lower at elevated curing temperature and is achieved earlier. Very similar temperature dependence of chemical shrinkage was observed by Geiker and Knudsen [20] through weighing of samples immersed in liquid paraffin.

Values of the chemical shrinkage and hence the actual water to cement ratio of the pastes calculated directly from the increase in sample mass are presented in Table 4 in the supplementary materials. These results are used in the next section.

▼ 10 ● 20 ◆ 30 ■ 40 ◀ 50 ▲ 60°C

Fig. 7. Chemical shrinkage as a function of hydration time for white cement pastes mixed at w_{mix}/c ratio 0.4 and cured underwater at different temperature: blue inverted triangles: 10 °C; black circles: 20 °C; cyan diamonds: 30 °C; red squares: 40 °C; orange left-triangles: 50 °C; and green triangles: 60 °C.

4. Analysis

4.1. C-S-H density and composition

All the experimental data required to calculate the C-S-H density at 28 and 90 days of hydration is presented in the previous section. The ettringite content at 50 days was used to represent ettringite content at both 28 and 90 days. This is justified on the basis that the ettringite content of the same cement (but different batch) remains constant after the first day of hydration [1] because all calcium sulphates react within the first days and the low C_3A content does not allow precipitation of AFm at later ages. The only additional parameters required are the densities of cement, water, Portlandite and ettringite, $\rho_{c,w,CH,Et}$, which were taken as 3.15, 1.00, 2.24 and 1.77 g/cm³ respectively [22].

Fig. 8 shows the calculated C-S-H ‘solid’ and ‘bulk’ densities as a function of curing temperature. The C-S-H ‘solid’ density increases with temperature from $\rho_{CSH} = 2.50 \pm 0.03$ g/cm³ at 10 °C to $\rho_{CSH} = 2.64 \pm 0.03$ g/cm³ at 60°C °C at 28 days of hydration; and from $\rho_{CSH} = 2.57 \pm 0.03$ g/cm³ at 10 °C to $\rho_{CSH} = 2.69 \pm 0.01$ g/cm³ at 60 °C at 90 days of hydration.

However, the largest rate of change with temperature is at the lower end of the temperature range. The results at 20 °C are in good agreement with our previous room temperature measurements [13]. They are also very close to the room temperature value obtained by SANS measurements for a fully saturated CM-II globule density of 2.604 g/cm³ [23]. The

SANS density also excludes water on the outer surface of particles. However, at 20 °C, the values are at the upper end of estimates by helium picnometry [22,24,25].

The C-S-H ‘bulk’ density also increases with temperature from $1.85 \pm 0.01 \text{ g/cm}^3$ at 10 °C to $2.01 \pm 0.01 \text{ g/cm}^3$ at 60 °C after 28 days hydration and from $1.90 \pm 0.01 \text{ g/cm}^3$ to $2.01 \pm 0.01 \text{ g/cm}^3$ after 90 days. As with the solid density, these measurements are in line with our previous room temperature measurements and also with values measured by Young and Hansen [26] using shrinkage weight loss curve and gas picnometry at 11% RH and with values evaluated using the CM-II model [27].

The observed density increase is in good agreement with the increase reported by Bahafid *et al.* [5] who evaluated the C-S-H bulk density change from 1.88 g/cm^3 at 7 °C to about 2.04 g/cm^3 at 60 °C. We notice however that the freeze-drying procedure that has been found to cause the damage to the pore structure [28], has been used in that study as a method of sample preparation for MIP and as a measure of the input parameters for the density calculation. A larger increase in ‘bulk’ density with temperature was reported in a recent study by Gallucci *et al* [4] for sealed cement paste hydrated between 26 days (at 60 °C) and 50 days (at 5 °C). The calculations were based on analysis of SEM images and quantification of phases using XRD. We note that these methods have a shortcomings once they are used to assess the capillary porosity (SEM) and mass fraction of the C-S-H (XRD). Therefore the density results (that were obtained by some of us) dependent on these parameters may be erroneous.

The recorded uncertainties of the C-S-H density and composition in our article represent the standard deviation of multiple samples and repeat measurements. The sensitivity of the resultant C-S-H characteristics on input parameters has been investigated and is described in more detail in [2,6].

Fig. 8. C–S–H density as a function of the curing temperature of white cement pastes mixed at w/c_{mix} ratio 0.4 and cured underwater 28 (squares and triangles) and 90 days (diamonds and circles). The red squares and black diamonds represent the C–S–H ‘solid’ density, exclusive of the gel pore water; green triangles and blue circles represent the C–S–H ‘bulk’ density, inclusive of the gel water. Error represents the standard deviation value.

4.2. Composition of C-S-H at various temperature

The C-S-H composition is expressed as $Ca_z(Si_y, Al_{(1-y)})O_{(z+y/2+3/2)}(H_2O)_x$. The water content within C-S-H excluding, x , and including, x' , gel pore water is presented in Fig. 9. The x and x' follow the inverse trend of the density curves. The ‘solid’ C-S-H water content decreases with temperature by $\Delta x = 0.49$ and 0.46 at 28 and 90 days of hydration respectively. The water content with gel water included also decreases with temperature, by $\Delta x' = 1.35$ and 1.01 at 28 and 90 days of hydration.

The actual water content at 20°C excluding the gel pore water is $x = 1.51 \pm 0.13$ and 1.39 ± 0.01 after 28 and 90 days of hydration respectively. The corresponding values for the water content including gel water are $x' = 4.58 \pm 0.03$ and 4.29 ± 0.01 . All these values are lower

than expectation based on our own previous measurements ($x = 1.7$ to 1.9 ; $x' = 4.66$ to 5.25) [1,13] and also compared to the SANS data ($x = 1.8$) [23] and CM-II model calculation ($x' = 5$ including large gel pores) [27]. The reason for the lower water content values obtained is not fully understood but may be a consequence of the high dependency of this calculation on the model input parameters. Notwithstanding, the water content results are broadly in line with a wider review reporting various calculated H_2O/Si ratio [29].

Fig. 9. C–S–H water content as a function of the curing temperature of white cement pastes mixed at w_{mix}/c ratio 0.4 and cured underwater 28 (squares and triangles) and 90 days (diamonds and circles). The red squares and black diamonds represent water in the C–S–H excluding the gel pore water (x); green triangles and blue circles represent the water in the C–S–H, including the gel water (x'). Error represents the standard deviation value.

There is no discernible change in the $Ca/(Si + Al)$ ratio, z , with increasing temperature, Fig. 10a. The average value across the temperature range studied is $z = 1.78 \pm 0.01$ at 28 days of hydration and $z = 1.67 \pm 0.01$ at 90 days. Likewise, the $Al/(Si + Al)$ ratio and Si content, y ,

are constant within experimental error, Fig. 10b and c. The average y value is $y = 0.97 \pm 0.01$ across all temperatures and both hydration times. The $\text{Ca}/(\text{Si} + \text{Al})$ ratio of sealed cement paste with w/c ratio 0.4 was reported by Gallucci *et al* [4]. Based on SEM-EDS analysis it remains the same in temperature range 5 to 60 °C at around 1.8. Lothenbach *et al* [14] used the same method to estimate the ratio for sealed Portland-limestone cement paste. The ratio was found to not differ significantly (1.62 to 1.72) with increase of temperature (5 to 40 °C); it remained fairly constant in the range of experimental errors.

Fig. 10. $\text{Ca}/(\text{Si} + \text{Al})$ ratio (a), $\text{Al}/(\text{Si} + \text{Al})$ (b) and Si content (c) in the C–S–H as a function of the curing temperature for 28 days (red circle) and 90 days old (black squares) white cement pastes mixed at w_{mix}/c ratio 0.4 and cured underwater.

4.3. Mass and volume composition

The mass and volume fraction phase composition diagrams after 28 and 90 days of hydration are shown in Fig. 11. An increase in curing temperature increases the overall production of hydrate phases. However, the amount of Portlandite produced remains almost constant between 10 °C and 60 °C and the amount of ettringite content actually decreases. It is observed that the mass and volume of the solid C-S-H is slightly greater at elevated temperature, while the gel water content is slightly reduced. Pastes cured at higher temperature are characterised by a larger content of readily evaporable interhydrate and

capillary water in coarser porosity. These findings indicate that production of the denser C-S-H at elevated temperatures requires relatively less water and more cement consumption.

Fig. 11. Mass and volume composition of white cement pastes mixed at w_{mix}/c ratio 0.4 and cured underwater for 28 days (a) and 90 days (b) at various curing temperatures. From bottom: Portlandite (grey squared region); ettringite (white stripped); C-S-H (grey dotted);

gel pore water (plain white); joint ‘free’ and voids water (plain grey); and unreacted cement (black).

5. Discussion and conclusion

5.1. Solid density increase with temperature

The most obvious statement is that the increase in solid density with temperature cannot be attributed to thermal expansion. This leaves two possible interpretations: (i) a decrease in the number of locally aggregated hydrate backbone layers and/or (ii) a decrease in the backbone basal spacing coupled with change in the backbone silicate chain length.

The first explanation arises from the NMR measurement and cannot easily be tested independent of NMR. A complete hydrate layer comprises a backbone and interlayer.

However a stack of layers as seen by NMR always comprises one more backbone than interlayer as shown for ‘solid’ C-S-H in Fig. 1 (five backbones and four interlayers). This is because water on external stack surfaces exchanges rapidly with the surrounding gel pore water and hence relaxes like gel pore water. As the backbone is more dense than water, and as the number of layers decreases so the *apparent* solid hydrate density as detect by the NMR measurement increases. We can make a reasonable estimate of this change. We previously deduced that the C-S-H comprises of stacks of three backbones and two interlayers for a 28 days hydrated cement paste underwater cured at 20 °C and with the C-S-H solid density of 2.68 g/cm³ [13]. Using mineral 14 Å tobermorite [30] as a simple model of C-S-H, it might be supposed that the interlayer water accounts for about 1/3 of the total layer repeat distance. If this has a density of 1.0 g/cm³, then the backbone (calcium silicate layer – solid line in Fig. 1) itself has a density of 3.24 g/cm³ – both of which are assumed not to depend on the temperature, especially considering that the calcium, aluminium and silicon content of the C-S-H does not change with temperature as shown in Section 4.2. Now suppose the number of

layers is reduced to just 2. The resultant 2 backbones and single interlayer of water as seen by NMR have a combined density of 2.79 g/cm^3 – more than for a stack of three backbones 2.68 g/cm^3 . Now suppose the number of layers is 10. The resultant 10 backbones and 9 interlayers of water as seen by NMR have a combined density of 2.54 g/cm^3 – less than for a stack of three backbones 2.68 g/cm^3 .

Of course, the number of layers at any temperature is not infinite. The calculation can be reverse engineered, in which case, we deduce based on obtained densities that the average number of locally stacked layers is 14 at 10°C decreasing to just more than 3 at 60°C . The calculation is very sensitive to the backbone density and to the fractional interlayer thickness, especially for a large number (> 5) interlayers but nonetheless these results are typical of what is obtained for “sensible” input data. They are also plausible as a mechanism behind the non-linear apparent increase in solid density.

The second explanation that sees a basal spacing decrease is less plausible. An increase in silicate chain length with temperature has been reported by Cong and Kirkpatrick [31]. They suggest that this drives out OH^- groups leading to a decrease in basal plane spacing. Gallucci *et al.* [4] go on to calculate that, based on an increase in chain length from 2.98 at 5°C to 4.13 at 60°C , this results in a reduction in the interlayer water equivalent to 0.15 water molecules per C-S-H unit. This is much less than we (and indeed Gallucci *et al.* [4]) observed and is insufficient therefore to account for the observed density changes. We also note that we do not see significant change in the interlayer T_2 – a measure of the interlayer thickness. While we are likely insensitive to a change equivalent to just 0.15 in 1.5 waters (10% reduction), we would most likely see a change in T_2 brought about by a 35% change in interlayer thickness that is required to change the density from 2.64 g/cm^3 (measured at 60°C) to 2.50 g/cm^3 (measured at 10°C) based on maintaining a locally stack of 3 layers. It is

possible that the water content of the interlayer decreases with increasing temperature independent of the basal spacing but we have no evidence of this.

5.2. Bulk density increase with temperature

The bulk density can be expected to increase in line with solid density if the amount of the gel pore water is constant. However an increase will also be observed if there is less gel porosity per unit volume of gel. Less gel porosity can arise from the same number of the smaller gel pores or fewer gel pores of the same size. Smaller gel pores should lead to a decrease in gel pore water T_2 relaxation time, but, if anything we observe the opposite (Fig. 4). Fewer gel pores result in a lower gel water fraction which is observed (Fig. 2c). We therefore conclude that, decrease in gel porosity, at least partially contributes to the C-S-H densification with increased temperature.

The C-S-H ‘bulk’ density increase can also arise as a result of greater inner C-S-H product fraction in comparison with the outer product – as the inner product has a higher density than the outer product. We however have no direct evidence of this phenomenon.

As an additional comment, we note that a study has been performed with cement paste samples cured at room temperature and subsequently exposed later to elevated temperature [3]. This study showed that a temperature increase for mature samples with well-developed microstructure causes redistribution of water populations due to either water migration and/or pore rearrangement; the decrease in the signal of interlayer water is accompanied by the increase of the gel and partially capillary water signal. In our study, the same temperature has been maintained throughout entire hydration process, with increase of temperature at mature ages we observe less interlayer and but also less gel pore water while the content of interhydrate and capillary water is higher.

5.3. Comparison with earlier measurements of density

The bulk density measured in this work by NMR are in striking agreement with those bulk density measured by Bahafid *et al.* [5] using a combination of methods including X-ray diffraction, thermogravimetric analysis and mercury intrusion porosimetry. They were unable to determine the solid density which was assumed based on the work of Jennings [27].

The data are not in agreement with those previously obtained by some of us based on analysis of electron microscopy and X-ray diffraction. It is now clear as also commented by Bahafid *et al.* [5] that discrepancy arises from the shortcomings of the SEM analysis and XRD for determination of the capillary porosity and C-S-H mass fraction, respectively.

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Appendix A. Supplementary data