The morphology of C-S-H:
Lessons from ^1H nuclear magnetic resonance relaxometry

A. Valori¹, P. J. McDonald^{1*}, K. L. Scrivener²

1: Department of Physics, University of Surrey, Guildford, Surrey, GU2 7XH, UK

2: Laboratory of Construction Materials, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

* Corresponding author

Abstract

¹H Nuclear magnetic resonance has been applied to cement pastes, and in particular calcium silicate hydrate (C-S-H), for the characterisation of porosity and pore water interactions for over three decades. However, there is now renewed interest in the method, given that it has been shown to be non-invasive, non-destructive and fully quantitative. It is possible to make measurements of pore size distribution, specific surface area, C-S-H density and water fraction and water dynamics over 6 orders of magnitude from nano- to milli-seconds. This information comes in easily applied experiments that are increasingly well understood, on widely available equipment. This contribution describes the basic experiments for a cements audience new to the field and reviews three decades work. It concludes with a summary of the current state of understanding of cement pore morphology from the perspective of ¹H NMR.

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70 **1 Introduction**

71 This paper reviews the use of ^1H or proton Nuclear Magnetic Resonance (NMR) to study
72 the pore structure of cement pastes. Unlike most classical techniques used for the
73 characterisation of pore structure, ^1H NMR does not require prior drying; just the opposite,
74 NMR uses the protons in the water molecules to interrogate the structure. For cements, this
75 is a major advantage. Water is an integral part of the microstructure of cement paste and
76 removal of water causes irreversible damage to the structure.

77 The first systematic analysis of cement pastes by ^1H NMR was by Blinc *et al.* in 1978 [1].
78 Since then there have been very many further studies yielding a wealth of results, in
79 particular during the 1980's and again during the last decade when major progress was
80 made. However, these studies have used different variants of the method and different
81 spectrometers with different operating characteristics at different frequencies, so it has not
82 always been easy to reconcile results across studies. It is the purpose of this review to
83 understand these differences. In order to do this it is necessary to understand the physics of
84 the NMR experiments and so these, too, are reviewed. The review then goes beyond
85 previous reviews [2,3] by pulling together the picture of C-S-H microstructure that emerges
86 from the ^1H NMR work.

87 Hydrogen NMR as a tool for the study of cement has developed out of a much broader field
88 of research. NMR relaxation analysis and related pulse-field-gradient methods have been
89 developed over many years as a tool for the characterisation of microstructure and liquid
90 dynamics in porous media. The methods have been applied successfully to the
91 characterisation of reservoir rocks and fluids within them for petroleum engineering; the
92 study of flow and process within chemical reactors; and to food, pharmaceutical and
93 biological systems amongst much else [4]. Two principal advantages of the methods are
94 clear. First, NMR can be both non-destructive and non-invasive. This means that repeat
95 measurements can be made on the same samples over the course of time. Sample variability
96 is thus removed from the equation. Second, the water that is itself a primary constituent of
97 the cement is also the primary probe. In general, there is no need to dry or otherwise prepare
98 a sample prior to measurement, a process that might disrupt the microstructure under
99 investigation. In cements, these important advantages are balanced by disadvantages. First,
100 compared to many other porous materials, cements contain small pores with relatively large

quantities of paramagnetic impurities. The consequence is that signal lifetimes are shortened compared to other systems. This leads to an extra degree of experimental complexity. The second stems from what is really an advantage. NMR is a complex and rich spectroscopy. This richness means that much is possible but also implies that great care must be taken in the interpretation of results.

The paper does not attempt to explore the application of NMR spectroscopy, such as ^{29}Si , ^{27}Al , ^{17}O or even ^{33}S spectroscopy which addresses the molecular structure of different C-S-H phases. These methods and their application have been widely reviewed, for instance by [5].

2 Essential NMR

2.1 Background and scope

The nucleus of many atomic species, including the hydrogen proton, is a sub-atomic magnet. In an applied magnetic field, $\mathbf{B}_0$, the rules of quantum mechanics allow hydrogen nuclei to align either parallel or anti-parallel to the magnetic field. The parallel, or “up”, orientation has slightly lower energy and so, according to a Boltzmann distribution, is slightly preferred. Explanations of NMR generally only concern themselves with the small excess of nuclei aligned with the field since, for the remainder, every “up” nucleus is always counteracted by another that is “down”. The small excess of nuclei aligned with the field creates a bulk nuclear magnetisation. The field direction is traditionally used to define a z -axis. If the aligned nuclei are tipped away from the z -axis, then they precess around the field, or “resonate” at a frequency ω_0 directly proportional to the field strength, B_0 , according to the Larmor equation

$$\omega_0 = \gamma B_0 \quad [1]$$

Here γ is the magnetogyric ratio, a constant that is a fundamental property of the nuclear species under consideration. For hydrogen protons, γ is approximately 42 MHz/T. Coherent precession of the nuclei can be stimulated by a short pulse of radio frequency waves transmitted into the sample at the Larmor frequency that both tips the magnetisation away from the z -axis and disturbs the equilibrium Boltzmann population. Coherent precession means all nuclei turning together in phase and results in a rotating macroscopic magnetisation that maybe detected by a radio receiver, “listening” for the response. The power of the method lies in three facts:

i The magnetic field experienced by the nuclei is not just the applied laboratory field. The applied field is enhanced by the small local fields within the sample itself, due for instance to neighbouring nuclei and unpaired electrons in chemical bonds. Different nuclei experience different local fields and measurement of the small resultant shifts in resonant frequency (chemical shift and scalar coupling) is a powerful, well-proven and widely available method of elucidating complex molecular structures. This is structural information at the atomic scale. In cements it has mainly been applied to ^{29}Si coordination. As stated above, this is not discussed further in this review.

ii Of particular relevance to the ^1H NMR of cements is that the local fields are time dependent as a result of molecular dynamics (rotations and translations) within the sample. Time dependent magnetic fields are responsible for nuclear spin relaxation, which is the recovery to equilibrium of the nuclei after excitation of coherent precession. There are two principle relaxation times: T_1 and T_2 .

T_2 is known as the spin-spin relaxation time. It characterises the rate at which the nuclei attain equilibrium amongst themselves. It may be viewed as the signal lifetime or the time required for the nuclei that are initially precessing together, in phase, to lose coherence; that is for them to “fan-out”. Since there is no net exchange of energy between the nuclei and the sample in which they are embedded (known in NMR literature as “the lattice”), there is no change in the Boltzmann populations of the “up” and “down” nuclear orientations during T_2 , only a change in rotational phase coherence.

T_1 is known as the spin-lattice relaxation time. It characterises the rate at which the nuclei return to alignment with the magnetic field and, as an ensemble, recover thermal equilibrium with the lattice through exchange of energy. It is the time for the Boltzmann equilibrium population distribution to recover.

Except for T_2 of chemically bound nuclei, both processes are generally considered exponential. Hydrogen T_1 relaxation times typically vary from milli-seconds to seconds at normal temperatures. T_2 times vary from microseconds in crystalline solids to seconds in bulk liquids. Measurements of relaxation times provide information on molecular dynamics and water movement over a very wide range of length and time scales. Hence, they also provide information on pore size and microstructure.

iii The experimenter has the option to apply magnetic field gradients. Gradients make the resonant frequency spatially dependent and hence encode spatial information. This can

be exploited either for the purpose of “imaging”: that is the mapping of NMR parameters in 1, 2 or 3-dimensions or for the purpose of encoding and measuring transport, either molecular self-diffusion or flow. Several authors have exploited NMR for imaging water ingress into cementitious materials. Imaging studies are not reviewed here. A brief review is made of self-diffusion studies where these probe pore structure.

So it is the second of these three aspects that is central to this review. It focuses on a subset of NMR measurements in cements and concretes, in particular, T_1 and T_2 analysis in one and two (time domain) dimensions and as a function of frequency. It focuses on ^1H measurements, which, in cements, largely (but not wholly) means a study of water.

2.2 Measurement methodologies

This section introduces the set of NMR experiments most commonly encountered in relaxation analysis. The presentation is not exhaustive nor overly detailed. For a more complete survey and analysis the reader is referred to any one of a series of excellent introductory texts such as Blümich: *Essential NMR for scientists and engineers* [6]. More advanced texts include those by Callaghan: *Principles of Nuclear Magnetic Resonance Microscopy* [7]; Callaghan: *Translational Dynamics and Magnetic Resonance* [8] ; and Kimmich: *NMR Tomography Diffusometry Relaxometry* [9].

Each experiment comprises a series of radio frequency pulses that initiate and manipulate coherent precession of the nuclei about the magnetic field. The observed signal is the vector sum of the precessing nuclear magnetic moments in the plane transverse to the applied magnetic field.

2.2.1 Free induction decay

The simplest experiment, Figure 1(a), comprises a single excitation pulse, known as a $\pi/2$ or P_{90} pulse that tips the magnetisation 90° away from alignment with the magnetic field to initiate free precession. The sample response is a short-lived free induction decay (FID) signal the lifetime of which is generally written T_2^* . T_2^* is related to the true sample T_2 by

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_2^{\Delta B}} \quad [2]$$

where $T_2^{\Delta B} \approx 2/\gamma\Delta B_0$ is a measure of magnet inhomogeneity, ΔB_0 . For many low frequency bench-top apparatuses, $T_2^{\Delta B}$ is of the order of 0.5 to 1 ms. Hence, only for very short true T_2

relaxation times such as might be encountered for adsorbed or chemically bound water in cements is $T_2^* \approx T_2$. For cements, there are two additional complications. Heterogeneity of the magnetic susceptibility, arising for instance from high levels of paramagnetic impurity in the sample, can distort the magnetic field and worsen T_2^* performance, especially at high frequencies. Second, the combined excitation pulse length and the detector “dead-time” following the excitation may be comparable to the shortest decay times in solids so that these parts of the signal are lost in this experiment (see solid-echo below).

2.2.2 CPMG

The CPMG (Carr Purcell Meiboom Gill) experiment [10], Figure 1(b), is a means of measuring T_2 , overcoming the T_2^* limitations of the free induction decay. As shown in section 2.3.2, in cements this experiment can lead to a simple measure of the pore size distribution. An initial excitation pulse is followed at time τ by the first of a series of π or P_{180} refocusing pulses. Refocusing pulses invert the rotational phase of the nuclei with respect to applied field. Hence, an echo signal is observed at 2τ that is unaffected by dephasing due to magnetic field inhomogeneities. Subsequent refocusing pulses applied at $3\tau, 5\tau, 7\tau \dots$ produce further echoes at $4\tau, 6\tau, 8\tau \dots$. The echo intensities decay with time constant T_2 . Care must be taken to ensure that τ is sufficiently short so that so-called “diffusive attenuation” in either applied or susceptibility magnetic field gradients does not limit T_2 . That is, the nuclei should not diffuse to regions of the sample with considerably different magnetic field during a single echo formation. A simple test is to repeat the measurement for more than one value of τ . A variation of this experiment is to logarithmically increase τ from echo to echo. The advantage of log spacing for cements is that the total radio frequency demand (that can lead to ohmic heating of the sample or sensor burnout) remains small while the experiment can span a large range of relaxation times and hence pore sizes. The disadvantages are twofold. First, unwanted signal “coherence-pathways” may not be eliminated with log spacing as effectively as with linear spacing. Second, with linear spacing, echoes at long echo times may be averaged together. With log spacing, less echoes are acquired and this is not possible: the signal-to-noise ratio of the data that is processed is therefore lower.

2.2.3 Saturation and inversion recovery

Saturation and inversion recovery, Figure 1 (c) and (d) respectively, are two pulse sequences used to measure the T_1 relaxation time. Like T_2 , T_1 can be used to measure pore size. Saturation recovery comprises a train of excitation pulses that force (saturate) the bulk magnetisation to zero and destroy any coherence between the nuclei. Following saturation a variable time gap τ is introduced during which magnetisation recovers towards the equilibrium. The recovered magnetisation is then detected by applying a single P_{90} pulse as in an FID experiment. The magnetisation detected is a function of the time τ with T_1 the exponential recovery time. Inversion recovery acts similarly, except that the initial saturation is replaced by a single pulse that inverts the magnetisation. The former experiment is faster to carry out because it is not necessary to wait for the magnetisation to fully recover between measurements since it is saturated at the start. The latter experiment has twice the sensitivity as the magnetisation recovers from minus-maximum to plus-maximum rather than from zero to maximum.

2.2.4 Field cycling

Field cycling (also known as nuclear magnetic resonance T_1 dispersion or NMRD) is a method for measuring the frequency dependence of the T_1 relaxation time [11]. This provides insight into water dynamics in cements over a broad, pseudo-continuous, range of frequencies, particularly low frequencies down to perhaps 10 kHz. In cements, the method is a powerful way of discriminating between different models of relaxation and hence between different models of water dynamics. Field cycling requires a dedicated high field spectrometer linked to a magnet that can be switched rapidly over a large field strength range, typically 0 to 0.5 T in 1 ms. The basic measurement is to saturate the magnetisation of the sample at high (fixed) field, switch rapidly to low field, allow relaxation to occur for a fixed time and then return to high field for a measurement of the magnetisation. The process is repeated as a function of the relaxation field strength.

2.2.5 Solid or quadrature echo

In all NMR spectrometers, there is a dead time following a radio frequency excitation pulse during which the detector is saturated and no signal can be detected. Although this time is usually only a few microseconds, it can obscure a significant fraction of the very shortest T_2 signals characteristic of bound or adsorbed ^1H . The short T_2 arises from inter-nuclear magnetic dipole-dipole interactions that are not averaged to zero by molecular motion. In cements, failure to observe properly the short T_2 decay signals can prevent accurate

quantification of the total signal intensity and hence prevent accurate measurement of the solid fraction. The so called solid or quadrature echo experiment, Figure 1(e) refocuses static dipolar interactions and enables the solid signal to be (partially) recovered [12]. A good estimate of the total signal intensity can be made by extrapolating the solid echo amplitude as a function of τ back to zero time. In cements, by measuring the fast and more slowly relaxing intensity fractions of the total signal, a quantitative measurement of the bound (solid)-to-mobile ^1H ratio can be better made. Other sequences, such as the “magic sandwich echo”, [13], are also available to overcome the dead time problem. Magic sandwich echoes are used successfully in other branches of materials science, [14]. However, to the authors’ knowledge, they have not yet been successfully applied to cements.

2.2.6 Double quantum filter

The double quantum filter pulse sequence comprises a series of three closely spaced pulses of appropriate relative phase. The power of this pulse sequence for porous media studies lies in its ability to discriminate between nuclei that do and do not experience an isotropic motion and environment on the time scale of the NMR experiment [15]. In cements the double quantum filter has been used to explore the lateral extent of planar pores [16].

2.2.7 Exchange and correlation measurements

Both T_1 - T_2 relaxation correlation and T_2 - T_2 exchange 2-dimensional measurements can be made, Figure 1(g) [17]. In the former T_1 relaxation is first encoded and then T_2 relaxation so as to build a 2D data set, which, upon 2D inverse Laplace transform (ILT), yields a map showing reservoirs of ^1H with corresponding T_1 and T_2 . The T_2 - T_2 experiment is similar except that T_2 is measured in both periods.

The T_1 - T_2 experiment is particularly useful for differentiating ^1H reservoirs that exhibit similar T_1 but differing T_2 or *vice-versa*, especially when there is ambiguity in the standard 1D experiments.

If ^1H exchanges between environments with different relaxation characteristics during the encoding period, then cross-peaks appear in the maps. In T_1 - T_2 experiments identification of exchange may be ambiguous and there are practical difficulties associated with the ILT due to negative correlations. These problems are avoided in the T_2 - T_2 experiment, which unambiguously reveals exchange occurring during a storage interval between the two encodings. Coupled with an interpretation of T_2 in terms of pore size, in cements the method

can reveal and quantify water moving between different pore types in a fully saturated system: inter-pore exchange (section 2.3.4). A disadvantage of the T_2 - T_2 experiment versus the T_1 - T_2 experiment is a much-increased experimental time, from circa 0.5 to circa 5.0 hours, for a comparable signal-to-noise ratio.

2.2.8 Cryoporometry

Pore size distributions are often inferred from T_1 and T_2 relaxation data as described in section 2.3.2. NMR cryoporometry [18] is a different, less common, method to monitor porosity using NMR. It is based on the fact that confined water freezes at a lower temperature compared to bulk water due to the relatively greater importance of surface energy terms to the free energy. For water in pores, there is therefore an inverse relationship between pore size and freezing point depression. The measurement, which is closely analogous to thermoporometry, consists of measuring the unfrozen (mobile) water fraction using NMR via T_2 discrimination. It is usually performed during thawing, following a quench of the sample temperature to about -100 °C, to avoid super-cooling and the effects of migration of water from large to small pores during freezing.

2.2.9 Pulsed field gradient diffusometry

A pulse of magnetic field with spatial gradient applied over and above the homogeneous static field encodes nuclei with an additional precession angle proportional to their position. Two field gradient pulses of opposite sign applied τ_D apart encode displacement of the nuclei occurring during the interval τ_D . The experiment is normally carried out with the equivalent formulation of two positive gradient pulses and a P_{180} inversion pulse leading to echo formation, Figure 1(f). A common further modification is to replace the P_{180} by two P_{90} pulses and a storage interval so as to increase the diffusion time [19]. It can be used to measure either water flow or self-diffusion. In the former case, the echo is “phase shifted” as all nuclei experience the same net rotation. In the latter, the echo is attenuated as the net rotations are randomly distributed. If the apparent diffusion coefficient, D_{app} , of water in a porous matrix is measured as a function of τ_D , then the time dependence can be used to reveal restricted diffusion. This provides an alternate probe of the microstructure. For short τ_D , D_{app} is comparable to that of the bulk liquid. At longer τ_D , it decreases since the mean square displacement of the molecules is restricted by the characteristic size of the microstructure (pore size). As discussed in section 4.4, the method has been applied to cement pastes but extreme care is required. Strong field gradients and other special variants

of the method are needed first to overcome field gradients inherent in the sample due to heterogeneity of the magnetic susceptibility and second to overcome short cement pore water T_1 and T_2 values that restrict the maximum τ_D possible. Two-dimensional variants of PFG such as T_1 -diffusion and diffusion-diffusion correlation experiments can be constructed to explore relaxation-diffusion correlations and pore anisotropy respectively.

2.3 Theory of T_1 and T_2 spin relaxation

2.3.1 BPP theory

The primary theory of relaxation was developed by Bloembergen, Purcell and Pound (BPP) [20]. According to the theory, the T_1 and T_2 relaxation of hydrogen is facilitated by dynamic fluctuations in the local magnetic fields arising from inter-nuclear magnetic dipole-dipole interactions. Most commonly, fluctuations are due to random molecular motion: rotations and translations. What follows is a simplified version of the relevant analysis. The molecular motion is expressed in terms of a spectral density function, $J(\omega)$, that specifies the amount of (random) motion occurring at any given frequency. For simple liquids in which the motion is dominated by isotropic Brownian motion, $J(\omega)$ is equal to

$$J(\omega) = \frac{2\tau_c}{1 + \omega^2\tau_c^2} \quad [3]$$

where τ_c is the correlation time of the motion.

T_1 relaxation is mediated by fluctuations at the NMR frequency, ω_0 , and at $2\omega_0$, while T_2 relaxation is additionally caused by fluctuations at low (zero) frequency:

$$\frac{1}{T_1} = \frac{3}{20} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\gamma^4 \hbar^2}{r^6} [J(\omega_0) + 4J(2\omega_0)] \quad [4]$$

$$\frac{1}{T_2} = \frac{3}{40} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\gamma^4 \hbar^2}{r^6} [3J(0) + 5J(\omega_0) + 2J(2\omega_0)] \quad [5]$$

where μ_0 is the vacuum permeability $\hbar$ is the Planck constant divided 2π , and r is the inter-nuclear distance.

For bulk liquids such as water, τ_c is short so $\omega_0\tau_c \ll 1$, $J(0) \approx J(\omega_0) \approx J(2\omega_0) \approx 2\tau_c$ so T_1 is equal to T_2 and both are long. With reduced mobility, τ_c increases and T_1 goes through a

minimum at $\omega_0\tau_c = 0.616$. However, due to the $J(0)$ contribution, T_2 decreases monotonically to the “rigid lattice limit”. This is the limit applicable to crystalline and glassy solids. Here the T_2 relaxation time is determined by the (static) distribution of inter-nuclear magnetic dipole-dipole interaction strengths. For this reason, T_2 of solids such as $\text{Ca}(\text{OH})_2$ is invariably short while T_1 is much longer. Figure 2 shows the T_1 and T_2 relaxation times as a function of correlation time based on the foregoing analysis for 3 different NMR frequencies. The calculations are based on an H-H distance of 0.15 nm, as in water. The rotational correlation time for water is of the order of a few ps at room temperature. The plot shows a corresponding relaxation time of the order of seconds. The experimentally observed value is circa 3.6 s [21].

2.3.2 Pore size analysis – the fast exchange model of relaxation

Following from the previous section, the T_2 relaxation time of the hydrogen proton in pure bulk water equals T_1 . However, the T_2 relaxation time of a water molecule adsorbed on a surface, such as the internal pore surface of cements, is very much shorter, a few microseconds. For water confined to a small pore, the observed relaxation rate is the weighted average of that for molecules adsorbed on the pore surface and in the pore bulk [22,23]. This is because, on the timescale of the experiment, the adsorbed molecules are in rapid exchange with those within the pore and diffusion ensures that all molecules experience both environments equally (fast exchange assumption). Since the number of adsorbed water molecules scales with the pore surface area, S , while the number within the bulk of the pore scales with volume, V , so a measure of the relaxation time affords a measure of a characteristic pore size, through the pore surface-to-volume (S/V) ratio according to:

$$\frac{1}{T_2^{obs}} = \frac{\varepsilon S}{V} \frac{1}{T_2^{surface}} + \frac{V - \varepsilon S}{V} \frac{1}{T_2^{bulk}} \approx \lambda_2 \frac{S}{V} + \frac{1}{T_2^{bulk}} \approx \lambda_2 \frac{S}{V} \quad [6]$$

where T_2^{obs} , T_2^{bulk} and $T_2^{surface}$ are the observed, bulk and surface relaxation times respectively and ε is the thickness of a surface layer, normally enfolded with $T_2^{surface}$ in λ_2 as the pore-surface relaxivity. The equalities hold because the “surface volume” εS is very much less than the pore volume, V , and because $T_2^{surface}$ (μs) $\ll$ T_2^{bulk} (s).

A similar relationship holds for spin lattice relaxation, T_1

$$\frac{1}{T_1^{obs}} \approx \lambda_1 \frac{S}{V} + \frac{1}{T_1^{bulk}} \approx \lambda_1 \frac{S}{V} \quad [7]$$

except that here, the T_1 of adsorbed nuclei is somewhat longer, perhaps ms.

Equations [6] and [7] imply that measured relaxation times scale uniformly with characteristic pore sizes $a \approx V / S$. If one pore size of a distribution is known, then all pore sizes are known so long as the surface relaxivity is unchanging. Absolute measurement relies on knowledge of the surface relaxivity which can be estimated by measurement of systems dried to mono-layer coverage or by calculation. Calibration is discussed further in section 2.3.3.

Equations [6] and [7] assume fast exchange between the surface-layer and bulk-pore environments. This assumption is normally valid, especially when small pores and fast diffusion are involved. As a rule of thumb, the method requires $6DT_{1,2}^{bulk} \gg a$ where D is the self-diffusion coefficient ($\approx 2 \times 10^{-9} \text{ m}^2/\text{s}$ for water). In the case of more open pore systems, for instance during the early stages of hydration, inter pore exchange may lead to partial averaging of the T_2 , and hence pore size, distribution. Measurement of inter pore exchange is developed in section 3.2.4. When fast exchange does not apply, the observed signal is multi-exponential [22]. Limitations of the model in the case of the very smallest pores, ($\approx 1 \text{ nm}$), are discussed in section 3.3.

2.3.3 Modified BPP theory (Korb-model) for porous media

A model of the dynamics and hence relaxivity of water adsorbed on pore surfaces was proposed by Korb and co-workers [24-27] – hereinafter called the “Korb-model”. This model has been found to explain a wide spectrum of experimental data in porous media generally and cements specifically, including the frequency dependence of T_1 and the ratio T_1 / T_2 . According to the Korb-model, water molecules adsorb to a pore surface for a residency time τ_s during which time they undertake a 2-dimensional walk across the surface with a hopping time step τ_m , Figure 3. On the surface, they repeatedly encounter surface relaxation centres, which, in cements, are paramagnetic impurities such as Fe^{3+} ions. After a time τ_s the water molecule desorbs to be replaced by another. Water not adsorbed on the surface behaves as bulk water. These dynamics lead to a modified spectral density function for adsorbed molecules:

$$J(\omega) = \frac{3}{40} \frac{\pi \sigma_s \tau_m}{\delta^4} \ln \left(\frac{1 + \omega^2 \tau_m^2}{\frac{\tau_m^2}{\tau_s^2} + \omega^2 \tau_m^2} \right) \quad [8]$$

where σ_s is the surface density of the paramagnetic impurities and δ is the distance of minimum approach of a water molecule to an impurity. This function is inserted into BPP theory, equations [4] and [5] adapted to electron-proton interactions. This yields the surface relaxation rate that, in turn, can be used within the fast exchange model, equations [6] and [7] to calculate the pore size.

2.3.4 Exchange experiments

The case of exchange between pore surface and bulk sites in single pores leading to an average relaxation rate is just a special case of exchange more generally. The solutions of equations for relaxation in systems comprising two magnetisation reservoirs with exchange between them are well known [27-31]. As an example, consider a system, such as cement, with pores of two different sizes. If the pores are isolated, then water in each type has a relaxation rate proportional to the pore size. They have different relaxation times. Now consider that the pores are connected and that molecules are rapidly exchanging between them. All molecules see the two pores types as one connected space with an average value of S/V . A single relaxation time is observed. The limit to this is simply that the molecules must sample the entire space within the bulk liquid relaxation time. The Einstein equation $D = \langle r^2 \rangle / 6t$ (where r is displacement and t time) with $t = T_2^{bulk}$ and $D = 2 \times 10^{-9} \text{ m}^2/\text{s}$, suggests a maximum range of circa 200 μm .

More complex relaxation behaviour is observed for slow exchange. 2D T_2 - T_2 exchange experiments (Figure 1g) are designed to exploit this phenomenon and include a period of magnetisation storage (t_2) during which molecules can move from one pore type to another sandwiched between periods (t_1 and t_3) of relaxation measurement. The results depend upon the product $t_2 k$ where k is the inter-pore-type molecular exchange rate. Figure 4 shows the results of simulations of 2D T_2 - T_2 experiments on a sample comprising two equal volume reservoirs of ^1H with exchange between them as a function of t_2 and k . The reservoirs have T_2 relaxation times of 0.25 and 2.5 ms respectively. In the lower left, characterised by slow exchange and a short exchange period, the two reservoirs are clearly distinguishable as two

peaks on the diagonal. The right hand column shows the limit of fast exchange. Here the system collapses so as to appear as a single peak: the reservoirs are averaged together with the signal becoming weaker as t_2 is increased. Under intermediate conditions, when t_2 is of the order of k^{-1} , off-diagonal exchange peaks appear. The intensity of the exchange peaks measured as a function of exchange time is of the form $(1 - \exp(-kt_2))$ and yields the exchange rate [30,32].

3 Relaxation in cements: experimental results

Relaxation measurements have been carried out on cement pastes by many groups over several decades. Different groups have reported broadly similar observations. The most common are that, upon initial mixing there is a single component of T_1 and T_2 relaxation characteristic of the bulk water. This rapidly evolves into a multi-modal distribution for both relaxation times. Different components are widely attributed to, and associated with, capillary-pore, gel-pore and C-S-H water and to water bound in solid phases. Except for the solid, which invariably has a long T_1 and very short T_2 , the trend is for components with shorter relaxation times to appear, in line with the development of hydrate phases and micro- and nano-scale porosity. However, there are considerable differences in the detail of reports that has led to confusion about the value of results. In particular, the number of components within the distribution, their relative intensities and the actual relaxation time values reported vary widely between different studies. The reasons are manifold.

- *Sample composition, conditioning and age:* Relaxation characteristics vary with sample composition and age. Due to a higher concentration of iron paramagnetic impurities, grey cements generally exhibit shorter, and less well differentiated relaxation times than found in white cements, which in turn are shorter than those in model systems such as C_3S and synthesised C-S-H. Well hydrated cements with a finer porosity exhibit shorter relaxation times than equivalent less hydrated material. Cements prepared at high water-to-cement (w/c) ratio tend to have more capillary water with slower relaxation (longer times) than those with low w/c ratio. Since NMR probes water, the sample condition during hydration (e.g. underwater, sealed or open cure) or any sample preparation such as drying is especially important. This too varies greatly between studies.

- *Measurement conditions:* These may lead to variation in results. For instance, NMR relaxation rates are sensitive to the measurement frequency according to BPP theory (section 2.3). Spectrometer frequencies in common use vary by more than 2 orders of

magnitude. Independent of BPP theory, T_2 relaxation is further sensitive to frequency due to diffusive signal attenuation of water through magnetic field gradients arising from heterogeneity of the sample magnetic susceptibility. Since susceptibility gradients increase with applied field strength, the diffusive attenuation increases with NMR frequency.

- *Data analysis methods:* Variation may arise from differences in data analysis methods. The fitting of exponential signal decay data with multiple relaxation times, or a distribution of relaxation times, is known to be a difficult problem without, in general, a unique “best-fit” solution. This difficulty is discussed further in section 6.

- *Spectrometer hardware:* Some spectrometers are unable to detect the very fastest relaxing T_2 components usually ascribed to chemically combined or highly confined water due to spectrometer dead-time following the excitation pulse. This can lead to ambiguities in terminology: for instance “fast / fastest relaxing component ...”. Even a measurement of T_1 which is generally longer in crystalline or glassy solids requires that the signal be seen, and hence that the dead-time is short.

3.1 Evolution of nuclear spin relaxation times during cement hydration

In their early study Blinc *et al.* [1] looked at T_1 and T_2 relaxation times of mobile water in cement ($w/c = 0.42$) and C_3S pastes ($w/c = 0.5$) prepared with both distilled water and D_2O at the NMR measurement frequency of 60 MHz. The hydration was monitored from 10 minutes after mixing through to 28 days. Three stages in the hydration process were identified from the changing relaxation characteristics: an induction period, showing slow changes (up to circa 2 hours); an intermediate stage with faster changes (between 2 and 20 hours); and a third stage (beyond 20 hours) during which the changes slowed down again. No attempt was made to resolve multiple relaxation components within the mobile water signal so the quoted values must represent an average. The cement pastes started with a typical T_1 of circa 15 ms in the first stage that quickly dropped during the second stage to circa 0.7 ms before decreasing slowly to circa 0.5 ms in the third stage. The initial T_2 value of 2 ms was tracked only up to 10 hours of hydration by which time it had decreased to 0.7 ms. C_3S pastes showed similar behaviour to cement, but with characteristically longer relaxation times (T_1 from 750 ms in the first stage to 65 ms in the third) as expected due to lower concentrations of paramagnetic impurities. T_2 values for C_3S pastes decreased from 70 to 5 ms between the first and third stages.

With significant foresight, Blinc *et al.* noted that the relaxation time ratio, T_1/T_2 , was equal to 12 rather than unity as expected by BPP theory. This, together with observations of the line width and T_1 of D₂O in cement and C₃S led to the conclusion that the relaxation mechanism must involve paramagnetic impurities. The authors commented on the possibility of two water environments (a mono-molecular layer of water adsorbed on the internal pore surface and the pore water itself) and of fast exchange between them.

Schreiner *et al.* [33] measured both T_1 and T_2 relaxation at ¹H NMR frequencies of 38 and 19 MHz in cement pastes cured at circa 70% relative humidity as a function of w/c ratio from 0.33 to 0.63 and hydration time from 10 minutes to almost 1 year. Four stages of hydration were identified from the relaxation data: the first 10 mins.; from 10 mins. to 2 hrs.; from 2 to 12 hrs and beyond 12 hrs. In stage 1, the T_1 relaxation is characterised by a single component of circa 30 ms. By stage 4 this has evolved into three distinct hydrogen reservoirs which the authors assigned to solid Ca(OH)₂ ($T_1 \approx 500$ ms; amplitude 25 %), to micro-pore water and water in mono-layers on the product surface ($T_1 \approx 5$ ms; amplitude 20 %), and to water in “solid-gel” ($T_1 \approx 1$ ms; amplitude 55 %).

Figure 5 shows the evolution of the micro-pore water T_1 as a function of hydration. The relaxation time decreases with hydration time as expected of a system developing finer porosity with greater surface area and is shorter for pastes with lower w/c ratio. So, this assignment is consistent with the fact that T_1 of liquid in increasingly confined spaces is increasingly reduced, while T_1 of solid is generally long. The shoulder between 12 and 24 hours is not fully explained. Shreiner *et al.* also measured T_2^* and T_2 values. These were discussed qualitatively in terms of paramagnetic relaxation and sample heterogeneity. The results generally supported the conclusions drawn from T_1 results.

Over time, there has been increasing preference to work with T_2 rather than T_1 since it is a more straightforward experiment and the solid is separated from pore-water more easily. This is because, while T_2 of liquid decreases with confinement like T_1 and is generally of comparable magnitude, the T_2 of solid is always very much shorter – indeed, in cements, is invariably the shortest component. Greener *et al.* [34] studied T_2 in a sealed $w/c = 0.42$ white cement paste using a “cross normalised” combination of FID and CPMG to increase quantification. These authors modelled the decay of the “solid like” components (defined as those with T_2 relaxation time shorter than 100 μ s) with Gaussians and the “liquid like” components (relaxation times longer than 100 μ s) with exponentials. The study was

followed up by the some of the same authors in 2007, [35]. T_2 distributions were measured using the same methods as a function of hydration time up to one year and temperature in the range 2 to 100 °C in parallel with an X-ray diffraction study. In the first few minutes after mixing, almost all the signal is in a single component with long T_2 , circa 40 ms, assigned to capillary water. Over the first 100 hours, the T_2 of this component drops rapidly, to circa 1ms and an amplitude fraction of about 20 %. Beyond 100 hours, its T_2 stays constant, but its amplitude continues to decrease monotonically towards zero. A component with T_2 about 4 ms appears shortly after hydration starts. At about 10 hours, its T_2 drops rapidly to circa 400 μ s whereupon it has an amplitude of 37 %. Thereafter, its T_2 drops only a little further, while its amplitude stays constant. It is assigned to gel pore solution. Two other components appear alongside the gel solution. The first rapidly attains a T_2 value of 100 μ s. Its amplitude increases throughout hydration, quite rapidly at first, more slowly later on, attaining about 25 % at 10000 hours. It is assigned to water in the C-S-H inter-layer space. The other has a very short, constant T_2 throughout hydration, circa 20 μ s. Its amplitude grows throughout hydration, again rapidly between 10 and 100 hours, more slowly thereafter to a total of about 43 %. It is assigned to solid, principally calcium hydroxide. Finally, there is a component with long T_2 , greater than 10 ms that appears only briefly at around 10 hours. It is assigned to water released into isolated spaces in the ettringite to monosulfate conversion. So, in summary, five T_2 components are identified. In ascending order of T_2 in the maturing paste, they are: solid; C-S-H inter-layer water; gel pore water; capillary water and water associated with ettringite to monosulfate conversion. Only the first three appear in the mature paste. This description and assignment of T_2 components is broadly in line with current understanding as developed further in subsequent sections.

3.2 Measurement of pore size distribution by fast exchange model.

Halperin *et al.* [36] studied a $w/c = 0.43$ paste assuming an interconnected pore structure. This was the first study to seek to interpret relaxation rates in terms of pore sizes by Laplace inversion of T_2 CPMG data and application of the fast exchange model (section 2.3.2). They calculated pores of characteristic radius 3, 15 and 200 nm as early as 2.5 h. after mixing. After 8 hours the largest pores reduced to circa 60 nm. From 1 day onwards all the porosity detected was below 20 nm to approach, at 59 days, a bimodal distribution around 3 and 12 nm.

Related studies include Bohris *et al.* [37] who reported two T_2 reservoirs at circa 20 μs and over 1 ms for early stages of hydration (1 hour) in a $w/c = 0.5$ cement paste. At later stages the magnetisation divided into three components: 350 μs (20 %); 80 μs (30 %); and 9 μs (50 %). A $w/c = 0.3$ paste behaved similarly, but with the longer component somewhat shorter during the early stages and of only small amplitude at long times. Pore sizes of 2.4 and 15 nm were inferred.

Plassais *et al.* [38] performed a study on mature, $w/c = 0.4$, C_3S paste hydrated under saturated $\text{Ca}(\text{OH})_2$ solution for 3 months in which they combined NMR relaxation analysis with magic angle spinning spectroscopy (MAS). The MAS resolves different chemical moieties such as SiOH , H_2O etc. The relaxation analysis resolves their mobility or environmental confinement. Put together, it is possible to see which chemical groups occur in which dynamical environments. Plassais *et al* interpreted their data in terms of 4 moieties: SiOH , confined $\text{SiOH} / \text{H}_2\text{O}$, mobile H_2O and CaOH each spanning up to 5 T_1 components at 0.1, 1, 10 100 and 1000 ms: so finding a total of 15 moiety / mobility combinations. Their primary conclusion was that different fractions of each chemical grouping relaxed at different rates dependent on their environment, and equally that each environment encompassed multiple groupings. This was taken as evidence that surface-site-hydrogen and bulk-pore-water were interacting with each other according to the fast exchange model of relaxation, differentiated by pore size with sizes ranging from 2 to 500 nm. The authors observed that the amplitude versus T_1 of the circa ten NMR moiety / environment combinations arising from mobile species is linear on a log-log plot spanning two orders of magnitude and hence well described by a power law. This has been interpreted as evidence for a fractal distribution of discrete pore sizes over the interval 2 to 500 nm with fractal dimension $D_f = 2.6$. The reservoirs that do not follow this fractal distribution are attributed to $\text{Ca}(\text{OH})_2$ and the silanol groups in the C-S-H inter-layer spaces, for which they suggest the fast exchange model is not applicable.

Most recently, Muller *et al.* [39,40] performed experiments on carefully controlled low alumina white cement pastes that build on the work of Holly *et al.* [35]. Quadrature echo experiments were performed to quantify better the solid phases, in preference to FID that suffers from dead-time limitations, combined with CPMG experiments to resolve the mobile water. Measurements were made both as a function of hydration age and, for a mature paste, as a function of equilibrated relative humidity (see section 3.6) The NMR measurements were considered alongside thermo-gravimetric analysis (TGA), X-ray diffraction (XRD)

with Rietveld analysis and scanning electron microscopy (SEM). Results were presented in terms of a cement composition map, Figure 6, the calculation of which is discussed further in the analysis of composition, section 3.5, and as a function of relative humidity during controlled drying, Figure 7. The authors showed that the combined $\text{Ca}(\text{OH})_2$ and ettringite fraction is consistent to within 1 % across NMR, TGA and XRD; so that the shortest mobile T_2 component (about 110 μs) must arise from C-S-H inter-layer space water and with the next component at about 330 μs arising from gel pore water. The next longest component, circa 1 ms, rapidly evolves from the free water signal and is attributed to inter-hydrate pore water. There is only a very small fraction of water with longer T_2 still, attributed to water in micron size capillary pores. This assignment broadly followed that of Greener *et al* [34] and Holly *et al* [35].

The C-S-H inter-layer space width derived by Muller *et al* on the basis of relaxation times is circa 0.95 nm, the gel pore width about 3-3.5 nm and the inter-hydrate pore size about 10 nm. The C-S-H inter-layer space and gel pore sizes are shown to be in good agreement with those calculated from the measured signal amplitudes (section 4) and vary little throughout hydration: they represent the sizes of spaces in the C-S-H as it forms. The inter-hydrate pore size is distinct in so much as it rapidly evolves down to the characteristic size of 10 nm, after which the size remains constant. The data in Figure 6 to be further discussed in section 3.5 show the total porosities assigned to these different pore types. It is seen that the gel porosity plateaus after about 3 days hydration even though the hydrate phases continue to grow as evidenced by continued increase of the inter-layer signal component. The inter-hydrate porosity diminishes monotonically to zero over about 2 months. The authors suggest that the transition at three days corresponds to the onset of the growth of denser product, with the denser product growing largely free of gel-porosity within the inter-hydrate space. Finally, the results also showed that the amount of large (micron sized) capillary porosity is much smaller than conventionally understood on the basis of the Powers-Brownyard model [41]. This is likely related to self-desiccation since NMR can only detect pores containing water. The Kelvin-Laplace radius at 90% relative humidity is of the order of 10 nm, so large micron pores are likely to be empty.

In summary, there has been a convergence of measured pore sizes by NMR relaxation time analysis using the fast diffusion model of relaxation towards a multi-modal distribution with sizes circa 1 nm and 2-5 nm and 10 nm in hydrated paste. Only a small fraction of larger (micron) capillary pores are seen. It is now believed that the 1 nm pores correspond to the

inter-layer spacing within the C-S-H, the 2 -5 nm pores to the gel pores, and the 10 nm pores to inter-hydrate spaces that decrease in total volume as the paste matures. The seeming absence of water in large, micron-sized, capillary pores may in part be related to self-desiccation, even in samples cured underwater. The pore sizes determined by relaxometry are in agreement with sizes derived from other NMR methods – section 4. Before that, however, in the following section, we address issues associated with the calibration of the pore size through the surface relaxivity, with why variations in this parameter exist across the literature and with how it impacts on the smallest size (1 nm) in particular.

3.3 Surface relaxivity and calibration of pore size by the fast diffusion model of relaxation.

Halperin *et al.* [36], Bohris *et al.* [37], Plassais *et al.* [38], Monteilhet *et al.* [30] and Muller *et al.* [39] all use the fast exchange model introduced in section 2.3.2 to interpret relaxation rates in term of pore sizes. According to this theory, the measured rate for both T_1 and T_2 of water in pores is a weighted average of the bulk pore water rate and the surface relaxivity for water interacting with the pore surface. Hence it is a measure of the pore S/V ratio. Bulk water relaxation rates are easy to measure and are well known but impact little on the inferred pore size. Measurement of the surface relaxivity presents a harder problem but impacts much more. Hence while the ratio of the characteristic size of different pore types may be known with reasonable accuracy, absolute calibration is harder.

The surface relaxivity is a combination of two parameters: the surface relaxation time and the “thickness” of the surface layer. Values used for the surface relaxation time vary from author to author. Equally, the effective layer thickness varies. Bohris *et al.* [37] adopted a value of 10 μs equal to the relaxation time of chemically combined water. Halperin *et al.* [36] observed that the surface of the solid cement gel structure, consisting of chemically bound water, had a relaxation time of 17 μs measured from FID, but used instead the asymptotic value of pore water T_2 as the sample was dried, circa 40 μs . In a similar experiment, Muller *et al.* [39] measured 75 μs at an NMR frequency of 20 MHz and room temperature. While these values differ, it is to be noted that the surface relaxation time is expected to be NMR frequency dependent, just as is the relaxation time for the full-pore fluid. Unfortunately, not all authors give the frequency of their experiments. The surface layer thickness is normally assumed to be the size of one water molecule, circa 0.28 nm, but up to 3 times this value has been taken in some cases.

Others have sought to calculate the surface relaxivity from first principles using the Korb-model for the pore surface water dynamics, section 2.3.3 [30]. A difficulty is that the model requires knowledge of several parameters for which there is a degree of uncertainty: the Fe^{3+} surface density (which has been inferred from electron spin resonance [26]), the distance of closest approach of a water molecule to the Fe^{3+} , correlation times for the water dynamics (available by fitting the frequency dependence of T_1) and, for the pore size via the fast exchange model, the thickness of a surface mono-layer of water. Taken together, there is uncertainty in the resultant pore size to within perhaps a factor of 2 either way.

The smallest pore size measured, now firmly established to be the inter-layer space of the C-S-H, is circa 1 nm. Such a small size begs the question as to whether “surface layer” and “bulk pore” water have distinct meaning. However this is answered, experimentally it appears that all hydrogen in a C-S-H inter-layer space experiences a common T_2 relaxation time of the order of 100 μs and that this relaxation time decreases as the water is progressively removed. Equations [6] and [7] can be applied, but the meaning of “bulk” and “surface” sites has to be treated with a degree of caution. Terms such as “fast” and “slow” relaxing sites, across which the observed relaxation rate is exchange averaged, may be more appropriate. Moreover, within the inter-layer space, Korb’s model of surface relaxation by 2D “surface” diffusion may start to break down. This may explain why the ratio T_1/T_2 deviates slightly from the otherwise constant value of the larger pores in some experiments and why inter-layer space sizes calculated with “surface” relaxation rates based on Korb’s model tend to overestimate the inter-layer size compared to e.g. diffraction studies of C-S-H analogues such as tobermorite and jennite.

More widely, the question has been raised [42] as to whether different T_2 reservoirs corresponded to water in pores of different sizes as widely interpreted in the literature, or to water in similarly sized pores but with different surface relaxivities due to inhomogeneous distribution of paramagnetic centres. This question was answered in favour of pore sizes by Valori *et al.* [43] using T_2 - T_2 measurements of essentially paramagnetic impurity free synthesised C-S-H as discussed in section 5.2.

3.4 Measurement of specific surface area.

Halperin *et al.* [36], estimated the total specific surface area of a $w/c = 0.43$ cement paste to be 225 m^2/g of anhydrous cement (equivalent to about 300 m^2/cm^3 of paste) from the T_2 relaxation decay intensity. Muller *et al.* [39] went further and calculated the pore specific

surface area obtaining $91 \text{ m}^2/\text{cm}^3$ of paste for the gel pores and $175 \text{ m}^2/\text{cm}^3$ for the inter-layer C-S-H spaces, a total of $266 \text{ m}^2/\text{cm}^3$.

At very low NMR frequencies, accessible only to field cycling experiments, the T_1 relaxation rate is limited by the transfer of magnetic dipolar energy within the solid, bound hydrogen reservoir. The relaxivity thus becomes proportional to the specific surface area of the porous sample. On this basis, Barberon *et al.* [26] calculate that the total specific surface area is the order of $100 \text{ m}^2/\text{g}$ and still increasing after 12 hours of hydration. It is not possible to make measurements by this method in older samples as the relaxation time becomes too short for the field cycling method.

3.5 Cement composition and C-S-H density.

Muller *et al.* [39,40] developed a series of conservation equations for total mass, total volume including chemical shrinkage, and Ca, Si, Al and water content. Product fractions were written in terms of NMR signal intensities. By combining the NMR data with an independent measure of the degree of hydration and ettringite content (both obtained by XRD) and a measure of the chemical shrinkage* they were able to determine both the “solid” C-S-H density (the sheets of Ca ions and SiO_2 tetrahedra and the inter-layer water but excluding gel pore water) and bulk C-S-H density (additionally including the gel pore water). They also obtained the C-S-H composition expressed as $\text{Ca}_z(\text{Si}_y\text{Al}_{(1-y)})\text{O}_{(z+1/2y+3/2)}\cdot(\text{H}_2\text{O})_x$ and the overall cement paste composition: $\text{Ca}(\text{OH})_2$; ettringite; C-S-H; gel porosity; inter-hydrate space and capillary void fractions. In paste cured underwater, the chemical shrinkage was derived from the NMR data. In sealed cured paste an independent measurement of the chemical shrinkage was required. The NMR derived composition of a sealed cured $w/c = 0.4$, low C_3A paste as a function of degree of hydration from this work is shown in Figure 6. The C-S-H composition was found to be $\text{Ca}_{1.70}(\text{Si}_{0.95}\text{Al}_{0.05})\text{O}_{3.67}\cdot(\text{H}_2\text{O})_{1.80}$ in the mature paste. The calculated C-S-H bulk density, which includes gel water, increased with degree of hydration providing evidence for overall densification of the C-S-H with time as expected. For instance, in $w/c = 0.4$ sealed cured

* Chemical shrinkage is the overall decrease in volume occurring when the reactants (anhydrous cement and water) are transformed into products (hydrates). Traditional chemical shrinkage measurement monitors the drawing down of water from a capillary and into a sample. NMR can access this shrinkage in an underwater cured sample similarly, by measuring the increase in total signal amplitude during hydration. In principle, NMR can measure also the “before” and “after” signal increase of a sealed cured sample exposed to water post hydration, although in practice it is very difficult to fill entirely the void space. In sealed samples, macroscopic shrinkage of the samples may also occur, but this is very small compared to the internal voidage created by the chemical shrinkage. NMR cannot measure the macroscopic shrinkage.

pastes it went from $\rho_{\text{bulk}} = 1.8 \text{ g/cm}^3$ at a degree of hydration $\alpha \approx 0.4$ to 2.1 g/cm^3 at $\alpha \approx 0.9$.
 On the other hand, the headline solid density decreased with degree of hydration. For
 instance in the same paste, $\rho_{\text{solid}} = 2.73 \text{ g/cm}^3$ at a degree of hydration $\alpha \approx 0.4$ decreasing to
 2.65 g/cm^3 at $\alpha \approx 0.9$. Contrary to first impression, this too is evidence for densification in
 so much as it shows that the average number of locally aggregated C-S-H layers increases.
 The solid density includes inter-layer water but excludes water adsorbed on external
 surfaces of locally aggregated C-S-H layers. The “surface water” contacts, and hence is part
 of, the more mobile water in the gel pore. It appears gel-like. If the average number of
 locally aggregated layers is s , then the number of inter-layers is $s-1$. As the number of layers
 increases during densification, so the ratio $(s-1)/s$ increases towards 1. Hence ρ_{solid} includes
 a greater overall fraction of water and decreases.

3.6 Measurement of the pore specific desorption isotherm.

Muller *et al.* [39], measured the pore-type resolved desorption isotherm of a white cement
 paste, Figure 7. The desorption isotherm derived from the total NMR signal has the same
 appearance as one obtained from gravimetric data. However, the pore-size specificity
 enables this to be decomposed into separate isotherms for the capillary, gel and C-S-H inter-
 layer spaces. The capillary pores are seen to empty between 100 and 90 % RH, the gel pores
 by 20 % RH and the inter-layer spaces below this. Re-plotted as a function of sample mass,
 the relative rate of decrease of the different components permits an estimate of the pore size
 independent of the relaxation time (section 4). The gel pore size thus obtained is in good
 agreement with that obtained by application of the fast diffusion model of relaxation. In the
 case of the inter-layer, the discrepancy is greater, perhaps because the underlying models of
 relaxation and of drying tend to break down in such a confined space.

3.7 Spatially resolved measurements

Authors such as Prado *et al.* [44], have studied T_1 and T_2 in the context of spatially resolved
 measurements. Whilst these studies have the power to visualise spatial gradients in
 hydration resulting from T_1 and T_2 weighted profiles and images, in general the spatially
 resolved methodology does not have the sensitivity to enable precise measurement of
 relaxation times. Hence, these studies, while not contradicting much of the above, are not
 discussed here further.

4 Results of NMR experiments not reliant on the fast exchange model of relaxation.

Section 3 discussed cement porosity as reflected in measurements of nuclear magnetic relaxation times interpreted using the fast exchange model of relaxation. This section reviews other experiments which do not rely on this model but rather interpret the data in other ways, including from the signal amplitude as a function of sample drying, and from the ratio of frozen to unfrozen water at low temperatures.

4.1 Cement pore sizes from signal amplitudes.

As described in section 3.3, absolute measurement of pore sizes based on relaxation times can be ambiguous due to the difficulty of measuring the surface relaxivity. To advance quantification, McDonald *et al.* [45] proposed an alternative technique independent of surface relaxivity calibration. In this work, measurements of the solid echo and FID long component intensity are made as a function of sample water content. The key to extracting pore size is the different rate at which these two components vary during drying compared to their sum, Figure 8. As a pore empties, a residual surface layer of water is left. In the full pore, surface molecules have a long T_2 characteristic of mobile water due to exchange. In the dried pore they have a short T_2 characteristic more akin to immobile water as the opportunity for exchange is removed. Hence, as the sample is dried, the mobile signal fraction decreases faster than the total, while the less mobile fraction actually increases. Measurement of the rate difference leads to an estimate of the pore size.

Figure 9 shows experimental results from drying the sample at elevated temperature. There are three regions: the first from relative mass of water 1.0 to circa 0.7; the second between circa 0.7 and 0.4; and the last below 0.4. The first two regions show the successive removal of water from pores of two distinct sizes. As water is removed, the residual surface layer appears less mobile. The measure of the pore sizes obtained with this technique are circa 1.5 and 4.1 nm for the C-S-H inter-layer and gel pores respectively. The former is much larger than expected. The reason is probably that the underlying concept of a surface-layer and bulk water within the confines of the inter-layer is breaking down. The same comments as made in section 3.3 about fast and slowly relaxing sites likely apply but are not yet quantified. The third region, where the apparent total signal amplitude decreases faster than the relative mass of water, has been explained in terms of carbonation. These experiments

have been repeated in samples dried in controlled relative humidity environments at room temperature, yielding comparable pore size results [46].

4.2 Double quantum filter experiments

Double quantum filter experiments were reported by Rodin *et al.* [16]. These experiments are sensitive only to bound water and to water in highly anisotropic pore environments. In essence, the experiment measures the circle of influence around a paramagnetic centre within a planar pore that leads to relaxation of a water molecule. The measurements were carried out with a view to learning the lateral extent of the inter-layer spaces in the C-S-H of cement. It was concluded that, in the white cement studied, the impurity separation was around 6 nm and so the inter-layers must be at least of the same lateral dimension.

4.3 Cryoporometry

Cryoporometry applied to cementitious materials includes the work of Jehng *et al.* [47]. For a white cement sample mixed at $w/c = 0.43$, and cured sealed for circa 4.5 months, they found that all water is frozen below 160 K. A comparison of results from cryoporometry and relaxation analysis found excellent internal agreement with a bimodal distribution of smaller pores peaking around 2.5 and 7.5 nm. These sizes are comparable to, but slightly larger than those reported elsewhere, perhaps because of the calibration factors used. Marginally less good agreement was found for coarser porosity that was estimated as 130 nm by cryoporometry and 110 nm from relaxation analysis. In further experiments, relaxation analysis was performed at different temperatures, showing the change in the distribution of unfrozen pores during thawing.

Valckenborg *et al.* [48] compared cryoporometry and relaxation analysis in a mortar cured under saturated lime solution for more than one year and thereafter stored in propanol. Before use, the samples were dried carefully at 40 °C to remove the propanol and capillary saturated under water for 2 hours before measurements. The extent to which this process disturbed the microstructure or failed to allow full re-saturation is unclear. Notwithstanding, almost no unfrozen water signal was detected below 203 K, a value higher than that reported by Jehng *et al.* When the temperature rose above 203 K a signal appeared with a relaxation time of circa 300 μs that was attributed to a monolayer of water molecules on solid surfaces. A second contribution at circa 1200 μs was reported to appear above 213 K, the intensity of which increased up to 243 K. In this range of temperature, the Gibbs-Thomson equation predicts a typical pore size between 1.4 and 2.8 nm while the fast exchange model of

relaxation using the measured low temperature value of the surface relaxation time gives 1.2 nm. At around 253 K a third contribution at 4500 μ s appears. This corresponds to a pore size of 4.3 nm according to the Gibbs-Thomson equation or 4.5 nm by relaxation analysis. At around 263 K a fourth long component ($\sim 15000 \mu$ s) appears that is attributed to capillary water in pores greater than 10 nm.

Leventis *et al.* [49] performed similar experiments starting from 193 K on a Portland cement at a $w/c = 0.6$. These authors infer a sharp peak in the pore size distribution around 1.8 nm and a broader peak at 10 nm, comparable with the results of Jehng *et al.* [47] already discussed.

Variable temperature magnetic resonance images do not have enough resolution to enable a direct measure of the pore size. However, as is pointed out by Mitchell *et al.* [50] they provide valuable insight into the homogeneity of the porosity throughout the sample. An example of such an application is to detect the effect of a superplasticiser [51]. Prado *et al.* [52] present the same technique.

4.4 Pulsed field gradient diffusion measurements

The first pulsed field gradient diffusion measurements relating to cements were incorporated within the pioneering work of Blinc *et al.* [1]. The method, a review and further results were presented by Nestle *et al.* [53]. Most recently, Rodin *et al.* [54] have used the method to determine the distribution of large capillary pore sizes in young (< 14 days) pastes and mature pastes (1 year). These pores contribute only a very small fraction ($< 5\%$) of the total porosity seen by NMR as discussed in section 3. Notwithstanding, the pulsed field gradient diffusion results suggest a log-normal distribution of pore sizes by volume with a mean size of 4.2 μ m and dimensionless width parameter 0.51. Two-dimensional experiments show no anisotropy of the capillary pore morphology. The pulse field gradient method is not suited to gel pores. The reason is that the T_2 and size of gel pores is too small to permit encoding of spatial information with switched magnetic field gradients.

5 Pore water dynamics: from ns to ms.

NMR experiments have measured water dynamics in cement pores on three very different timescales. Two relate to the Korb-model. The first of these is the hopping time for adsorbed water diffusing across the pore surface. It is about 1 ns and is inferred from the frequency dependence of T_1 as measured by field cycling. The second is the residency time for water molecules adsorbed on the pore surface. It is about 13 μ s and is inferred from the

ratio T_1/T_2 which can be measured in 2 dimensional T_1 - T_2 correlation experiments. The third timescale is that for water exchange between different pore types (inter-layer and gel). It is about 5 ms and is measured in T_2 - T_2 exchange experiments.

5.1 The nano-second timescale: pore-surface hopping.

Field cycling methods measure the NMR frequency dependence of T_1 . They add an extra dimension to relaxation rate data. This is because, as shown in section 2.3, relaxation times are strongly dependent on the spectral density function of the water dynamics at the Larmor frequency. Changing the NMR frequency therefore tracks the frequency dependence of the possible water dynamics.

Field cycling experiments on cementitious materials have been performed mainly by Korb and co-workers, [26,38,55,56]. A typical result is shown in Figure 10, where the relaxivity, normalised to unity at low frequency, is plotted against frequency in a lin-log plot for a series of different hydration ages out to 12 hours of hydration for a sample of white cement at $w/c = 0.4$. The relaxation is too fast to continue measurement by field cycling beyond 12 hours, but measurements made at specific frequencies using conventional spectrometers and in the so-called “rotating reference frame” ($T_{1\rho}$) have been found to be in agreement with the general trend in samples out to 1 year in age, [38]. The typical pattern is a plateau at low frequencies (below circa 22 kHz), with a bilinear decrease at higher frequencies. There is a peak at circa 60 MHz (not seen in Figure 10) if the experiment ranges this far, due to direct Fe^{3+} electron paramagnetic relaxation of ^1H (irrespective of ^1H diffusion) which is the rate controlling process at this frequency. The fact that a universal curve is seen as a function of degree of hydration suggests that an unchanging process is governing the relaxation and dynamics throughout hydration.

The T_1 dependence on frequency shown in Figure 10 can only be explained by the Korb model of water in pores (section 2.3.3). Fitting the curve yields an estimate of τ_m , the hopping time of water on cement pore surfaces. Best estimates are $\tau_m = 0.7$ ns during the first 7 h of hydration, increasing to $\tau_m = 1.3$ ns after 12 h [26]. White cement, OPC pastes and a mortar have been compared. It is found that τ_m depends very little on the cementitious material studied: it is near universal [56]. This is a clear signature that the overall dynamics and physics are the same within all the samples. The only sample that differed significantly from 1 ns was one in which the pore surface was modified by the addition of 10% PVA.

The timescale of nano-second surface hopping has been confirmed by molecular dynamics simulations of water interacting with tobermorite surfaces [57,58].

5.2 The micro-second timescale: pore surface residency.

McDonald *et al.* [27] performed T_1 - T_2 correlation experiments and compared the results to theoretical analysis. The results show a series of discrete features lying on the line $T_1 = 4T_2$, Figure 11. The features are interpreted as water in different pore sizes. The fact that $T_1 = 4T_2$ at the NMR frequency used (20 MHz) is consistent with the Korb-model. Given an estimate of the surface hopping time (1.3 ns, see section 5.1), the T_1/T_2 ratio leads to an estimate of 13 μ s for the adsorption time for water molecules on the pore surface. Further validation of the model is provided in [59] where results of the same experiment performed over more than 2 orders of magnitude in frequency confirm the predicted frequency dependence of the T_1 / T_2 ratio.

5.3 The milli-second timescale: inter-pore exchange

The off diagonal peak in Figure 11 could have been interpreted either as hydrogen in a solid like environment, characterised by $T_1 \gg T_2$, or as the result of water exchange between pores of different sizes. The exchange explanation is more probable since the value of T_2 of the exchange peak is much longer than that reported for chemically bound hydrogen in solids. However, the T_1 - T_2 experiment was not able to fully discriminate between the two hypotheses.

Subsequent T_2 - T_2 experiments on cement have been presented in [30] and unequivocally point to exchange, Figure 12. Comparisons between simulated and measured data on a $w/c = 0.4$ white cement paste cured saturated at 20°C for 3 days lead to an order of magnitude estimate of the exchange time of circa 5 ms. A further observation is that exchange has only been seen to date in relatively young samples: no more than 3 to 5 days old. The interpretation of this apparently very long exchange time has not been simple and remains controversial. An early hypothesis was based on the fact that the typical size of a cement grain used in this experiment was 7.5 μ m. From this value and the 5 ms exchange time, a diffusion coefficient of the order of that of bulk water is obtained which led to a hypothesis that it is exchange between inner and outer product. This hypothesis has been shown to be incorrect by an experiment on synthesised C-S-H [43], Figure 12, which shows a similar exchange time for homogeneous material. The same experiment also discounts an alternate hypothesis to explain the exchange based on an assumption of uniform pore size

but different surface relaxivity due to the distribution of paramagnetic impurities. This leaves as a more plausible explanation exchange between C-S-H inter-layer and gel pore water. The long exchange time in this case may be related to the energetic “trapping” of water in the sheets due to the presence of the Ca ions in the restricted space. Moreover, as the sample ages, so the confinement and gel tortuosity may become greater explaining why exchange is not seen in older samples.

6 Some practical issues affecting the interpretation of NMR in cements

As much of the preceding text has made clear, NMR can yield remarkably reproducible results across different studies. However, this relies on careful quantification, and quantification requires that all the water in the sample is accounted for. Experiments in which short T_2 components are not seen are of less value than those in which they are. In experiments based on discrimination of T_2 components, observation of solid phases such as $\text{Ca}(\text{OH})_2$ or ettringite requires excitation pulse lengths less than 10 μs , ideally 1 to 2 μs and commensurably short detector dead times. Examination of the solid is facilitated by the use of solid or quadrature echo methods. Such pulse lengths and dead times are normally associated with small radio frequency coils and hence sample sizes of 1 cm characteristic size or less. Spectrometers for larger samples, with pulse lengths and dead times of the order of 50-150 μs , that are often designed primarily for imaging, fail to detect the gel water in mature pastes. T_1 is sometimes cited as an alternative relaxation time to measure in preference to T_2 . However, the same considerations apply since the detected signal is observed in the form of a transitory signal that decays with time T_2 after the detection pulse. Moreover, measurement of T_1 is generally a more time consuming process than measurement of T_2 . This can be an issue in young cements, which are changing rapidly due to on going hydration.

Quantification may be based on comparison of the signal intensity against a standard. In these cases it is important to ensure that the standard and unknown sample are as “NMR-similar” as possible since the sample generally de-tunes the detector coil and causes a systematic change in the gain of the receiver amplification.

Fitting relaxation data to distributions of relaxation times is a notoriously ill posed problem. Satisfactory results can often be obtained by assuming an *a priori* number of relaxation reservoirs to be fit. However, this can result in difficulties if, for instance, one mode of a distribution dominates another. Then a two component fit may simply adjust to a value

typical of the upper and lower sides of the dominant distribution and miss the minor component entirely. Adding a third component may be ambiguous. ILT algorithms potentially overcome this problem but all current algorithms include a regularisation parameter that generally serves to “smooth” the output distribution. If this parameter is not chosen with care, then misleading results may be obtained. A quirk of ILT algorithms is that they tend to “pearl”. That is, a distribution may move towards a finite number of modes of low width if the analysis is pushed too far. The widths of these modes, that correspond to pore size ranges, is then under-estimated although the integrated intensity of each tends to remain faithful to reality. In the case of solids, careful investigation of different solid phases such as Ca(OH)_2 and ettringite in isolation may reveal that they have identifiably different relaxation signatures, but these differences seem not to be sufficiently large to enable quantifiable discrimination between them when more than one phase is present. Only in the most recent studies [39,40] have all these issues been systematically addressed and the results compared to those for established methods such as scanning electron microscopy, X-ray diffraction, thermo-gravimetric analysis and mercury intrusion porosimetry.

7 Summary

Viewing ^1H NMR studies as a whole, a picture emerges of the nature of cement paste microstructures as comprising ^1H in solid (e.g. Ca(OH)_2) and in water in a hierarchy of pores of different size. Specifically:

- The relaxation component with very short T_2 (few μs), long T_1 (ms) is attributed to crystalline solids phases such as Ca(OH)_2 and, e.g., to crystal (non zeolitic) water in ettringite. It is only detected in studies that utilise spectrometers and methods suited to short T_2 systems, even if the object of study is T_1 . However, when it is detected, the fractional intensity of this component corresponds closely with measurement of crystalline solid content by other techniques, such as thermal gravimetric analysis or X-ray diffraction so long as the molar mass of water in the solids is properly accounted.
- Other relaxation components are attributed to mobile water in pores of successively larger size as T_1 and T_2 increase. The relaxation rates are proportional to the pore size. The constant of proportionality is determined by the paramagnetic impurity concentration of the cement. The two relaxation times are characterised by the ratio $T_1/T_2 > 1 = \text{constant} \approx 4$ at 20 MHz NMR frequency. The ratio is frequency dependent and increases with frequency. Quantitative study is thus possible.

- 958 • Numerous experiments lead to the conclusion that, in white cement, the component
 959 with T_2 of the order 100 μs at 10 – 20 MHz NMR frequency is due to C-S-H inter-layer
 960 water. This conclusion is supported by the fact that, in quantitative experiments in which all
 961 the water is “seen”, the only component with shorter T_2 is fully accounted for by the
 962 crystalline solid. Hence this reservoir must include all the hydrogen associated with the
 963 inter-layer space: hydrogen in silanol groups, water associated with Ca ions and “free”
 964 water. The inter-layer size, based on the fast exchange model of relaxation and using the
 965 relaxation time for dried material as the surface relaxivity, is estimated to be 1 nm.
- 966 • The next component with T_2 of the order 300-400 μs is due to gel pore water.
 967 According to the fast exchange model of relaxation, the gel pores have a size of a few nm,
 968 with 2 – 5 nm being most commonly reported. At 100% RH, the hydrogen associated with
 969 the gel porosity is typically $1\frac{1}{2}$ times the volume associated with the sheet porosity.
- 970 • The total volume of free water decreases throughout hydration. After circa 1-2 days
 971 of hydration, most of the free water is in small inter-hydrate pores of about 10 nm. NMR
 972 “sees” far fewer larger (micron-sized) capillary pores than normally expected. ^1H NMR
 973 requires water to be in the pores in order to “see” them. It is likely that self-desiccation
 974 empties these pores in open and sealed cured samples: a Kelvin-Laplace radius of 10nm
 975 corresponds to 90% relative humidity. Full capillary pores can be ensured by curing small
 976 samples of paste under water. Where this is done, the volume is still small (typically <5%)
 977 and only about $\frac{1}{3}$ - $\frac{1}{2}$ that predicted on the basis of the Powers-Brownyard model.
- 978 • The pore sizes can also be measured by analysis of NMR signal amplitudes in
 979 controlled drying experiments and by NMR cryoporometry. All three methods show
 980 excellent consistency and moreover there is agreement with measurements by other, non-
 981 NMR based techniques, such as small angle neutron scattering [60].
- 982 • Since NMR is non-invasive, it is possible to follow the evolution of the porosity
 983 during hydration. The basic measurement takes minutes and the early stages of hydration in
 984 particular can be followed in considerable detail. There are changes in relaxation rates that
 985 correspond to different stages of the hydration. After the induction period, the gel porosity
 986 evolves rapidly. There is indication that the gel porosity stops increasing after 2-3 days
 987 hydration. However, the C-S-H inter-layer porosity continues to grow and the inter-hydrate
 988 porosity decreases progressively to zero. Hence it is speculated that 2-3 days marks a

transition from the formation of lower density to higher density C-S-H product and that dense product is forming in the inter-hydrate pores.

- The evolution of the filled porosity during controlled drying experiments of mature pastes may be followed. This leads to the measurement of pore-size resolved desorption isotherms. The picture that emerges is consistent with conventional understanding of pore drying inferred from purely gravimetric experiments.

- The specific surface area has been measured. The total is about $270\text{-}300\text{ m}^2/\text{cm}^3$ in mature, $w/c=0.4$ white pastes.

- The C-S-H density and composition of never-dried material, but excluding the gel pore water, have also been inferred given the degree of hydration and ettringite fraction as measured by other conventional methods. The average density result is 2.71 g/cm^3 for the solid density of a $w/c = 0.4$ paste, including the inter-layer water but excluding gel pore water (and hence excluding water adsorbed on aggregated C-S-H layer surfaces). The average value conceals the fact that the NMR results show strong evidence for C-S-H densification during hydration. The corresponding C-S-H composition is $\text{Ca}_{1.70}(\text{Si}_{0.95}\text{Al}_{0.05})\text{O}_{3.67}(\text{H}_2\text{O})_{1.80}$.

- NMR relaxation analysis and 2D relaxation together measure dynamic phenomena on 3 timescales: 0.7 ns for the surface hopping time of water molecules on pore surfaces during the first few hours of hydration, increasing to 1.3 ns at later stages; $13\text{ }\mu\text{s}$ for the pore surface residency time in mature pastes and 5 ms for the exchange time between the C-S-H inter-layer spaces and gel pores in the first few days of hydration. The first of these times (surface hopping) has been confirmed by molecular dynamics simulations.

- Exchange of water has been observed in young pastes (typically up to 3 days). The most plausible explanation is that this is exchange between inter-layer water and gel pore water. The exchange time is surprisingly long, 5 ms . A long exchange time likely arises due to the difficulty of escaping the confines of the inter-layer space due to the Ca ions. Exchange has not been observed in older samples where confinement and microstructure tortuosity are likely to inhibit further any exchange between these two populations. Exchange is seen in synthesised C-S-H and confirms the fact that exchange is between water environments of different size and not between environments with different surface relaxivity characteristics (density of paramagnetic impurities).

Parameters describing the morphology of C-S-H, such as pore sizes and density, that emerge from NMR relaxometry are generally consistent with parameters of the revised colloidal model of cements (CM-II) due to Jennings [61]. CM-II parameters have emerged primarily from examination of the results of scattering experiments. However, there are key differences. First, CM-II differentiates between so called intra-globular gel pores due to imperfect C-S-H sheet stacking within globule particles, small globule pores between particles within flocs and large globular pores between flocs. These are additional to the inter-layer spaces. NMR only sees three reservoirs of nano-sizes pores: inter-layer spaces of size circa 1 nm, gel pores of size circa 2-5 nm and inter-hydrate pores of circa 10 nm. These last, however, are not seen as integral to the C-S-H since their amount decreases with ongoing hydration, rather than increases. Second, and more philosophically, NMR views C-S-H as a solid matrix with water filled pores. CM-II views it as colloidal particles in a continuous water phase. The critical observation is that while both NMR and scattering experiments are primarily sensitive to the solid–water interfaces, neither can easily distinguish between the differing points of view.

8 Conclusion

It is seen that NMR relaxation analysis and related techniques offer considerable opportunity to study the formation and characteristics of cement microstructures and of water within them. The methods have several major advantages compared to other techniques. NMR is non-destructive and non-invasive and does not require sample drying. Indeed it is the sample water that is the probe. The method is quantitative. NMR spectrometers for this kind of study are relatively inexpensive and widely available. The experiments may be performed rapidly.

To conclude, NMR characterisation is now at a stage where basic questions of methodology and data interpretation have largely been answered on model systems and carefully controlled pastes. Potential pitfalls and reasons for potential discrepancies have been identified. There is therefore significant opportunity for much greater use to be made of NMR in the characterisation of cement based materials and for the method to sit equally alongside other, more established, methods. Only the issue of high iron content in some practical materials remains a major limiting factor. Notwithstanding, NMR relaxometry of cements is now at a stage where cement scientists can begin to explore unknown materials confident in the robustness of the methodology.

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Figures

Figure 1 Schematics of the different pulse sequences described in the text: a) FID. A single pulse is followed by a short spectrometer dead time (light grey) after which the signal may be observed. The signal due to the solid decays more rapidly than that due to the liquid. It is partially obscured by the spectrometer dead time (dotted line, shaded region). The signal due to the liquid decays with a time constant $T_2^* < T_2$ that is a function of the magnet homogeneity. b) CPMG. The initial pulse and FID (dotted line, T_2^* decay) is followed by a series of refocusing pulses that invert dephasing due to magnet inhomogeneity leading to a

train of signal echoes that decay with time constant T_2 (slowly relaxing magnetisation, dashed line). c) Saturation Recovery. A train of pulses destroys the equilibrium magnetisation. It recovers, unobserved, with time constant T_1 (dotted line). An inspection pulse after time τ measures the recovered magnetisation at that time. d) Inversion recovery. This is the same as saturation recovery, except that the initial magnetisation is inverted; e) Quadrature (or solid) echo. The solid signal decays due to inter-nuclear magnetic-dipolar interactions. A second 90° pulse of shifted phase reverses this decay but leaves the liquid signal un-touched. There is no simple, non-quantum mechanical, explanation for the solid echo formation. The solid line shows the observed signal, the sum of solid and mobile components (dotted lines) f) The simplest pulse field gradient sequence for measuring self diffusion. The sequence is the same as for the generation of the first echo in CPMG except that two magnetic field gradient pulses are additionally applied τ_D apart. These encode the nuclei with their macroscopic displacement within the sample during τ_D . Diffusion is manifest as a reduced echo intensity. g) A schematic of 2D correlation or exchange experiments. The two boxes (duration t_1 and t_3 respectively) either side of the magnetisation storage interval of variable length t_2 are used to encode any of T_1 , T_2 or self-diffusion in order to build a correlation or to measure inter-pore exchange. The reader is referred to the references for further details.

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Figure 2. ^1H T_1 and T_2 relaxation times as a function of correlation time, τ_c , calculated according to the BPP model as described in the text for NMR frequencies of 1, 10 and 100 MHz. The inter-nuclear distance r is set to 0.15 nm. In each case, T_1 goes through a minimum with increasing correlation time whereas T_2 , which initially equals T_1 , decreases monotonically down to the rigid lattice limit, set here to 10 μs . The correlation time for bulk water is a few picoseconds leading to T_1 of the order of a few seconds, as observed experimentally.

Figure 3 Schematic representation of the 2D diffusion of water molecules across a pore surface in the vicinity of paramagnetic impurities and relative characteristic times (reprinted from [27]).

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1267 Figure 4 Calculated 2D T_2 - T_2 spectra for (left to right) slow, medium, and fast
 1268 exchange rates, k , and (bottom to top) short, intermediate, and long storage times, t_2 .
 1269 Plots span T_2 from 0.1 to 10 ms. (reprinted from [30]).

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Figure 5. A plot of the T_1 of the pore water in cement paste as a function of hydration time and w/c ratio. T_1 decreases as the porosity develops and is generally longer in systems with higher w/c ratio. (Reprinted from [33])

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1281 Figure 6 Mass (left) and volume (right) composition of $w/c = 0.40$ sealed cured
 1282 white cement paste as a function of degree of hydration. From top, the shaded
 1283 regions correspond to free water, gel pore water, C-S-H, ettringite, Ca(OH)_2 and
 1284 unreacted cement. (Reprinted from [40])

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Figure 7 The NMR “water-environment” resolved desorption isotherm of 28 day, $w_{\text{mix}}/c = 0.4$ underwater cured ($w_{\text{actual}}/c = 0.46$, see inset) white cement paste calculated from CPMG and solid-echo T_2 analysis. Circles show the total signal intensity and inverted triangles filled capillary and inter-hydrate water. Other traces show the Ca(OH)_2 (diamonds, $T_2 \approx 10 \mu\text{s}$), C-S-H inter-layer water (squares, $T_2 \approx 100 \mu\text{s}$) and gel pore water (triangles, $T_2 \approx 400 \mu\text{s}$). Notice that, as the gel porosity empties, so residual water on the C-S-H surface appears sheet-like. Hence this signal increases. (Reprinted from [39]).

Figure 8a to d. A schematic picture of the drying of a planar pore. Circles represent mobile water molecules, crosses represent surface adsorbed molecules. a) Pores completely filled; all the water appears as mobile. b) Two possible modes of emptying a pore showing mobile and adsorbed water. In b(i) all the remaining water appears mobile but with an increased S/V ratio and decreased relaxation time. This is not observed experimentally. In b(ii) there are two environments. The mobile component is decreased in volume but with the same surface-to-volume ratio and hence T_2 . A region of monolayer coverage also appears that has a short relaxation time. c) A pore with surface adsorbed water only. d) An empty pore. The pore size is calculated from the rate of increase with drying of the adsorbed fraction. (Redrawn after [45]).

Figure 9 The total NMR signal (squares), solid (circles) and mobile (triangles) signal fractions as a function of the actual relative mass of the sample (top axis); of the relative mass of water assuming a w/c ratio of 0.4 as mixed (middle axis); and of the relative mass of water assuming a w/c ratio of 0.52 as derived from extrapolation of the total signal to zero intensity (bottom axis). The small sample is cured underwater, hence the increase in w/c . The indicative drying temperatures are shown above the plot. The solid lines are least squares fits to the data from the gradients of which the pore sizes are calculated as 1.5 and 4.1 nm. (Reprinted from [45])

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1330 Figure 10 Field cycling measurements of $1/T_1$ as a function of NMR frequency.
1331 Multiple data sets are shown for different degrees of hydration, all normalised to
1332 unity at low frequency. A master curve is obtained from which universal dynamics
1333 are inferred including calculation of an adsorbed-water pore-surface hopping time
1334 of circa 1 ns using the Korb-model of relaxation. (Reprinted from [56]).

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Figure 11 The T_1 - T_2 correlation spectrum of a white cement paste cured for 4 days. A series of diagonal peaks from lower left to upper right are progressively attributed to C-S-H inter-layer water; gel pore water, capillary pore water, water in cracks and bulk-water on the sample surface. The off-diagonal peak at $T_1 = 10$ ms, $T_2 = 70$ μ s is the result of exchange of water between the C-S-H and the gel porosity. (Reprinted from [27]).

Figure 12 Top, a T_2 - T_2 spectrum recorded from a 1 day old white Portland cement sample cured at 20 degrees. The off-diagonal peaks in the spectrum show unambiguous exchange between the two diagonal reservoirs. Bottom, the same experiment performed on synthesised C-S-H. The lower impurity concentration shifts the spectrum up the diagonal, from which it is concluded that the reservoirs are pores of different size: C-S-H inter-layers and gel pores. (Reprinted from [43]).