

STUDY OF THE NANO-STRUCTURE OF C-S-H USING NUCLEAR MAGNETIC RESONANCE

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Introduction

Calcium-silicate-hydrate (C-S-H) is the active component of cement, the binder phase of concrete. Cement production exceeds 3 billion tonnes per annum and contributes 5-8% of global CO₂ [1]. Our reliance on cement for infrastructure is global, yet there is clearly a need to reduce the CO₂ impact. A way forward is to incorporate more environmentally favourable supplementary cementitious materials. However, their use depends on maintaining and predicting concrete properties. Since water underpins performance and is central to all concrete degradation mechanisms, progress requires thorough understanding of C-S-H nanostructure, the role of water within it and a rapid means to characterise C-S-H in new, candidate materials.

Nuclear Magnetic Resonance relaxation time analysis is an established technique for non-invasive and non-destructive characterization of pore size distributions and pore-water interaction in porous media such as cement and concrete [2,3].

The purpose of this project is to show that the NMR experiment is quantitative, simply to carry out and provide a greater level of detail concerning microstructure than other techniques. We present how quantitative NMR data can lead to the full description of cement paste, C-S-H density and chemical composition and how it can be used to create a pore-type resolved sorption isotherm. We show how ¹H NMR can be used to determine the evolution of nanoscale porosity of white cement pastes, with and without addition of silica fume, cured at different temperatures. The impact of silica fume addition on characteristics of C-S-H is investigated.

NMR probes the water, or more precisely the hydrogen protons, within filled pores. The NMR signal amplitude is proportional to the mass of water. The signal lifetime, known as the spin-spin relaxation time T_2 , is very sensitive to pore size, for the so-called fast diffusion limit for pores filled with water $\frac{1}{T_2} \propto \frac{\lambda S}{V}$ where λ is the surface relaxivity, S is the surface area and V is the volume of the pore [4]. T_2 of water in pore therefore varies from 100 μ s to 100 ms. The T_2 of water bound in solid is even shorter, circa 10 μ s. NMR has advantage over other methods of studying porosity of cement paste in that it does not require drying or vacuum preparation of the sample. The delicate structure of C-S-H gel is not disturbed by the NMR measurement.

By applying combined CPMG (Carr-Purcell-Meiboom-Gill) and Quad-Echo pulse sequences, all hydrogen protons in the cement paste can be measured and quantified in their different environments [5]: crystalline phases (Portlandite and Ettringite), C-S-H interlayer water, C-S-H gel pore water and capillary pore water. The quantitative analysis is supported by parallel X-Ray diffraction (XRD) and thermal analysis (TGA) measurement. In order to complete mass and volume analysis, the chemical shrinkage volume, not seen by NMR, is required. A conventional technique of measuring chemical shrinkage is used.

An NMR update to Powers and Brownyard's diagram

Based on the different NMR signals, the water mass in different environments can be quantified at any measurement time. Throughout mass balance and oxides conservation equations, the C-S-H chemical composition can be found; volume balance gives C-S-H density [6]. Summarizing the data, mass and volume composition of the paste can be drawn against, for instance, degree of hydration.

White cement paste at water-to-cement ratio 0.4 is studied throughout the hydration from mixing up to 300 days. The paste is kept sealed at 20°C. The results, presented in Figure 1, display an "NMR update" of Powers and Brownyard's well-known model from 1948 [7]. The evolution of C-S-H density, inclusive and exclusive of gel water is also presented in the Figure 1.

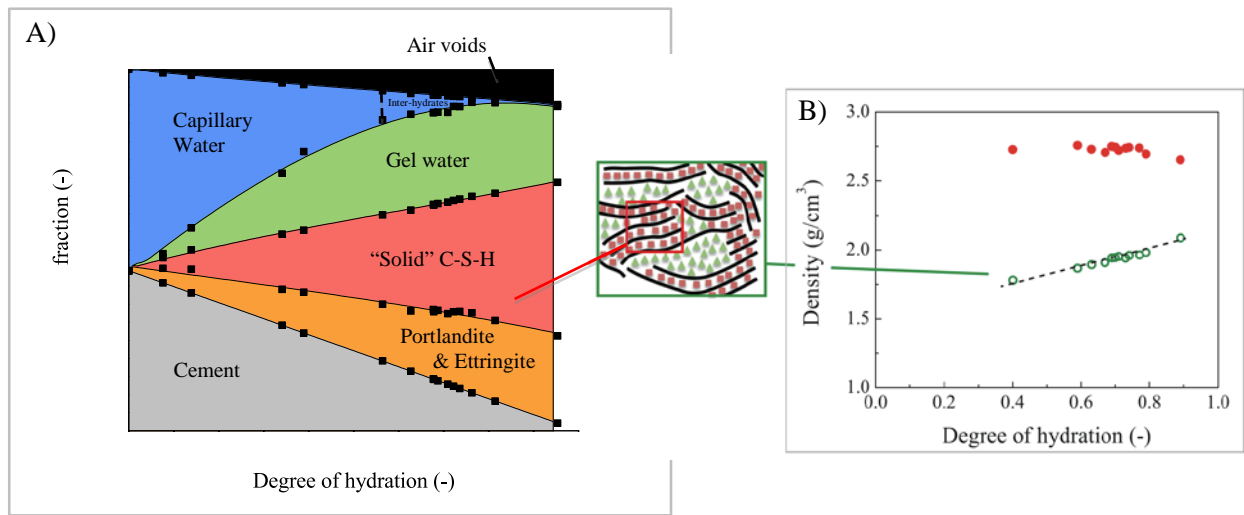


Fig. 1: (A) Volume composition of white cement paste $W/C = 0.4$ as a function of degree of hydration (B) associated C-S-H densities inclusive of the gel water (red dots) and for the “bulk” C-S-H (green empty dots).

The diagram displays the continuous consumption of cement and capillary water leading to the formation of hydration products. Portlandite plus Ettringite as measured by NMR are in very good agreement with XRD and TGA results within 1%. The capillary water rapidly goes down with degree of hydration and becomes what we call water in “interhydrate” pores above $\alpha=0.6$ (about 2.2 days of hydration). At this point, the interhydrate pores are about 10 nm in size. After 2.2 days, the interhydrate water continues to be consumed to form more hydration products but no further decrease in size is observed. We believe this is the distance between the growing C-S-H needles. In parallel, calculations give 0.85 nm for the C-S-H interlayer spacing and 2.5 nm for the C-S-H gel reservoirs. More discussion can be found in reference [6].

The main difference between this model and Powers’ model is the non-linear behaviour of the gel water with degree of hydration. The C-S-H gel is formed mainly during the first 2 days of hydration and then plateaus. This highlights a densification of the C-S-H (inclusive of the gel water) with time. Figure 1B displays the rate of this densification, with density increasing from 1.7 g/cm³ at 1 day up to 2.1 g/cm³ at 300 days. On another hand, the solid C-S-H density (exclusive of the gel water), tends to be roughly constant with time at around $\rho_{\text{solid}} = 2.7$ g/cm³.

The average solid C-S-H chemical composition is found to be $\text{Ca}_{1.7}(\text{Si}_{0.95}, \text{Al}_{0.05})\text{O}_{3.7}(\text{H}_2\text{O})_{1.8}$ for high degree of hydration. This is in agreement with previously reported data in the literature [8,9].

Desorption isotherm

Water desorption and adsorption has long been used as a way to study cement structure. Powers and Brownard’s work led to an early analysis of cement composition and pore morphology that is still widely quoted and used today [7]. However, the state of water in that study was inferred from the mass loss curve. By using NMR relaxometry, we have measured the first drying, re-adsorption and second drying isotherms with water-environment specificity [5].

NMR analysis of water has been performed on white cement paste during progressive drying and rewetting in a controlled relative humidity environment at room temperature. Measurements were made on white cement paste ($w/c = 0.4$) cured under water for 28 days and then subsequently equilibrated to constant relative humidity.

Figure 2 (inset) shows that the loss of total NMR signal intensity with sample mass is linear during controlled drying and implies an effective $w/c = 0.463$. The increase reflects underwater curing of samples and proves that there is no “hidden” water - the NMR experiments sense all the water inside the sample.

The normalized total signal intensity over one and a half cycles presents a normal gravimetric isotherm hysteresis loop, Figure 2B.

The NMR signal can be decomposed into water fractions corresponding to chemically combined water, water in C-S-H interlayer, gel and capillary pores. In this way the first pore size specific sorption isotherm can be generated. The Figure 2A shows the total signal decomposed into particular water fractions as a function of water mass and relative humidity. These plots show how the capillary porosity empties above 90% RH. The gel pore water dries in the range between 100 and about 25% RH. At the same time the C-S-H

interlayer water signal increases. This arises since as the pore empties an immobile surface layer is left. This layer is no longer able to exchange with more mobile water in the bulk of the gel pore, hence, in NMR terms, is seen as interlayer water with shorter T_2 . Below 25% RH, water is rapidly lost from the C-S-H interlayers. In the same RH range an increase in the solid signal occurs. Similar to the gel, as interlayer water is lost, so any residual water molecule appears solid-like. Hence, in this range, the solid signal increases.

Pore sizes are independently calculated from the spin-spin relaxation times in accordance with fast diffusion model of relaxation [4] and from the rate of signal amplitude loss with drying [10]. The C-S-H interlayer and gel pore thickness from primary desorption based on amplitudes model are 1.6 and 3.4 nm respectively. While the values obtained by the relaxation time model are 3.1 nm and 0.94 nm. Given the pore widths from fast diffusion model, the specific surface area (SSA) is evaluated; it is $91 \text{ m}^2/\text{cm}^3$ for gel pores and $175 \text{ m}^2/\text{cm}^3$ for interlayers [5].

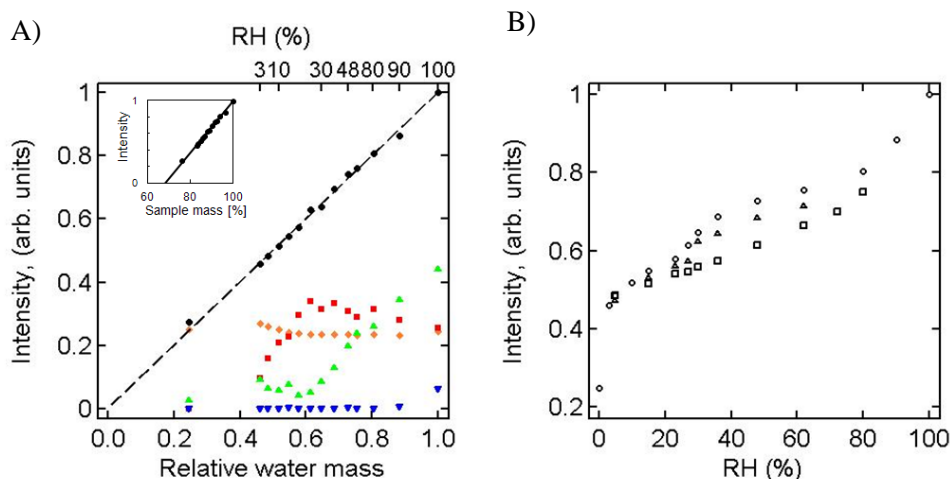


Fig. 2: (A) The total signal plotted against relative water mass and humidity (black rounds) and decomposed into a chemically combined fraction (orange diamonds), water within the C-S-H interlayer (red squares), gel pore water (green triangles) and capillary pore water (blue inverted triangles) for primary desorption. Inset: Total NMR signal intensity as a function of sample mass. (B) The normalized total NMR signal intensity as a function of humidity – first desorption (rounds); adsorption (squares); second desorption (triangles).

Silica fume dependence at room temperature

The addition of 10% of silica fume is known to improve drastically the durability of concretes. The reasons might be numerous: chemical effect of silica fume on the pore solution, filler effects due to its very small size or change in the morphology when C-S-H precipitates from the pozzolanic reaction. Many studies focus on the changes due to addition of silica fume. ^{27}Al and ^{29}Si MAS NMR techniques [11,12,13] are used to quantify the degree of reaction of silica fume. As silica fume reacts, the C-S-H mean chain length is found to increase. Other authors have tried to quantify C-S-H composition in the presence of silica fume based on non-evaporable water measured by TGA using chemical equilibrium[14,15]. The C/S ratio is known to decrease with addition of silica fume leading to a decrease in C-S-H water content within the interlayer space [16]. However, there is no clear/full description on the changes happening to the nanostructure of C-S-H in never dried systems as the hydration proceeds.

We have used NMR relaxometry to characterise the composition and evolution of cement paste with silica fume. White cement paste with 10% of cement mass replacement by silica fume is mixed at a water-to-binder ratio of 0.4. Silica fume is pre-dispersed in water for 8 minutes in an ultrasonic bath before addition of cement and paste mixing. The sample is then sealed into glass tube and measured by NMR throughout the hydration at 20°C , following the same procedure as for the plain white cement. The evolution of the mass fractions of the different populations of mobile water is presented in Figure 3A for the silica fume mix (colours) and compare to plain white cement signal from reference [6] (in black). For clarity of the graph, the solid signal is not shown in this figure.

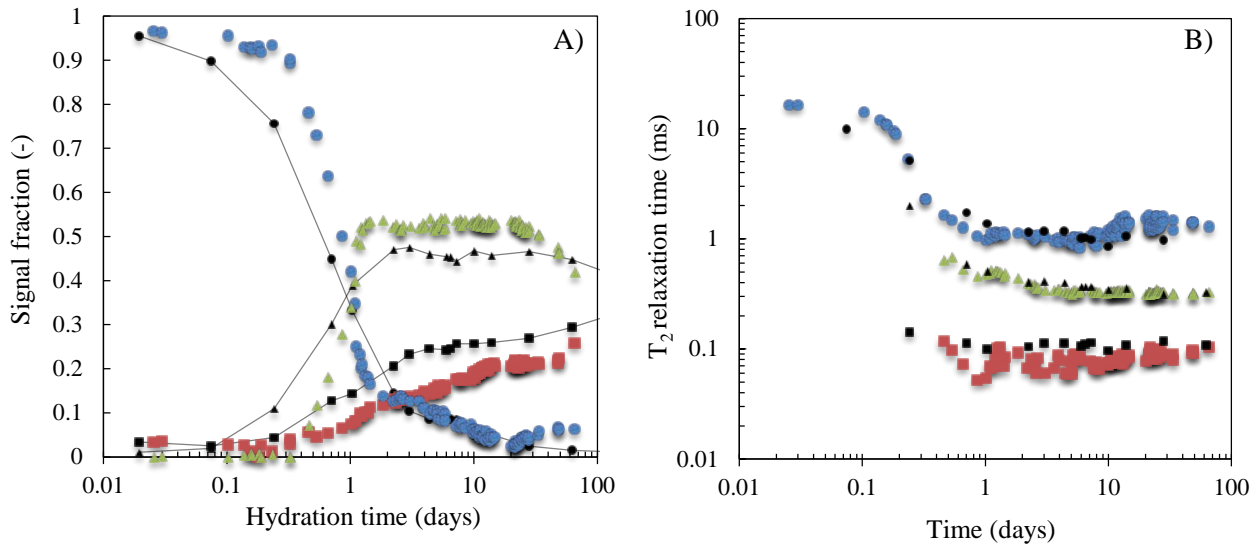


Fig. 3: (A) Evolution of the different mobile water populations against time for white cement + 10% silica fume (colours) and for the reference plain white cement (black), all at $w/b = 0.4$. Rounds are capillary water signals, squares C-S-H interlayer water signals and triangle C-S-H gel water signals. The NMR solid signal is not shown on this graph. (B) Evolution of the associated T_2 relaxation times for the different water populations. Symbols are in accordance with signal amplitudes.

At first sight, the cement with silica fume behaves very similarly to plain white cement. However, there are important differences.

The first difference is that the transition from low density (LD) C-S-H to high density (HD) C-S-H happens earlier. It is illustrated by the change in consumption rate of capillary water and the end of gel pores formation. This transition happens at about 1 day for the silica fume mix compare to 2.2 days previously observed for plain white cement paste. For the silica fume mix, an increase in rate of hydration reactions is observed, as evidence by the slope of capillary water consumption. This increase rate is explained by the extra surface provided by the silica fume, acting as nucleation sites for C-S-H to form [17]. Therefore, the bulk capillary water space in between the unreacted particles becomes filled-up earlier in time. This can be equally observed on the evolution of pore sizes presented in Figure 3B. The interhydrate pore size (10 nm) of the main water reservoir is reached earlier in time in the presence of silica fume. These observations are in a good agreement with the “space-filing” model [18], as already discussed in our earlier publication [6].

The second difference is that the fraction of C-S-H interlayer water is 30% lower in the presence of silica fume. In parallel, the gel water fraction increases. The shortest T_2 relaxation times of the interlayer spacing shown in Figure 3B further suggests that the layers of C-S-H incorporates less water in the presence of silica fume. In terms of pore sizes, it brings the C-S-H interlayer spacing from 0.85 nm for plain white cement down to 0.65 nm when silica fume is added to the mix.

In addition, a higher capillary water fraction is observed at later ages in the presence of silica fume. The density of C-S-H needs to be calculated according to our calculation model to take further this analysis.

Temperature dependence

The curing temperature significantly influences the mechanical and microstructural properties and hence durability of cement, concrete and mortars. The influence on compressive strength is well established – higher curing temperature causes increase of initial strength and long term decrease [19]. Straight changes have been correlated with structural changes [20,21]. Mercury intrusion porosimetry, scanning electron microscopy and backscatter electron image analysis have shown that when temperature increases the total porosity rises with the biggest difference in the volume of the larger pores. The C-S-H distribution is more inhomogeneous.

The NMR experiments have been performed to identify quantitatively the influence of curing temperature on the location of water inside cement paste over the time of hydration. Measurements were made on cement pastes prepared with white cement and white cement with 10% addition of silica fume, mixed at water-to-binder ratio of 0.4 and cured under water.

One way to interpret the data is to compare the time at which a given amount of capillary pore water is consumed inside the sample (Figure 4). The age of sample at which the initial fraction of capillary water is consumed by 50% and 80% decreases with increase in curing temperature for cement pastes, with and without addition of silica fume. However, for samples with silica fume, the capillary water decreases faster. The striking feature is that the consumption of 90% of capillary water is achieved at much longer ages for samples cured at elevated temperatures, both with and without silica fume.

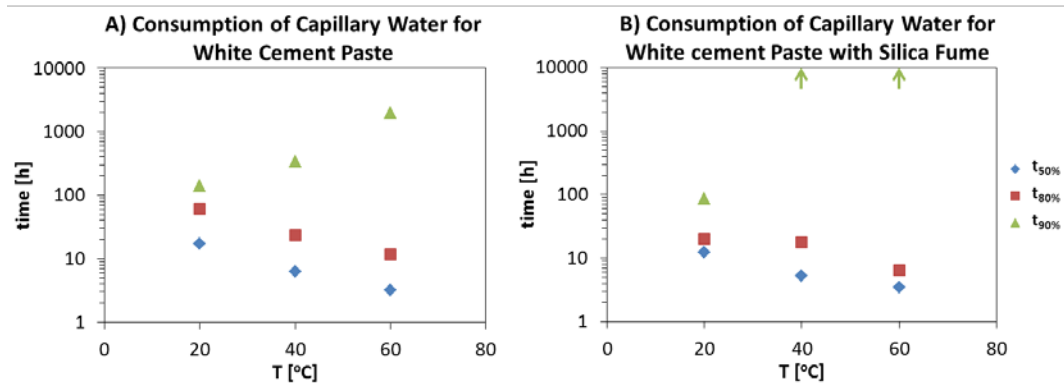


Fig. 4: Consumption of capillary pore water for white cement paste, without (A) and with (B) silica fume.

Figure 5 presents the evolution of water that is chemically bound and water in pores of different sizes (C-S-H interlayer, C-S-H gel and capillary pores) over the time of hydration at three curing temperatures (20, 40 and 60°C). The fraction of water is normalized to the initial mass of water at the mixing point. The total signal fractions go above 1 indicating the underwater curing of the samples. At elevated temperature the capillary water of paste with and without silica fume is consumed faster at early age and much more slowly when samples are older.

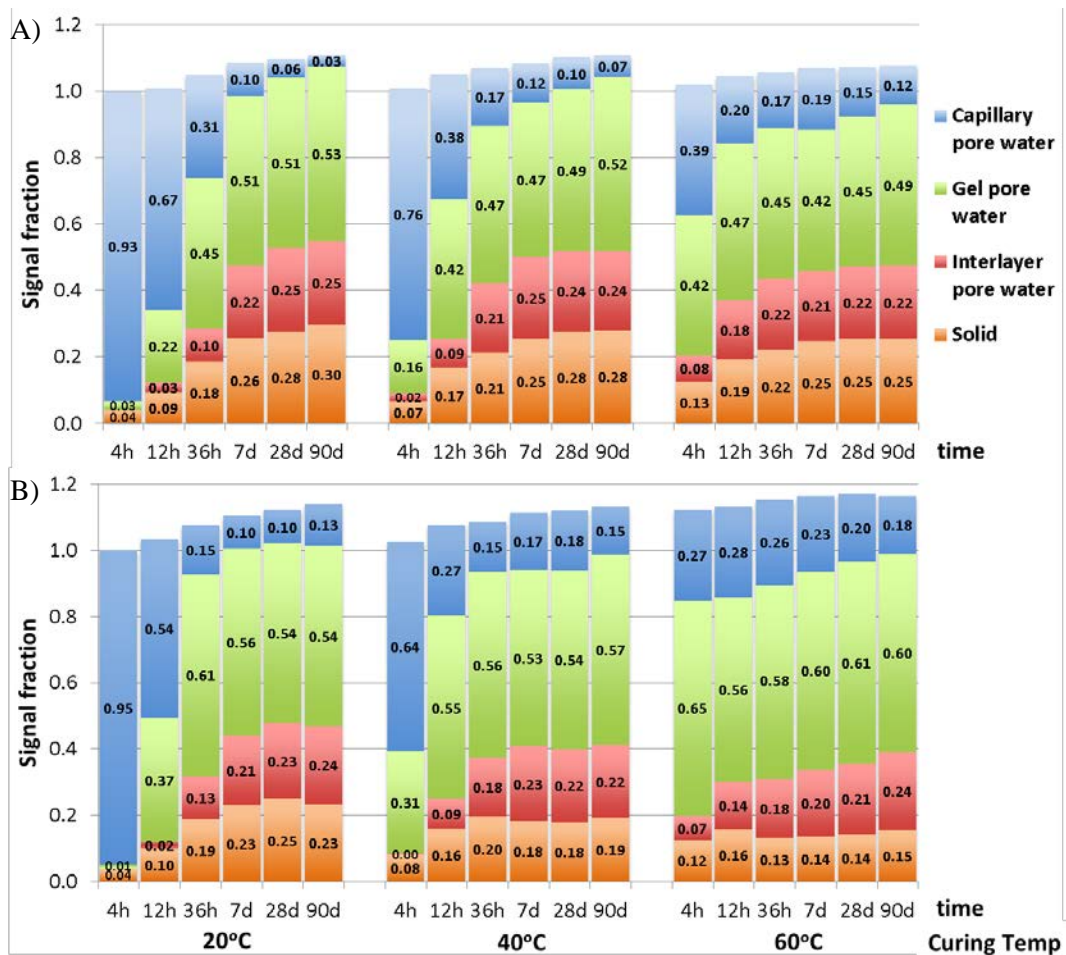


Fig. 5: The evolution of different water population for white cement paste (A) and white cement paste with 10% addition of silica fume (B) over the time of hydration for samples cured at 20, 40 and 60°C.

The development of crystalline phase (Portlandite and Ettringite), C-S-H interlayer and gel pores of white cement paste proceeds faster when the curing temperature is increased (Fig. 5A). However, it is shown that beyond 7 days of hydration the quantity of water content associate with those components has higher values for reference curing at 20°C in comparison with the amounts obtained at the highest applied temperature.

Figure 5B shows that the replacement of cement by 10% of silica fume causes the significant differences in content of chemically combined water. At the younger age the solid signal for samples with silica fume follows the signal of plain white cement paste. Above 2 days of hydration at 20°C, 36h at 40°C and 6h at 60°C the differences in signal can be seen as it decreases by up to 7, 10 and 11% respectively. There is an apparent maximum in the content of solid signal fraction, which moves toward shorter hydration times at higher temperature (20°C – 28days, 40°C – 36 hours, 60°C – 12 hours). It is shown that the paste with silica fume addition contains much more gel pore water in its structure comparing to white cement paste specimens cured at the same temperature for the same period of time. Opposite to white cement paste, the quantity of gel pore water increases with raise of curing temperature. The amount of capillary pores is lower at the earlier age for silica fume mix than for white cement without addition of silica fume. However, in the long term at every given temperature it exceeds it.

Activation energy

The activation energy characterises the minimum kinetic energy required for reaction to occur. The Arrhenius equation relates the rate of reaction with temperature at which this reaction occurred. We have adopted this theory for NMR analysis and relate the relaxation rate with temperature. As water in different pore environment has specific relaxation rate, by looking at the changes in this rate with temperature we are able to define activation energy for water motion in associated pore types.

Inversion recovery (T_1 relaxation) measurements were performed for white cement paste as a function of temperature (-20 to 60°C) at which the relaxation parameters are measured. White cement pastes cured underwater (w/c=0.4) for 28 and 90 days were studied. The data for the 28 days old paste are presented in Figure 6.

The activation energy for C-S-H interlayer and gel pore water molecular motion, at 28 days of hydration, is calculated to be 0.034eV and 0.012eV respectively. In the range between 28 and 90 days of hydration those values do not change considerably.

The dependence of activation energy on T_1 relaxation time shows that molecular motion and its activation energy depends on the pore size. Surface water interaction has significant influence on activation energy.

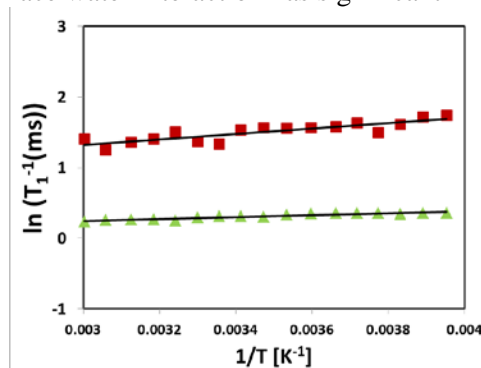


Fig. 6: Distribution of T_1 as a function of temperature for 28 days old white cement paste, green triangles – C-S-H gel pore water, red squares – C-S-H interlayer water.

Conclusions

This work has shown that NMR can provide a lot of information about cement microstructure as a function of hydration time, temperature and mix composition. Changes in the fine nanostructure of C-S-H are tracked with accuracy in never dried material.

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REFERENCES:

- [1] World Business Council for Sustainable Development, Cement Sustainability Initiative, <http://www.wbcscement.org>, (accessed 1st December 2011).
- [2] R. Blinc M. Burgar, G. Lahajnar, M. Rozmarin, V. Rutar, J. Ursic, NMR Relaxation Study of Adsorbed Water in Cement and C3S Pastes" *Journal of the American Ceramic Society*, 61 (1978) 35-37
- [3] A. Valori, P.J. McDonald, K.L. Scrivener, The morphology of C–S–H: Lessons from ¹H nuclear magnetic resonance relaxometry, *Cement and Concrete Research* (49) 65–81
- [4] W. P. Halperin, J.-Y. Jehng, Y.-Q. Song, Application of spin-spin relaxation to measurement of surface area and pore size distributions in a hydrating cement paste, *Magnetic Resonance Imaging* 12 (1994) 169 – 173
- [5] A.C.A. Muller, K.L. Scrivener, A.M. Gajewicz and P.J. McDonald, Use of bench-top NMR to measure the density, composition and desorption isotherm of C-S-H in cement paste, *Microporous and Mesoporous Materials* 178 (2013) 99-103
- [6] A.C.A. Muller, K.L. Scrivener, A.M. Gajewicz and P.J. McDonald, Densification of C-S-H measured by ¹H NMR relaxometry, *Journal of Physical Chemistry C* 117 (2013) 403-412.
- [7] T. C. Powers, T. L. Brownyard, Studies of the physical properties 742 of hardened Portland cement paste; Portland Cement Association 743 (Bulletin 22): Chicago, 1948; reprinted from Proc. J. Am. Concr. Inst. 744 1947, 43, 101, 249, 469, 549, 669, 845, 993.
- [8] A. J. Allen, J. J. Thomas & H. M. Jennings, Composition and density of nanoscale calcium–silicate–hydrate in cement, *Nature Materials* 6 (2007) 311-316
- [9] S.A. Rodger, et al., Microstructural development during the Hydration of Cement. in *Material Research Society Symposium Proceedings*. 1987: Material Research Society.
- [10] P. J. McDonald, V. Rodin, A. Volari, Characterisation of intra- and inter-C-S-H gel pore water in white cement paste based on an analysis of NMR signal amplitudes as a function of water content, *Cement and Concrete Research* 40 (2010) 1656-1663
- [11] H. Justnes, I. Meland, J.O. Bjoergum, J. Krane, A ²⁹Si MAS NMR study of the pozzolanic activity of condensed silica fume and the hydration of di- and tricalcium silicates, *Advances in Cement and Research*, 3 (1990) 111–116
- [12] J. Skibsted, O.M. Jensen, H.J. Jakobsen, Hydration kinetics for the alite, belite, and calcium aluminate phase in Portland cements from ²⁷Al and ²⁹Si MAS NMR spectroscopy, 10th International Congress on the Chemistry of Cement, Göteborg (1997) 2ii056
- [13] H. Zanni, M. Cheyreyzy, V. Maret, S. Philippot, P. Nieto, Investigation of hydration and pozzolanic reaction in reactive powder concrete (RPC) using ²⁹Si NMR, *Cement Concrete Research*, 26 (1996) 93–100
- [14] E. Helsing Atlassi, Nonevaporable water and degree of cement hydration in silica fume-cement systems, in: V.M. Malhotra (Ed.), *Proceedings of the 5th International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete*, American Concrete Institute, Detroit (1995) 703–717
- [15] H. Justnes, E. J. Sellevold, G. Lundevall, High strength concrete binders. Part A: reactivity and composition of cement pastes with and without condensed silica fume', 4th International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Istanbul (1992) 873–889
- [16] S. Brunauer, S. A. Greenberg, The Hydration of Tricalcium Silicate and (β-Dicalcium Silicate at Room Temperature, *Proceedings of the 4th International Symposium on the Chemistry of Cement*, Washington, Vol. 1(1960) 135–163
- [17] W. Gutteridge, J. Dalziel, Filler cement. The effect of the secondary component on the hydration of portland cement: Part 1. A fine non-hydraulic filler, *Cement and Concrete Research*, 20 (1990) 778–782
- [18] S. Bishnoi, K. L. Scrivener, μic: a new platform for modelling the hydration of cements, *Cement Concrete Research* 39 (2009) 266–274
- [19] M. Zajac, S. Garrault, A. Nonat, Effect of the hydration temperature on mechanical resistance of Portland cement mortar and paste, *Cement Wapno Beton* 2 (2007) 68–75
- [20] K.O. Kjellsen, R.J. Detwiler, O.E. Gjörv, Development of microstructures in plain cement pastes hydrated at different temperatures, *Cement and Concrete Research* 21 (1991) 179–189
- [21] K.O. Kjellsen, R.J. Detwiler, O.E. Gjörv, Pore structure of plain cement pastes hydrated at different temperatures, *Cement and Concrete Research* 20 (1990) 927–933