A $^1$H double-quantum-filtered NMR study of water in cement pastes

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Abstract. The results of a $^1$H double-quantum-filtered (DQF) nuclear magnetic resonance (NMR) study of water in cement pastes are reported. It is shown that the DQF signal increases with curing time and in sympathy with the loss of mobile single-quantum signal, suggesting strongly that a signal from $^1$H in chemically combined and strongly confined water is selectively observed. The DQF signal in white cement comprises at least two components: the first is assigned to portlandite (Ca(OH)$_2$); the second is assigned to water in the planar, nanometre-wide, calcium–silicate–hydrate (C–S–H) gel pores. The pore water signal is significantly broader than that expected for bound water. The width is interpreted in terms of the water undergoing a two-dimensional walk in the vicinity of Fe$^{3+}$ impurities. A simple model is presented and found to be consistent with experiment and the known Fe$^{3+}$ concentration. In grey cements, a third component is identified and associated with Fe-rich phases. The analysis places a lower bound on the lateral extent of planar C–S–H pores. The change in DQF signal components upon drying a sample mirrors the loss of the single-quantum components observed in a parallel study.

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1. Introduction

There is ongoing interest in characterizing the nano- to microscale structure of cement pastes, the morphology of the porosity to which this structure leads and the dynamics of water confined within it \([1, 2]\). This is because of the importance of cement porosity and water in determining the macro properties of cement and the fact that water transport is at the root of many degradation mechanisms of concrete. An improved understanding of water in cement is expected to lead to improved models of new cementitious materials.

Nuclear magnetic resonance (NMR) relaxometry has played an important role in advancing new understanding. Different experiments have led to the identification of translational motions on three timescales (ns, \(\mu s\) and ms) within the calcium–silicate–hydrate (C–S–H) gel structure of cement pastes and to estimates of characteristic gel pore sizes of the order of a few nanometres and a few tens of nanometres \([3]–[5]\). Gel pores in cements are often considered to be planar \([6]\). Hence, relaxation methods tend to yield an estimate of the pore width.

In this work, we explore the contribution that can be made using double-quantum-filtered (DQF) \(^1\text{H}\) NMR spectroscopy to the characterization of water in cement pastes. Multiple quantum NMRs of spin-1/2 nuclei, such as \(^1\text{H}\), are distinct from more standard single-quantum NMRs. In single-quantum experiments, a signal is seen from all nuclei in the sample in response to a single excitation pulse, whereas in multiple quantum experiments, signals are only seen in response to a multiple pulse excitation that selectively tracks magnetization that has evolved coherently between strongly coupled nuclei. Since, in particular, rapid isotropic molecular tumbling averages magnetic dipolar coupling to zero, this means that double-quantum NMR of water is specifically sensitive to immobile bound and anisotropically confined water.

Our study of cement by DQF NMR is motivated by two driving issues. Firstly, a detailed understanding of pore morphology requires an estimate of the lateral extent of anisotropic planar pores as well as of pore width. Such an estimate has not been forthcoming from NMR measurements. Secondly, the extent to which bound water in solid phases, such as portlandite (calcium hydroxide, Ca(OH)$_2$ or in cement notation CH), is well distinguished from strongly adsorbed water in the narrowest C–S–H gel pores has been unclear. Clarification is needed to better assure the current interpretation of relaxation data.
While DQF NMR was applied extensively to other materials [7]–[10], we believe that this is the first time that it has been applied to cement. We chose to use DQF NMR because signals originate from water in strongly anisotropic, bound and confined environments, whereas water in mobile environments is suppressed. In this work, we report:

1. The growth of the $^1$H NMR DQF signal during hydration and cure of cement paste, and show how this mirrors the loss of the longer spin–spin relaxation time, $T_2$, components in the normal single-quantum experiments.

2. How the constituent components of the DQF signal vary in amplitude as a cured cement paste sample is progressively dried. We show that this behaviour is consistent with a model of pore drying developed elsewhere [11].

3. How the DQF line shape evolves in a series of materials starting with pure Ca(OH)$_2$, through white cement and onto two different grey cements, enabling us to assign different line shape components to hydrogen in different environments.

4. A model for the DQF spectrum of water in planar cement pores relaxed by Fe$^{3+}$ paramagnetic centres. The model leads to an estimate of the spacing of the Fe$^{3+}$ impurities and puts a lower bound on the lateral extent of the planar pores.

2. Materials and methods

White cement and two grey cements were obtained from the Nanocem consortium materials bank. Ca(OH)$_2$ was purchased from Sigma-Aldrich. Table 1 shows the chemical composition of the three anhydrous cements.

The cements were mixed into pastes with a water-to-cement ratio of 0.4 using methods established by the Nanocem consortium. In short, the procedure involved mixing for 3 min at 500 rev min$^{-1}$, pausing for 2 min, followed by re-mixing for 2 min at 2000 rev min$^{-1}$. Except for measurements made as a function of curing time, samples were cast in cylindrical moulds 8 mm in diameter and 20 mm deep. Once set, the samples were removed from the moulds and cured under a small quantity of saturated calcium hydroxide solution at room temperature for 28 days. Prior to analysis, samples were dabbed dry, crushed to a coarse powder and placed in small NMR tubes with stoppers. Care was taken to see that the sample was contained within the volume of the probe coil to ensure good radio frequency field homogeneity. For the progressive drying study, samples were weighed before and after drying in a vacuum oven. Drying was initially for a few minutes just above ambient temperature, gradually increasing to

| Phase (‘cement chemistry’ notation) | White cement ‘A’ (%) | Grey cement ‘B’ (%) | Grey cement ‘C’ (%) |
|-----------------------------------|---------------------|-------------------|-------------------|
| Alite (C$_3$S)                    | 67.1                | 51.4              | 62.3              |
| Belite (C$_2$S)                   | 23.6                | 21.1              | 18.4              |
| Ferrite (C$_4$AF)                 | 0.0                 | 10.0              | 7.1               |
| Aluminate (C$_3$A)                | 3.5                 | 6.5               | 6.0               |
| Total others                      | 5.8                 | 11.0              | 6.2               |
longer times at temperatures of up to 200 °C. An oven without a vacuum was available for even higher temperatures. For the progressive curing study, samples were cured in the NMR tube and placed under a small reservoir of the calcium hydroxide solution between measurements. All measurements were made at room temperature.

NMR measurements were performed using a 400 MHz Chemagnetics (now Varian Inc) Infinity spectrometer equipped with a 10 mm Fraunhofer Institute 1H probe and an 89 mm bore Magnex superconducting magnet. A standard DQF sequence comprising three π/2 excitation pulses (P90), with an additional π refocusing pulse (P180), was used [13]: P90–τc/2–P180–τc/2–P90–τc–P90 measure. Here, τc is the DQF creation time and τc is the evolution time. The former, τc, was optimized for maximum signal from a white cement sample and was thereafter kept constant; the latter, τc, was kept as short as practically possible, a few μs. Full phase cycling to remove unwanted coherences was adopted [13]. The P90 pulse width was 8 μs and the spectrometer dead time was 4–5 μs. Typically, 512–1024 averages with a repetition time of 1 s were recorded per spectrum. Careful tests were carried out to ensure that residual signal from mobile 1H samples, such as water and oil, was negligible compared to the DQF signals observed from cement. A very small empty cavity signal was routinely subtracted. All DQF magnetization spectra, M (see section 3), as a function of frequency, f, were phased and then anti-symmetrized using $M'(f) = (M(f) - M(-f))/2$ to remove any residual phasing artefact prior to data analysis.

DQF spectra have been fitted to one or more pairs of anti-phase Lorentzian lines of area $A$, width $w$ and offset $d$ according to

$$M'(f) = \sum_i \frac{2A_i w_i}{\pi} \left( \frac{1}{w_i^2 + 4(f + d_i)^2} - \frac{1}{w_i^2 + 4(f - d_i)^2} \right).$$  \hspace{1cm} (1)$$

The choice of a Lorentzian is arbitrary but empirically the fits are better than using Gaussians. A least-squares analysis using multiple overlapping Lorentzian functions is relatively unstable and the resultant parameters are generally dependent on the initial (guess) values. Similarly shaped curves are achieved for widely different combinations of $A$, $w$ and $d$ due to the way in which two ‘up and down’ Lorentzians overlap and cancel in the middle. Consequently, fitting was constrained by requiring $w = nd$, where $n$ is a constant of the order of unity across all analyses.

3. Theoretical model

We consider a model in which water molecules (proton spins $I_1$ and $I_2 = \frac{1}{2}$) reside in the vicinity of an Fe$^{3+}$ paramagnetic impurity (spin $S = \frac{3}{2}$) and calculate the 1H DQF spectrum. The calculation was performed using standard spin operator formalisms [14] using the interaction Hamiltonians

$$H_{II} = \frac{\mu_0}{4\pi} \frac{\chi_I^2 \hbar^2}{r_{II}^3} \left( 1 - 3 \cos^2 \theta_{II} \right) (3I_1zI_2z - I_1I_2) = C_{II} (3I_1zI_2z - I_1I_2)$$  \hspace{1cm} (2)$$

and

$$H_{IS} = \frac{\mu_0}{4\pi} \frac{\gamma_I \gamma_S \hbar^2}{r_{IS}^3} \left( 1 - 3 \cos^2 \theta_{IS} \right) (I_zS_z) = C_{IS} (3I_zS_z).$$  \hspace{1cm} (3)$$

Here, $r_{II}$ and $r_{IS}$ are the nuclear–nuclear and nuclear–electronic impurity spin distances, respectively, and $\theta_{II}$ and $\theta_{IS}$ are the angles between the inter-spin vectors and the applied
magnetic field. \( I \) and \( S \) are the spin angular momentum operators. The remaining constants are \( \mu_0 \), the magnetic permeability of free space, \( h \), Planck’s constant divided by \( 2\pi \) and \( \gamma_{I,S} \), the magnetogyric ratio of the nuclear and electron spins, respectively.

The calculation of the spectrum is straightforward, if tedious. The essential method is to evaluate, in an appropriate basis set, the initial spin density matrix, \( \rho(0) \), spin rotation matrices \( R_{\varphi,\xi} = \exp(-j\varphi I_\varphi) \) corresponding to the excitation pulses \( P_{\varphi}\xi \) applied to the nuclear spins and the spin Hamiltonian evolution matrix acting between the pulses, \( E(\tau) = \exp(-jH\tau) \). Here, \( \varphi \) and \( \xi \) are the rotation angle and phase of the pulses. The spin density matrix at time \( t \) after the third pulse is given by

\[
\rho(t) = E(t)R_{90}\rho(0)E(\tau_c)R_{90}E(\tau_c/2)R_{180}E(\tau_c/2)R_{90}\rho(0)\cdots R_{90}E^+(\tau_c/2)R_{180}^+E^+(\tau_c/2)R_{90}^+E^+(\tau_c)R_{90}E^+(t).
\]

The magnetization is then given by the trace

\[
m(t) = \text{Tr}(I_x + j I_y, \rho(t)).
\]

The problem is much simplified in the basis set \( |\frac{1}{2}, \frac{1}{2}\rangle|m_s\rangle, (|\frac{1}{2}, -\frac{1}{2}\rangle + |\frac{1}{2}, \frac{1}{2}\rangle)|m_s\rangle/\sqrt{2}, |\frac{1}{2}, -\frac{1}{2}\rangle|m_s\rangle \) and \( (|\frac{1}{2}, -\frac{1}{2}\rangle - |\frac{1}{2}, \frac{1}{2}\rangle)|m_s\rangle/\sqrt{2} \), where \( \pm\frac{1}{2} \) represent the two proton spin states and \( m_s = -\frac{3}{2}, \cdots +\frac{3}{2} \) the electron states. The advantage of using the simplified electron–nuclear interaction Hamiltonian implicit in equation (3) is that the matrices are block diagonal with one block for each electron state, so simplifying the analysis significantly. Only the symmetric nuclear states actively contribute and the electron interaction appears Zeeman like. The maximum matrix size is \( 3 \times 3 \) and matrices are readily evaluated from results in standard texts, for instance [14].

We assume that \( r_{1:S} = r_{1:S} \) and \( \theta_{1:S} = \theta_{1:S} \). This geometric assumption is good except for the very closest approach of the water molecule to the paramagnetic impurity corresponding to the very broadest parts of the line. Given the diminishingly small weighting of nuclei at closest approach in a powder average (see below), this is not seen as a major limitation to the accuracy of the results.

With phase cycling of the pulses to remove residual single-quantum coherences, the measured DQF magnetization at time \( t \) following the third pulse is given by

\[
m(t) = \sum_{m_s=-\frac{5}{2}}^{\frac{5}{2}} 2\sin \left( \frac{3C_{II}\xi}{2} \right) \exp(j2C_{IS}m_s t) \left( \exp \left( j\frac{3C_{II}t}{2} \right) - \exp \left( -j\frac{3C_{II}t}{2} \right) \right).
\]

Fourier transformation of \( m(t) \) yields the spectrum, \( M(f) \). Figure 1 shows DQF spectra evaluated for \( (\theta_{II}, \theta_{IS}) = (\frac{\pi}{2}, \frac{\pi}{2}) \), \( r_{II} = 0.16 \) nm (i.e. a water molecule) and for short \( \tau_c \) and \( \tau_e = 0 \) as a function of radial distance \( r_{IS} \). For fixed angles, the spectrum comprises a multiplet of six antiphase doublets, each corresponding to a different value of the Fe\(^{3+}\) spin quantum number, \( m_s \).

For small \( r_{IS} \), the total width varies as \( 1/r_{IS}^3 \). At large \( r_{IS} \), the spectrum collapses to that for a dipolar-coupled spin-1/2 pair. Thus, to a reasonable approximation, the width of the spectrum defined as twice the maximum shift of a resonance singularity from the centre, \( 2\Delta f \) varies as

\[
2\Delta f = \frac{a}{r_{IS}^3} + b,
\]

where \( b \) is the width characteristic of a spin-1/2 pair far from the Fe\(^{3+}\) (see below for further discussion) and \( a \approx \left( \frac{45}{32} \right) \Delta f r_{II}^3 \).

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Figure 1. The lower series shows $^1$H DQF NMR stick spectra for a water molecule at different distances $r_{IS}$ from an Fe$^{3+}$ impurity for fixed angles $(\theta_{II}, \theta_{IS}) = (\pi/2, \pi/2)$. The distances are (from bottom) $5r_{II}$, $10r_{II}$, $20r_{II}$ and $40r_{II}$ with $r_{II} = 0.16$ nm. For short distances, the total width varies as $1/r_{IS}^3$. At large distances, the spectrum reduces to that of an isolated water molecule. On top is a numerically integrated spectrum for water in a powder average of planar pores with a cut-off radius of $r_c = 2.4$ nm. The full width, calculated as twice the second moment of the symmetrized spectrum, is 123 kHz.

At large $r_{IS}$, the spectrum is reminiscent of an anti-symmetric version of the symmetric two-line spectrum that is observed in single-quantum NMR experiments of oriented, rigid dipolar-coupled spin-1/2 pairs, such as in a single crystal of gypsum. The magnetic dipolar field of one nucleus shifts the resonance of its partner by an amount dependent on the distance between the two nuclei and the orientation of the inter-nuclear vector relative to the applied magnetic field. In general, powdered samples rather than single crystals are available. The distance between different pairs of nuclei is constant but the relative orientations are not. The observed spectrum comprises a powder average over all orientations. Since the probability of the angle between the inter-nuclear vector and the field $(\theta_{II})$ varies as $\sin(\theta_{II})$, some splittings are far more likely than others. As a result, the powder spectrum exhibits a complex shape dominated by two strong lines or singularities corresponding to $\theta_{II} = \pi/2$. For the case of the single-quantum experiment, the shape is the well-known Pake doublet [15]. It is the separation of these singularities that defines the width parameter $b = 1.5C_{II}$ in equation (7).

The model we envisage is one in which the water molecule randomly walks in two dimensions across the surface of a planar pore repeatedly encountering paramagnetic Fe$^{3+}$ relaxation centres (figure 2). This model is consistent with previous analyses of nuclear spin relaxation rates in cements [3, 4]. To develop it further for DQF analysis, we assume that the angle between the inter-proton vector and the normal to the pore surface is assumed constant. Interactions that couple water in one pore to Fe$^{3+}$ in a neighbouring or parallel pore are not included. There is a powder average of pore orientations. The calculation is performed in a frame of reference aligned to the pore-plane $(O_{x}, O_{y}, O_{z})$, as shown in figure 2, by first averaging over all angles $\phi_{I}$ and $\phi_{IS}$ followed by $\alpha$ with $\sin(\alpha)$ weighting. If the walk is bounded by the edges of the pore or if the Fe$^{3+}$ concentration is sufficiently high, then the resultant powder spectrum is equivalent to a weighted sum over all distances from that of closest approach of the water to the Fe$^{3+}$ ($r_{\text{min}} = 3$ nm [4]) out to a maximum cut-off radius, $r_c$, roughly equal to the

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Figure 2. The geometry of the Fe$^{3+}$ (spin $S$) and water (spins $I_1$ and $I_2$) system. The water undergoes a 2D walk in a planar pore, within a cut-off radius, $r_c$, of the Fe$^{3+}$. Both spins $I$, separated by $r_{II}$, are assumed to be $r_{IS}$ from $S$. The angles $\theta$ are the between the inter-spin vectors, $\mathbf{r}$ and the applied magnetic field, $\mathbf{B}_0$. For ease of calculation, the spins $I$ are located within the plane.

Figure 3. The dependence of the powder-averaged spectral width $2\Delta f'$ for water undergoing a 2D random walk between a distance of closest approach to the Fe$^{3+}$ and a cut-off radius $r_c$. The horizontal line corresponds to 108 kHz, the measured value in white cement.

The resultant fit is shown in figure 3. The best-fit parameters are $b' = 43.5$ kHz and $a' = 70.8$ kHz nm$^3$. The constant $a'$ is smaller than expected, probably reflecting the manner in which wider parts of the line phase cancel in the powder average, while $b' \approx b = \frac{3}{2}C_{II}$ within 1%, the small discrepancy arising from, firstly, the finite value of $r_c$ and secondly, the fact that the second

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Figure 4. (a) Top trace: the measured DQF spectra for powdered Ca(OH)$_2$ (circles) compared to the calculated spectrum without broadening, (solid line). Second trace: the measured DQF spectra for white cement (circles) and the fit to the data (line, almost totally obscured by data points). Third trace: as second trace but for grey cement C. Bottom trace: as second trace but for grey cement B. The fits to the data are discussed in the text. (b) The difference between the Ca(OH)$_2$ and white cement spectra (Ca(OH)$_2$ minus cement) when they are both plotted so as to have equal half-integral area.

moment is a different measure of the line width compared to the separation of the singularities. Further details of this model and calculation have been presented by Valori [16].

4. Results and analysis

4.1. Double-quantum-filtered (DQF) creation time dependence

Figure 4(a) (second trace) shows the $^1$H DQF spectrum recorded from a sample of white cement A recorded using a creation time, $\tau_c$, of 37 $\mu$s after 28 days of curing together with a fit to the data. The spectrum comprises a pair of anti-phase lines as expected and is typical of all those recorded from white cement. The line shape and fit are discussed further in section 4.3. Figure 5 shows the $\tau_c$ dependence of the total signal intensity, defined as the integral area of the half ($-\infty$ to 0 Hz) spectrum, of the three cements studied and of Ca(OH)$_2$. All samples have a single maximum occurring between 30 and 40 $\mu$s. The fact that only one maximum is observed is discussed in section 4.5.

4.2. DQF dependence on sample curing

Figure 6 shows the DQF signal intensity of white cement as a function of time during curing. The growth of the DQF signal mirrors the growth of a short $T_2$ component (about < 50 $\mu$s) in
Figure 5. The creation time dependence of the DQF intensity for white cement (open circles), grey cements C (closed circles) and B (open triangles) and for Ca(OH)$_2$ (closed triangles).

Figure 6. The intensity of the DQF spectrum as a function of curing time (circles) compared to the loss of the long $T_2$ components in the single-quantum spectrum (squares). The intensities are normalized to 1 at the end and start of the experiment, respectively.

single-quantum experiments, which we have seen and which has also been extensively reported by others [17, 18]. The growth occurs concurrently with the loss of longer $T_2$ components (about $>50 \mu$s) that are more easily measured experimentally. Hence, for direct comparison, the amplitude of the long $T_2$ component is shown in figure 6. These observations are entirely consistent with mobile water in the original mix becoming increasingly confined by, and chemically bound in, the hydration products of the cement and give confidence in the general observation that DQF NMR is measuring the bound and confined water fraction.

4.3. DQF line shape—results

Figure 4(a) (top trace) shows a $^1$H DQF spectrum recorded from a sample of powdered Ca(OH)$_2$ recorded under identical conditions to the white cement. As expected for DQF NMR, the spectrum comprises a pair of anti-phase lines that, for a simple crystalline structure such as Ca(OH)$_2$, resembles an asymmetric version of the single-quantum Pake doublet [15]. The
positive maximum and negative minimum are separated by $2\Delta f = 30.8$ kHz. We have carried out the corresponding single-quantum experiment and observed the Pake doublet: our results are very similar in detail to those reported in the literature [19, 20]. The line in figure 4(a) top trace is the theoretically calculated DQF spectrum without lifetime broadening. The calculation is based on an inter-hydrogen distance of 0.175 nm. The literature reports the inter-hydrogen distance in Ca(OH)$_2$ to be in the range of 0.202–0.218 nm [21, 22]. We note that a Pake doublet splitting (here the DQF splitting) is generally regarded as a very sensitive measure of this distance. The fact that this distance as determined by neutron scattering and by NMR measurements disagrees so significantly across studies has not, to our knowledge, been adequately addressed. However, there is clearly a significant degree of broadening in the NMR data compared to theory due to spin relaxation, to longer-range interactions, to the finite experimental pulse length and to spectrometer dead time. The degree of broadening is similar to that seen in the single-quantum Pake doublet by us and by others. In passing, we note that Lee and Khitrin [23] have performed numerical simulations of the broadening of Pake doublets in the context of experiments to measure $^{13}$C–$^{15}$N inter nuclear distances. They present an empirical result from which the broadening may be estimated and a correction made for spectrometer dead time. Applying their equation (2) to our single-quantum Pake doublet spectrum, we find that both effects are significant but that they act in opposition, leaving a net underestimation of less than 4% in the inter-nuclear distance. It is probable that their result could be extended and adapted to DQF spectra. While this requires analysis and simulations that have not been carried out to date, it is probable that the magnitude of the correction is comparable$^2$.

Comparing the top two traces in figure 4(a), it is apparent and we consistently observe that there is greater relative spectral width in the wings of the spectrum of cement compared to Ca(OH)$_2$. This can be appreciated from figure 4(b), which shows the difference between the two spectra when they are plotted so as to have the same half-integral intensity. Outside the central ±8 kHz region, the plot is consistent with taking intensity from the centre to the sides of the spectrum on going from Ca(OH)$_2$ to cement. The wiggle at the centre arises from a slight narrowing of the Ca(OH)$_2$ line shape, as discussed below. We suggest that the white cement spectrum comprises two components: the first is a relatively narrow anti-phase doublet due to crystalline phases such as Ca(OH)$_2$; the second a wider anti-phase doublet due to confined water in the planar C–S–H gel pores.

The more narrow component in white cement is slightly narrower than that for pure Ca(OH)$_2$, a result that mirrors the findings of Dolinšek et al for the Pake doublet [20]. We measure $2\Delta f = 25.5$ kHz between the singularities. A speculative reason is that the Ca(OH)$_2$ lattice spacing/structure is slightly modified in cement because it occurs only as nano-crystals for which the surface energy plays a more significant role. Notwithstanding this difference, the white cement spectrum has been fit to a function comprising a linear combination of the line shape recorded for powdered Ca(OH)$_2$ (we have used the measured line shape, rather than any Lorentzian-based fit function) and one anti-phase Lorentzian doublet, equation (1). The width of each Lorentzian, $w$, is a forced multiple, $n$, of its offset from the central frequency, $d$. Empirically, a factor $n = 2$ yields the best fits with $d = 50$ kHz for the wide line. The fit is stable to different starting parameters and the location of the maxima/minima in the summed asymmetric Lorentzian pair are well defined. These occur at ±54 kHz, i.e. $2\Delta f = 108$ kHz. Approximately 12% of the total cement DQF intensity resides in the wide component.

$^2$ We are grateful to an anonymous referee for bringing Lee and Khitrin’s work to our attention.
Figure 7. The intensity of the DQF spectrum as a function of sample relative mass for a progressively dried sample of white cement paste (squares, the line is a guide to the eye). The DQF spectrum is fitted to two components attributed to Ca(OH)$_2$ and water in C–S–H gel pores. The intensities of the separate fit components are shown as circles and triangles, respectively. Each set of relative intensities is normalized to 1 at the start, making clear how the Ca(OH)$_2$ fraction initially increases as water is lost. This behaviour mirrors that for the different $T_2$ components of the single-quantum spectrum [11]. Closed symbols are for drying temperatures below 200°C in a vacuum oven where carbonation is not thought to be significant.

Figure 4(a) (lower traces) show spectra for grey C and B cements in which the Ferrite concentration in the anhydrous material increases from one to the next. The spectra are recorded under identical conditions to those above. There is now a clear additional shoulder to the spectrum that increases in intensity with the Ferrite content of the cement. It is likely that the shoulder arises from $^1$H strongly associated with poorly crystalline, Fe-rich AFm and AFt mineral phases, such as monosulfate and ettringite, respectively [24].

Grey cement C has been fitted based on a linear combination of the Ca(OH)$_2$ spectrum, a Lorentzian pair with offset $d = 50$ kHz and $n = 2$ representative of water in C–S–H and an additional Lorentzian pair for the Fe-rich phases. The fit is shown in figure 4. The additional component of the best fit has an offset $d = 32$ kHz. Grey cement B is less amenable to fitting in this way. Using Gaussians in place of the second Lorentzians improves the fit significantly, but this is achieved at the expense of the component for the C–S–H water that the fitting algorithm reports as small but negative. Since there is little information available to us about the differentiation of Fe in the different mineralogical phases of these cement pastes, this analysis cannot be taken further.

4.4. DQF dependence on sample drying

Figure 7 shows the DQF signal intensity of white cement as a function of sample water content during controlled drying. The DQF signal decreases at an accelerating rate as water is removed. Each spectrum has been decomposed into two fractions, as discussed in the previous section. The relative intensity of these fractions, both normalized to the initial values, are also shown in the figure. It is evident that the component assigned to the C–S–H water decreases
monotonically, while that associated with the solid Ca(OH)$_2$ first increases before decreasing. We suggest that as evaporable water is removed, initially an adsorbed layer is left behind that has DQF characteristics closely akin to those of Ca(OH)$_2$. The adsorbed layer increases the ‘solid’ component in the early stages of drying. Once mobile water is removed, then at higher temperatures the surface layer is lost and eventually crystalline products break down, leading to a total loss of signal. A distinction is made between results obtained at drying temperatures less than 200 °C, where a vacuum oven was available and carbonation is not thought to have been a serious issue, and results from drying above 200 °C, where the reverse is true. This result and interpretation are entirely consistent with the results of a parallel study published elsewhere [11], which explored the single-quantum amplitude during drying. Decomposition of that signal into short and long (less than and greater than about 50 µs) $T_2$ components, as measured using a solid echo and FID, showed the long-component intensity decreasing faster than the total, while the short component increased as water was removed. Analysis led to an estimate of pore widths.

4.5. DQF line shape—analysis

The separation of the DQF maximum/minimum for the signal component assigned to gel pore water in white cement, $2\Delta f_{\text{exp}} = 108$ kHz, is significantly greater than that expected for water based on a hydrogen separation of 0.16 nm, $2\Delta f_{\text{theory}} = 44$ kHz between the peaks. We suggest that residual Fe$^{3+}$ impurities in the C–S–H provide additional broadening, as described in section 3. In order to estimate the cut-off radius for the two-dimensional (2D) diffusion of the water in the vicinity of Fe$^{3+}$ in the C–S–H planar pores, we compare the experimental result to the numerically calculated second moment of the symmetrized theory spectrum (figure 3). Based on this, we infer $r_c = 3$ nm and hence that the surface Fe$^{3+}$ density in white cement is approximately $3 \times 10^{16}$ Fe$^{3+}$/m$^2$. For comparison, this density has previously been estimated [3, 4] as $2.5 \times 10^{15}$ Fe$^{3+}$/m$^2$ from calibrated electron spin resistance measurement of similar, but not identical, materials.

Although these numbers are intriguing, they do not yet meet the goal of providing an estimate of the lateral extent of C–S–H gel pores. The calculated value of $r_c$ merely provides a lower bound. Had the Fe$^{3+}$ density been lower, ideally less than 1 Fe$^{3+}$/per pore on average, then this may have yielded a cut-off radius equal to the pore size, rather than the Fe$^{3+}$ density. Further ongoing work on synthesized C–S–H and on C$_3$S where the Fe$^{3+}$ concentration is controlled and much lower may help increase the $r_c$ bound, notwithstanding limits placed by likely microstructural differences.

In passing, we note that previous NMR field cycling and 2D $T_2-T_2$ relaxation experiments [4] yielded an estimate of the hopping time and residency time (1.3 ns and 13 μs, respectively) for water adsorbed on internal pore surfaces in cement gel. These times suggest that an adsorbed water molecule undergoes $p = 10^4$ steps before desorbing from the pore surface. If it is assumed that the hop length is comparable to the water hydrogen separation, 0.16 nm, and that the diffusion is unbounded, then the adsorbed water ranges approximately $\sqrt{10^4 \times 0.16} \approx 16$ nm per adsorption event. The value of $r_c$ is consistent with this in so much as the water is not predicted to range further than the distance suggested by relaxation rates. Equally, the time to range $r_c = 3$ nm is approximately 0.5 μs, significantly less than the NMR measurement timescale.

Finally, we consider the signal amplitudes. The fit in figure 4 has 12% of the signal assigned to gel pore water and 88% to Ca(OH)$_2$. X-ray diffraction suggests that Ca(OH)$_2$
hydrogen accounts for about 28.8% of the total hydrogen content of this white cement [12]. Hence, the calculated water fraction is surprisingly small. In part, this is because DQF NMR is sensitive to rigid, anisotropic water. Diffusing water will undergo a degree of isotropic tumbling in the planar pore. In part it is due to the creation time dependence of the signal intensity (which, in the simple spin-1/2 pair model, and in the absence of relaxation, varies with dipolar coupling strength as \( \sin(3C_{II}t_{c}/2) \)) and to other relaxation effects. Hence, little meaning can be derived from the relative signal amplitudes. These observations may also help to explain the fact that only one peak is observed in the creation time build-up curves (figure 5). With multiple environments corresponding to different dipolar coupling strengths, one expects multiple maxima in the build-up curves. Experimentally, the curves are seemingly dominated by Ca(OH)\(_2\). Other components have a very broad spread of build-up rates (distribution of \( C_{II} \)) and presumably therefore no clear maximum. Nevertheless, there remains the possibility that the Ca(OH)\(_2\) spectral component is masking water not in the vicinity of Fe\(^{3+}\) and hence not further broadened. Such a conclusion is already suggested by the interpretation of figure 7.

5. Conclusion

We have presented the first \(^1\)H DQF NMR study of water in cement pastes. We have shown that the build-up of the signal with curing time and the loss of signal with sample drying are both consistent with expectation and the results of single-quantum relaxation experiments. We have shown that the line decomposes into at least two parts: one for Ca(OH)\(_2\) and one for water diffusing in planar C–S–H gel pores. The latter is wider than normally expected for water and this is attributed to the presence of Fe\(^{3+}\) impurities. A cut-off radius of 3 nm has been deduced that places a lower bound of 6 nm on the lateral extent of these pores. This distance is consistent with measurements of the Fe\(^{3+}\) impurity surface density. A third line component is observed in grey cements initially containing a significant ferrite fraction.

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