1 The relative humidity dependence of the permeability of cement paste measured
2 using GARField NMR profiling.

3
4 S. Zamani, R. M. Kowalczyk, P. J. McDonald*

5
6 Department of Physics, University of Surrey, Guildford, Surrey, GU2 7XH, UK

7 * Corresponding author

8
9 Abstract

10
11 The relative humidity (RH) dependence of the water permeability of cement is
12 calculated from the water concentration profile of a paste exposed to an RH
13 gradient and the desorption isotherm. The profile is measured using GARField,
14 standing for *Gradient at Right Angles to Field*, NMR. The isotherm is derived from
15 other earlier NMR measurements. The Darcy equation gives the intrinsic
16 permeability as $4.6 \times 10^{-21} \text{ m}^2$. The apparent intrinsic permeability to water flow
17 shows a broad “U” shape dependence on RH, with a minimum of $7 \times 10^{-22} \text{ m}^2$ at
18 RH 55%. The “U” shape is attributed to the fact that the transport mechanism
19 involves a coupling of liquid and vapour modes. The data is further analysed in
20 terms of a model of coupled liquid and vapour diffusion and Darcy flow due to
21 Baroghel-Bouny *et al.* (*Cem. Con. Res.* 2011 **41** 828) from which the relative
22 liquid water and vapour permeabilities are calculated. They are strongly RH
23 dependent. The former increases with increasing RH; the latter decreases.

24
25 Keywords

26 C: Permeability; C: Diffusion; D: Cement Paste; Other: NMR

1. Introduction

A factor common to nearly all forms of degradation of concrete materials is water transport into, and out of, the solid matrix and in particular the binder phase, cement. In consequence, characterisation of the porosity of cement, and of properties related to water transport within it, are seen as valuable indicators of durability. Intrinsic permeability is one such indicator. Intrinsic permeability, K , is the macroscopic property that relates volume liquid flow through the matrix, Q , to the driving pressure P according to Darcy's law,

$$K = \frac{LQ\mu}{AP} \quad \text{Eq. 1}$$

where A is the cross sectional area of a test sample of length L and μ is the dynamic fluid viscosity. The intrinsic permeability relates to a fully saturated system.

The intrinsic permeability of cement paste is unusually low compared to many other porous media. This makes its measurement extremely difficult since, at moderate pressures, the flux of liquid through a representative volume is extremely slow. Literature reports a very wide range of experimental values from 10^{-17} m^2 measured using O_2 gas as the permeating fluid [1] through to values in the range 10^{-20} down to 10^{-22} m^2 using liquid water [2,3]. Clearly, these values are not fluid independent. The most likely hypothesis, advanced previously [4-6], is that these discrepancies may be explained if it is appreciated that in almost all, if not all, measurements the fluid does not fully saturate the system. In the case of O_2 gas measurements, the C-S-H gel phase that percolates the paste is not normally completely dehydrated while in the case of liquid water measurements, self-desiccation of larger pores invariably causes the capillary network to be partially desaturated. Hence, a combination of both liquid water and vapour/air fills the pore space.

In the case of partially saturated media with liquid and vapour flow, the relative permeability of the liquid and vapour should be considered. Moreover, it is then necessary to measure the permeability as a function of saturation. This is not possible with most conventional methodologies where a macroscopic sample is

57 exposed to a pressure gradient as in, for instance, a so-called “cup-test” without
58 making many measurements that each span different small ranges of RH and
59 hence saturation - a difficult and time consuming process. Imaging is required to
60 overcome this difficulty. NMR imaging (MRI) has previously been used to
61 measure water concentration, ingress and drying profiles in cement based
62 materials [7-10]. However, in general, MRI has only visualised the water in the
63 larger pores with long spin-spin lattice relaxation times, T_2 . A lack of full T_2
64 resolution coupled with spatial resolution has limited the analyses. Lesser
65 known NMR methods that do access less mobile water with much shorter T_2 in
66 more confined spaces as well as water in larger pores are known and have been
67 used. These include so called single-point imaging (SPI) methods [11,12].
68 However, SPI lacks discrimination between water in different environments, as
69 only a single relaxation decay time, albeit short, is interrogated unless the
70 experiment is repeated for different interrogation times [13,14]. Stray field
71 imaging (STRAFI) techniques have also been used [15,16]. In this case the
72 observed relaxation time bridges between T_2 and $T_{1\rho}$, the so-called spin lattice
73 relaxation time in the rotating frame. STRAFI is closely analogous to GARField
74 NMR as used in this work.

75 This paper reports measurements of the permeability of cement paste to water
76 transport as a function of the degree of saturation obtained using magnetic
77 resonance profiling. The profiles are recorded with a GARfield MR magnet that
78 affords an unusually high magnetic field gradient so as to allow sufficiently short
79 magnetic resonance echo times to see signals from short T_2 liquid fractions¹. As a
80 result, it is possible to quantify the capillary pore, C-S-H gel pore and C-S-H
81 interlayer water of the sample. Moreover, the method has sufficiently high
82 spatial resolution (sub millimetre) so as to use samples that are small enough to
83 equilibrate relatively quickly. The profile intensities are calibrated through
84 recent advances in the understanding of NMR relaxation experiments applied to
85 cement pastes and by cross reference to a saturated packed sand sample of

¹ With GARField, using short pulse gaps and a quadrature echo train as here, the observed relaxation time is a mix of T_2 and $T_{1\rho}$. However, in practice, we find that the measured times are very similar to those reported for bulk measurements of T_2 of pastes using bench top instruments in, e.g. reference [17]

known porosity. Finally, the pore type specific desorption isotherm of cement paste is taken from the recent work of Muller *et al.* [18] in order to link water saturation to RH in the calculation of permeability.

The data is analysed in three ways. First, the simple macroscopic permeability as would result from a conventional test is calculated. Second, the effective water permeability as a function of RH or saturation is calculated, making no attempt to separate liquid and vapour. Third, the data is fit to a model of coupled liquid and vapour transport in cement materials due to Baroghel-Bouny *et al.* [19].

2. Theory

The NMR experiment yields the (calibrated, and pore-type resolved) dynamic equilibrium profile of water saturation across a cement paste sample, $S(z)$ where z is the space coordinate exposed to a spatial gradient of the RH. Darcy's law, Eq, [1], can be written in terms of the reciprocal of the profile gradient as

$$K(\varphi) = J\mu \frac{\partial z}{\partial S} \frac{\partial S}{\partial \varphi} \frac{\partial \varphi}{\partial P} \quad \text{Eq. 2}$$

where $\varphi(z)$ is the local (external) RH that would yield the local (internal, equilibrium) saturation, S ; P is the corresponding vapour pressure; and $J = Q/A$ is the water flux. The term $\partial z/\partial S$ may be calculated from the gradient of the measured dynamic equilibrium profile. The term $\partial S/\partial \varphi$ is the gradient of the desorption isotherm. Finally, the term $\partial \varphi/\partial P$ derives from the partial vapour pressure of saturated air, taken to be a constant equal to 4.33×10^{-4} m²/N. The analysis presupposes a single fluid flow, and liquid water is assumed by default. The dynamic viscosity is therefore set equal to 8.9×10^{-4} N.s/m².

Figure 1. A schematic representation of the water transport model due to Baroghel-Bouny *et al* [19]. The liquid comprises water and dissolved ions, the gas comprises dry air and water vapour. Both are subject to a Darcy flow. The air and vapour inter-diffuse, as do the ions and liquid water, although the ions are neglected in this work.

108

109 The alternate analysis applies the model of coupled liquid water and gas
 110 transport in cement developed by Baroghel-Bouny *et al.* [19]. Figure 1 shows a
 111 schematic of the processes involved. There is inter-diffusion of liquid water and
 112 dissolved ions within liquid filled paste porosity. The remainder of the pore
 113 space is occupied by gas comprising water vapour and dry air. Within the gas,
 114 there is inter-diffusion of water vapour and dry air. The water vapour and liquid
 115 are locally maintained in dynamic equilibrium according to the desorption
 116 isotherm. Finally there is a separate mass transport of liquid and gas due to
 117 Darcy flow. Under conditions of dynamic equilibrium, the liquid saturation
 118 profile, $S(z)$ is constant with time so that $\partial S/\partial t = 0$. As the timescales are long, it
 119 is inferred that the gas pressure is uniform, and everywhere equal to
 120 atmospheric pressure. Finally, the role of ions in driving a diffusive liquid flux is
 121 ignored. According to this model, and with these assumptions, the dynamic
 122 equilibrium saturation profile is given in differential form by:

$$J = \frac{Q}{A} = \frac{\partial S}{\partial z} \left\{ \frac{-Kk_L c_w}{\mu} \frac{\partial P_L}{\partial S} + \frac{D_v f}{R\theta} \frac{\partial P_v}{\partial S} \right\} \quad \text{Eq. 3}$$

where P_L and P_V are the liquid and vapour pressure respectively, k_L is the relative liquid permeability, R and θ are the gas constant and temperature respectively, D_V is the vapour diffusivity within the gas (here taken as $2.47 \times 10^{-5} \text{ m}^2/\text{s}$), c_w is the molar density of water and f is a diffusion hindrance factor due to the matrix tortuosity and partial liquid saturation.

Apart from constants, application of Eq. 3 requires expressions for four quantities in terms of the saturation: the liquid and vapour pressures, the relative permeability and the hindrance factor.

Baroghel-Bouny *et al.* follow Millington and Shearer [20] in writing

$$f = f(\Phi, S) = \Phi^x (1 - S)^y \quad \text{Eq. 4}$$

where Φ is the cement porosity and x and y are fitting parameters. For the liquid permeability, they follow van Genuchten [21] in writing

$$k_L(S) = S^{0.5} \left(1 - (1 - S^{1/m})^m \right)^2 \quad \text{Eq. 5}$$

and also, for the gas

$$k_G(S) = (1 - S)^p \left(1 - S^{1/m} \right)^{2m} \quad \text{Eq. 6}$$

where p and m are fitting parameters. As already stated, at dynamic equilibrium the gas pressure is taken everywhere as atmospheric pressure, $P_G = P_{ATM}$, in which case

$$P_L = P_{ATM} - P_C \quad \text{Eq. 7}$$

where P_C is the capillary pressure given by

$$P_C = a \left(S^{-1/m} - 1 \right)^{1-m} = \frac{-\rho_L}{M_L} R \theta \ln(\phi) \quad \text{Eq. 8}$$

after van Genuchten and using the Kelvin Law respectively. In equation 8, ρ_L and M_L are the liquid water density and molar mass of water respectively and a is a

141 further fitting parameter. The parameters a and m can be calculated by fitting
 142 the desorption isotherm through a reworking of equation 8 such that

$$\varphi = \exp\left(\left(\frac{-M_L a}{\rho_L R \theta}\right)\left(S^{-1/m} - 1\right)^{1-m}\right) \quad \text{Eq. 9}$$

143 This leaves the parameters x, y and K to be found by fitting the dynamic
 144 equilibrium profile given the measured water flux J . The parameter p is required
 145 only for the relative gas permeability and is not used in the primary analysis.

146

147 3. Materials and Methods

148 3.1 Cement pastes

149 Short lengths of thin walled, 10 mm outer diameter, glass NMR tubes were cut so
 150 as to be open at both ends. The cut ends were ground flat and “square on”. The
 151 tubes were cleaned using dilute hydrochloric acid. Having sample tubes open at
 152 both ends, allowed samples to be exposed subsequently to an RH gradient. The
 153 cleaning procedure greatly facilitated the adhesion of the paste to the tube wall
 154 so preventing wicking of water up the outside of the paste cylinders. The sealing
 155 procedure was found to either “work” or “not work” in the ratio about 1:2.
 156 Samples that adhered successfully to the glass maintained a uniform optical
 157 appearance around the circumference and along the length of the tubes. In
 158 others that leaked, water wicked up channels where adhesion was lost such that
 159 the optical appearance was no longer uniform. Streaks of wetted glass could be
 160 seen. Other methods of sealing samples were tried but were not successful.
 161 Common sealants, tapes and epoxies yielded significant background ^1H NMR
 162 signals or were not stable in the vicinity of the high pH pore solution. Pressurised
 163 fluorinated oil sleeves tended to leak or to take up too much space within the
 164 NMR system for small samples.

165 Low C_3A white cement, the same as we have previously studied [17], was mixed
 166 in the water to cement ratio 0.4 by mass and deposited in the tubes. Paste was
 167 retained in the tube at the lower end by standing the tube on the bottom of a flat
 168 dish. A small amount of additional paste was placed around the base of the tube

to prevent it from easily falling over. A small amount of saturated $\text{Ca}(\text{OH})_2$ solution was added to the dish and above the sample in the tube so that the cement was effectively cured underwater from both ends. The whole assembly was sealed in a plastic container.

After 28 days hydration, the tubes containing the samples were removed from the dishes. The original top containing saturated $\text{Ca}(\text{OH})_2$ solution was plugged by a tightly fitting rubber cap and the tube inverted so that this end of the sample was now exposed to the vapour of the solution with the solution retained by the cap. The RH was measured as 98%. The inverted tube was mounted in a plastic support and the whole assembly placed above self indicating silica gel in a glass jar and the jar sealed. In this way the original lower end of the sample, now open and at the top, was exposed to a low RH environment measured as 15%.

The tubes were stored in this condition for more than one year, save that periodically the jars were opened and the samples removed to allow NMR profiling. On these occasions, the tube plus cap and saturated $\text{Ca}(\text{OH})_2$ solution was weighed, the solution removed without wetting the sample and the sample re-weighed, allowing for the (known) mass of the tube. A glass rod was added to the tube to fill the free volume, the tube ends covered with plastic film to limit evaporation, and the NMR profiles recorded. After profiling, the cap was replaced on the inverted tube and the $\text{Ca}(\text{OH})_2$ solution restored using a syringe through the cap. The assembly with solution was weighed again and returned to the jar. By these means the samples never contacted liquid after the initial 28 days, the sample mass was periodically recorded and so was the water flux through the sample, via the change in mass of the inverted solution between measurements. Dynamic equilibrium was judged to have been reached when, within experimental error, the water flux through the sample, the sample mass and the integrated signal intensity all became constant.

3.2 NMR

The profile was measured using GARField NMR [22]. In this method, the bandwidth of the excitation pulse of length t_p , ($\delta\nu = 1/\pi t_p$), is much less than the

length of the sample, L , expressed in frequency units ($\Delta\nu = \gamma g L / 2\pi$) due to the strong magnetic field gradient. Here γ is the magnetogyric ratio of the hydrogen proton and, for this study, $g = 12\text{T/m}$ and $t_p \approx 3\mu\text{s}$. A NMR profile is obtained by stepwise lifting the sample through the field gradient and measuring progressively the signal from a series of resonant slices. So long as the step size in frequency units exceeds the pulse bandwidth, then the resolution is determined by the step size.

The measurement at each slice consists of a quadrature NMR echo train. The pulse gap, τ , was set to $21\mu\text{s}$ and echoes collected so that the NMR T_2 decay was interrogated at times $2n\tau$ with $n = 1, 2, 3, \dots$. The quadrature, rather than Carr-Purcell-Meiboom-Gill, train was used to maintain a constant bandwidth of all pulses. Given the typical T_2 relaxation time of crystalline solids ($\approx 10\mu\text{s}$), C-S-H interlayer water ($\approx 100\mu\text{s}$), gel pore water ($\approx 400\mu\text{s}$) and capillary water ($> 1\text{ms}$), this means that the capillary, gel pore and C-S-H interlayer water are readily detected, while only a weaker signal is obtained from the crystalline solid. Typically 1024 averages of 64 echoes each were recorded for every spatial location with a repetition time of 0.66 s. For the spatially equilibrated profile, the sample was stepped 0.5 mm between measurements so that a whole profile took about 10 hours to record. In other cases lower, variable resolution was used to minimise sample time out of the RH gradient. The cement paste signal amplitudes were converted to water filled porosity by comparison with a measurement of saturated sand of known porosity (32%), which, along with a rubber sample, also acted as a standard to mitigate against long term drift in the spectrometer sensitivity.

In order to check on the gradual equilibration of the profile, a simple profile was constructed as an echo sum. For more quantitative analysis, the echo trains at each location were fitted to three-component exponential decays, with fixed time constants of 120, 420 and $1400\mu\text{s}$. The fits were made using the MATLAB® (The Mathworks Inc, USA) function *lsqcurvefit*. Components with these time constants correspond to the C-S-H interlayer, gel pore and capillary pore water respectively as previously reported [17]. A small systematic baseline offset was subtracted from the data. Only even numbered echoes were analysed. This is for

two reasons. First, it is known from theory that the first echo amplitude is $2/3$ the “expected” intensity in a GARField experiment, and that the factor $2/3$ is very sensitive to accurate pulse length calibration [23]. Second, with the pulse spacing used, the first echo includes a poorly quantified contribution from crystalline $\text{Ca}(\text{OH})_2$ water that is not present in later echoes. A small residual echo modulation was removed by reference to the rubber sample decay that was assumed to be mono-exponential. A four-component fit including the first echo (multiplied by $3/2$) was notably less stable. A full inverse Laplace transform of the data was not attempted, as the signal to noise ratio of the echo trains was insufficiently good.

3.3 Profile analysis

To use the model embodied by equation 2, smooth functional representations of the profile data and isotherm are required. Cubic spline fits were generated using the MATLAB® function *csaps*. To use the coupled liquid-vapour transport model, the isotherm was also fit to equation 9 over the RH range spanned by the profiling experiment using the MATLAB® function *lsqcurvefit* so as to find the parameters a and m . Finally a simulated thermal annealing algorithm was written in MATLAB and used to search for sets of parameters x, y and K yielding the best (least squares deviation) fit of the coupled liquid water – vapour transport model to the experimental profile shape. Given the number of parameters involved, multiple “best fits” were obtained. The overall best fit was chosen and the sensitivity of the fit to changes in the parameters investigated. Correlations between multiple pairs of “best fit” parameters were also investigated.

4. The desorption isotherm and paste porosity

The desorption isotherm for an identical paste to that used in this work has been measured previously using NMR [18]. As shown in Figure 1 of reference [18], it is pore type resolved and includes the water bound in crystalline $\text{Ca}(\text{OH})_2$. In that earlier work, it was pointed out that the interlayer and solid water signals apparently increase as the gel water is removed. This is due to the shorter

relaxation time of residual surface water layers in dry pores, compared to the relaxation time of the same surface layer water in contact with bulk water in full pores. The isotherm shown in Figure 2 of this work is constructed from the earlier data, save that here the signal due to water bound in crystalline solid is excluded, while the signal associated with residual surface layers has been added back into the “proper” pore reservoirs. The isotherm is scaled in terms of degree of saturation as well as filled porosity. The total porosity is calculated to be about 0.51 on the following basis. The mix volume of the paste is $(0.4 + 1/3.15) = 0.717$ cm^3 given that the anhydrous cement density is 3.15 g/cm^3 . Since macroscopic shrinkage of small underwater cured samples is negligible, (indeed there may be slight swelling), this is taken as the hydrated paste volume. On the other hand, due to microscopic chemical shrinkage, the final water to cement ratio of small samples of this cement cured underwater is closer to 0.46, of which circa 20% is combined into crystalline solids [18]. Hence the C-S-H interlayer and pore water at 100% RH occupies $(1 - 0.2) \times 0.46 = 0.368 \text{ cm}^3$, equivalent to a porosity of 51%.

Figure 2 also includes the smoothed cubic spline fit to the isotherm data and the fit according to equation 9. The best fit parameters of the latter are $a = 3.4 \times 10^7 \text{ MPa}$ and $m = 0.29$. It is evident that equation 9 fails to capture the double step in the isotherm resultant from the multi-modal pore size distribution of the paste.

Figure 2. The desorption isotherm measured by NMR taken from reference [18], modified to include the interlayer, gel and capillary pore water only and to add back in the residual surface water layer that appears NMR solid-like as mobile pore water is removed. The data is shown both in terms of filled porosity of the paste and paste saturation. The solid line is a smooth cubic spline fit to the data over the region of interest defined by the profile; the dashed line is a fit using equation 9. The fit parameters are given in the text.

284 5. Profile results and analysis

285 Figure 3 shows the profile of the sample as originally hydrated (i.e. aged 28 days)
 286 and again aged 609 days, after exposure to a RH gradient from 98% at the right
 287 hand end of the sample to 15% at the left. The sample is 22.5 mm long. The data
 288 is reconstructed from the sum of the echoes recorded at each position. This
 289 presentation dramatically over-weights the contribution of long T_2 components
 290 such as capillary water. However, it serves to illustrate well the spatial
 291 uniformity of the sample immediately after hydration, save at the end in contact
 292 with water where there is evidence of surface water remaining.

Figure 3. The water concentration profile in the as prepared paste (28 days, squares) and after equilibration in the relative humidity gradient (609 days, circles). The RH gradient is from 98 down to 15% (right to left). The profile is constructed from the total integrated signal (echo-sum) so that long T_2 components are over weighted.

Figure 4. The equilibration of sample mass with time shown as grams water per gram anhydrous cement (squares, right hand axis) and water flux through the sample (circles, left hand axis). Inset: the equilibration of the integrated NMR signal intensity. The solid lines are guides to the eye.

294

295 Figure 4 shows the equilibration of the same sample in terms of sample mass
 296 loss and water flux through it. The flux data points are placed at the mid point of
 297 two NMR / mass measurements. The inset in Figure 4 is constructed from the
 298 integrated intensity of the NMR echo sum profile. Taken together, these plots
 299 reveal that the system is approaching dynamic equilibrium on a timescale of 200
 300 days. The full 600 days ensures that dynamic equilibrium is reached. The flux at
 301 equilibrium is estimated to be $J = 4.4 \times 10^{-7} \text{ kg.m}^{-2}.\text{s}^{-1}$.

Figure 5. Exemplar log-linear T_2 echo intensity decays, these recorded at 5 (squares), 12.5 (circles) and 20 mm (triangles) across the sample after equilibration in the RH gradient together with multi-component exponential fits to the data as described in the text. The inset shows the same data in linear-linear fashion.

302

303 Figures 5 shows the echo train intensity decays recorded from positions 5, 12.5
 304 and 20 mm on the scale of Figure 3. The overall signal is significantly smaller at 5
 305 mm compared to 20 mm, with a substantially reduced contribution from the gel
 306 pore water. There is negligible capillary water measured at any location in the
 307 equilibrium profile. The figure also shows the three component exponential fits
 308 to the data.

309 Figure 6 shows the dynamic equilibrium profile reconstructed from the fit
 310 component amplitudes, together with a smooth interpolation through the data
 311 using the MATLAB® function *csaps*. At the wet end of the sample, where it is
 312 exposed to 98% RH, the fit to the isotherm suggests that the saturation should be
 313 93% saturated. Given the estimated porosity of 51%, 93% saturation
 314 corresponds to a filled porosity of 47.5%, in reasonable agreement with the
 315 measured value of, coincidentally, 51% from Figure 6. At the other end of the
 316 sample, the saturation is about 42% corresponding a filled porosity of 22% and
 317 to an RH of 19%. This is in accord with expectation, since the vapour above the
 318 silica gel is nominally at 15% RH.

Figure 6. Closed circles: The dynamic equilibrium water saturation profile calculated from T_2 fits to the echo decays. The solid line is a smooth cubic spline fit to the profile. The open circles, squares and triangles show separate contributions from the interlayer, gel pore and capillary pore water respectively.

319

320 Figure 6 also shows the separate components for C-S-H interlayer, gel pore and
 321 capillary pore water across the sample resultant from the data fitting. At the wet
 322 end, the gel pore water component comprises about 75% of the total evaporable
 323 water. Our previous work suggests it should be closer to 60% at 93% saturation.
 324 Likewise, the interlayer component fraction is 25% rather than 40%. The
 325 discrepancy is likely due to the inadequacy of the multi exponential fitting used
 326 here, which, while getting the overall amplitude about right, misrepresents the
 327 component splits. Notwithstanding, there is good evidence that the gel pore
 328 water decreases to zero in going across the sample to the dry end, while the
 329 interlayer component, if anything, increases due to the residual surface layer as
 330 previously described [18]. The capillary component is effectively zero
 331 everywhere, again as expected for a sample equilibrated to RH values of 98%
 332 and less.

333

334 6. Analysis and discussion

335 6.1 Effective permeability

The permeability calculated using equation 1 is $4.5 \times 10^{-21} \text{ m}^2$. This result takes account only of the pressure difference across the whole sample and assumes single fluid, liquid water, flow. The analysis replicates standard measurements and the result is very much in accord with previous estimates for water permeability of cement paste published elsewhere. It gives confidence that the sample preparation and procedures are working as expected.

Figure 7. The RH dependence of the effective water permeability calculated using equation 2. The broad minimum centred on 50% RH is stable to small variations in the data analysis, whereas the detail below about 25% RH (the decrease on the left of the plot) depends critically on the echo train fitting. The dashed lines show the calculated permeability derived from alternate fits of the echo train data in which the T_2 values are varied by 20% as described in the text.

An effective permeability as a function of relative humidity has been calculated using equation 2, with data derived from the cubic spline fits to the isotherm and to the profile. This effective permeability also assumes single fluid (liquid water) flow. The result is shown in Figure 7. The permeability has a broad minimum at intermediate relative humidities, rising steeply at both low and high values. This result is consistent with expectation. As the humidity is reduced from 100%, so the pore network becomes partially filled with both liquid and vapour hindering

mass transport. At low humidity, the gel porosity is largely free of liquid, enabling free vapour transport. However, the calculated porosity continues to assume liquid as the permeating fluid, so the values obtained are little more than a characteristic of the system. The detail at low RH, and especially the final decrease in permeability, depend strongly on the precise fitting of the echo train data in this region. We therefore place much less reliance on the results below about 25% RH. These statements are exemplified by the dashed lines in Figure 7. Analyses of the echo trains were made in which the T_2 values assigned to the interlayer and gel pore water were systematically increased and decreased by 20% in all possible combinations. One dashed line is for the interlayer and gel pore water T_2 set to 96 and 336 μs respectively and the other 144 and 336 μs respectively. These two cases had the most significant effect on the effective permeability, with the latter yielding the second minima at low RH where the filled porosity was clearly underestimated. Notwithstanding, that the permeability is little affected across the broad minimum reflects the insensitivity of the overall signal amplitude to the detail of the fit across most of the profile. Understood another way, when in Figure 6 the interlayer signal is low compared to the average of the immediately surrounding data points, so the gel signal is high, and *vice versa*. The two are anti-correlated.

6.2 Coupled liquid – vapour transport model

In the case of the coupled liquid-vapour transport model, equations 3 to 9, multiple runs of the simulated annealing algorithm yield multiple “best” fits to the data. The overall best fit is shown in Figure 8. It is obtained using the isotherm parameters $\Phi = 51\%$, $a = 3.4 \times 10^7 \text{ MPa}$ and $m = 0.29$ with a permeability of $K = 2.3 \times 10^{-21} \text{ m}^2$ and hindrance function parameters of $x = 5.1$ and $y = 0.84$. The standard deviation of K from the multiple analyses is $\Delta K = 0.5 \times 10^{-21} \text{ m}^2$.

Figure 8. The profile data from figure 6, this time shown with the overall best fit (solid line) according to equations 3 to 9, the coupled liquid water – vapour transport model, obtained by simulated annealing. Fit parameters are given in the text. The remaining curves illustrate the sensitivity of the best fit to these parameters. The dashed line that is lower than the best fit on the right hand side of the plot is obtained by increasing m by 20%. The other dashed line is obtained by decreasing K by 20%. The dotted line, almost obscured by the best fit, is the result of fixing K at the “best” value, increasing the parameter x by 10% and re-fitting for y only.

378

379 Figure 8 also shows the sensitivity of the overall best fit to changes in different
 380 parameters. In two of the alternate analyses, a single parameter, m or K , is varied
 381 by 20% from the overall best value. The fits, shown as dashed lines in the figure,
 382 are noticeably less good. In particular they extend over the wrong spatial range
 383 (the simulated annealing treats position as the dependent variable).

384 Figure 9 shows the saturation dependence of the relative permeability to liquid
 385 water and vapour transport, equations 5 and 6, calculated using the overall best
 386 fit parameters. The liquid relative permeability is high at high saturation and
 387 decreases markedly as the liquid filled porosity is reduced in volume and
 388 connectivity at lower humidity. Not surprisingly, the vapour relative
 389 permeability, behaves oppositely. This parameter depends on the variable p that
 390 arises in equation 6 and that is not accessible from these experiments.

391 Accordingly, the relative vapour permeability is calculated using the
 392 value $p = 5.5$ following reference [19].

Figure 9. The liquid water and vapour relative permeability calculated using Equations 5 and 6 respectively with best fit experimental parameters as given in the text and $p = 5.5$.

Figure 10. The correlation between the fit parameters x and y for different “best fits” to the data found by the simulated annealing algorithm. The overall best fit has $x = 5.1$ and $y = 0.84$ in Equation 4.

Figure 11. The correlation of the hindrance parameter, f , with permeability for high ($S = 0.9$, squares), intermediate ($S = 0.5$, circles) and low ($S = 0.25$, triangles) saturation for different “best fits” to the data found by the simulated annealing algorithm. The overall best fit has $K = 2.3 \times 10^{-21} \text{ m}^2$.

394

395 One thing is striking from the multiple local minima found by the simulated
 396 annealing algorithm. It is that the three fit parameters, x , y and K are strongly
 397 correlated. Figure 10 shows that as x increases, so y decreases almost linearly.
 398 Figure 11 shows that the hindrance parameter, a function of x , y and S correlates
 399 strongly with permeability K , although differently for different values of the
 400 saturation. The hindrance factor is associated with the vapour diffusivity. At
 401 lower humidity, or equivalently, saturation, where vapour diffusivity dominates,
 402 the “best fit” permeability resultant from different analyses increases strongly as
 403 the hindrance factor decreases. The reverse is true at high saturation where
 404 liquid transport dominates. The hindrance factor shows little permeability
 405 dependence at intermediate saturation. This result might have been expected
 406 from study of equation 4. For the specific case of porosity 0.5 as is well
 407 approximated in this work, and an intermediate saturation of 0.5 as occurs
 408 across the centre of the profile, and given that $y + x \approx \text{constant}$ from figure 10, so

f is a constant. The correlation between x and y is further explored in the final analysis presented in Figure 8. In this case (the dotted line), the permeability has been fixed at the overall best value, the overall best x has been incremented by 10%, and a new fit value of y has been found. The new fit line is comparably good to the overall best line.

The form of the apparent intrinsic permeability through equation 2 and of the respective liquid and vapour relative permeabilities through the coupled liquid-vapour transport model are consistent with recent Lattice Boltzmann simulations of water permeation flow through cement paste by Zalazale *et al.* [24]. This study uses effective media theory to show the importance of transport through the C-S-H gel as well as through the capillary porosity. It shows that, as water is removed from the largest pore spaces, so the liquid permeability decreases. It also shows that at lower saturations, the vapour permeability increases dramatically. The general U-shape form of the apparent liquid permeability is also reminiscent of studies water capacity and humidity diffusivity in cement materials discussed by, for instance, Xi *et al.* [25,26]. The close connection between permeability and humidity diffusivity is discussed in that work and references therein.

7. Conclusion

It has been shown that GARField NMR profiling is a suitable means to obtain profiles in small cement paste samples with high spatial resolution that separately quantitate water in C-S-H interlayer, gel pore and capillary pore environments. As a result, this methodology goes further than earlier MRI studies that have largely accessed water in only the larger pore environments. We have shown that the data can be used to evaluate models of cement permeability with a good degree of accuracy, beyond that which can be achieved by gravimetry alone. In principle, the method can be extended to other, more industrially relevant, cement pastes and to mortars and concretes. The potential difficulties are (i) a lack of published NMR isotherms as used in the analysis and (ii) the large aggregate size relative to the small sample size used with current GARField facilities.

For the white cement paste, the NMR isotherm captures a level of detail not present in equation 9. Thus the work opens the way to testing advances in modelling which develop the concept of transport in a multi-modal pore size network. In particular, it has become possible to visualise water in the different pore environments across the profile and thus potentially achieve a level of analysis and testing not previously possible.

8. Acknowledgements

SZ thanks the Kwan Trust for financial support. This work was funded by the UK Engineering and Physical Sciences Research Council (Grant No. EP/H033343/1).

References

- [1] H.S. Wong, M. Zobel, N.R. Buenfeld, J.R. Zimmerman, Influence of the interfacial transition zone and microcracking on the diffusivity, permeability and sorptivity of cement-based materials after drying, *Magazine of Concrete Research*. 61 (2009) 571–589.
- [2] G. Ye, Percolation of capillary pores in hardening cement pastes, *Cem. Conc. Res.* 35 (2005) 167–176.
- [3] W. Vichit-Vadakan, G.W. Scherer, Measuring permeability and stress relaxation of young cement paste by beam bending, *Cem. Conc. Res.* 33 (2003) 1925–1932.
- [4] R.K. Dhir, P.C. Hewlett, Y.N. Chan, Near surface characteristics of concrete: intrinsic permeability, *Magazine of Concrete Research*. 41 (1989) 87–97.
- [5] A. Abbas, M. Carcasses, J.P. Ollivier, Gas permeability of concrete in relation to its degree of saturation, *Mater. Struct.* 32 (1999) 3–8.
- [6] H.S. Wong, N.R. Buenfeld, J. Hill, A.W. Harris, Mass transport properties of mature wasteform grouts, *Advances in Cement Research*. 19 (2007) 35–46.

468 [7] R.J. Gummerson, C. Hall, W.D. Hoff, R. Hawkes, G.N. Holland, W.S. Moore,
 469 Unsaturated water flow within porous materials observed by NMR imaging,
 470 Nature. 281 (1979) 56–57.

471 [8] C. Hall, Water sorptivity of mortars and concretes, Mag Concr Res. 41
 472 (1989) 51–61.

473 [9] A.J. Bohris, U. Goerke, P.J. McDonald, M. Mulheron, B. Newling, B. Le Page,
 474 A broad line NMR and MRI study of water and water transport in portland
 475 cement pastes, Magn. Reson. Imag. 16 (1998) 455–461.

476 [10] P.F. Faure, S. Caré, J. Magat, T. Chaussadent, Drying effect on cement paste
 477 porosity at early age observed by NMR methods, Construction and Building
 478 Materials. 29 (2012) 496–503.

479 [11] S.D. Beyea, B.J. Balcom, T.W. Bremner, P.J. Prado, D.P. Green, R.L.
 480 Armstrong, et al., Magnetic resonance imaging and moisture content profiles of
 481 drying concrete, Cem. Conc. Res. 28 (1998) 453–463.

482 [12] A.M. Olaru, B. Blümich, A. Adams, Water transport in cement-in-polymer
 483 dispersions at variable temperature studied by magnetic resonance imaging,
 484 Cem. Conc. Res. 44 (2013) 55–68.

485 [13] S.D. Beyea, B.J. Balcom, P.J. Prado, A.R. Cross, C.B. Kennedy, R.L.
 486 Armstrong, et al., Relaxation time mapping of short T_2^* nuclei with single-point
 487 imaging (SPI) methods, J. Magn. Reson. 135 (1998) 156–164.

488 [14] S.D. Beyea, B.J. Balcom, T.W. Bremner, R.L. Armstrong, P.E. Grattan-
 489 Bellew, Detection of drying-induced microcracking in cementitious materials
 490 with space-resolved ^1H nuclear magnetic resonance relaxometry, J. Am. Ceram.
 491 Soc. 86 (2003) 800–805.

492 [15] P.J. McDonald, B. Newling, Stray field magnetic resonance imaging,
 493 Reports on Progress in Physics. 61 (1998) 1441–1493.

494 [16] M. Van Landeghem, J.-B. d'Espinose de Lacaillerie, B. Blümich, J.P. Korb, B.
 495 Bresson, The roles of hydration and evaporation during the drying of a cement
 496 paste by localized NMR, Cem. Conc. Res. 48 (2013) 86–96.

497 [17] A.C.A. Muller, K.L. Scrivener, A.M. Gajewicz, P.J. McDonald, Densification of
498 C–S–H Measured by ^1H NMR Relaxometry, *J. Phys. Chem. C*. 117 (2013) 403–412.

499 [18] A. Muller, K.L. Scrivener, A.M. Gajewicz, P.J. McDonald, Use of bench-top
500 NMR to measure the density, composition and desorption isotherm of CSH in
501 cement paste, *Microporous and Mesoporous Materials*. 178 (2013) 99–103.

502 [19] V. Baroghel-Bouny, M. Thiéry, X. Wang, Modelling of isothermal coupled
503 moisture–ion transport in cementitious materials, *Cem. Conc. Res.* 41 (2011)
504 828–841.

505 [20] R.J. Millington, R.C. Shearer, Diffusion in Aggregated Porous Media, *Soil*
506 *Science*. 111 (1971) 372–378.

507 [21] M.T. Van Genuchten, A closed-form equation for predicting the hydraulic
508 conductivity of unsaturated soils, *Soil Science Society of America Journal*. 44
509 (1980) 892–898.

510 [22] P.S. Aptaker, P.J. McDonald, J. Mitchell, Surface GARField: a novel one-
511 sided NMR magnet and RF probe, *Magn. Reson. Imag.* 25 (2007) 548–548.

512 [23] T.B. Benson, P.J. McDonald, Profile Amplitude Modulation in Stray-Field
513 Magnetic-Resonance Imaging, *J. Magn. Reson. A*. 112 (1995) 17–23.

514 [24] M. Zalzale, P.J. McDonald, K.L. Scrivener, A 3D lattice Boltzmann effective
515 media study: understanding the role of C-S-H and water saturation on the
516 permeability of cement paste, *Modelling Simul. Mater. Sci. Eng.* 21 (2013)
517 085016.

518 [25] Y. Xi, Z.P. Bažant, H.M. Jennings, Moisture diffusion in cementitious
519 materials Adsorption isotherms, *Advanced Cement Based Materials*. 1 (1994)
520 248–257.

521 [26] Y. Xi, Z.P. Bažant, L. Molina, H.M. Jennings, Moisture diffusion in
522 cementitious materials Moisture capacity and diffusivity, *Advanced Cement*
523 *Based Materials*. 1 (1994) 258–266.

524

525

526

527

528 Figure captions

529 Figure 1: A schematic representation of the water transport model due to
530 Baroghel-Bouny *et al* [19]. The liquid comprises water and dissolved ions, the
531 gas comprises dry air and water vapour. Both are subject to a Darcy flow. The air
532 and vapour inter-diffuse, as do the ions and liquid water, although the ions are
533 neglected in this work.

534 Figure 2: The desorption isotherm measured by NMR taken from reference[18],
535 modified to include the interlayer, gel and capillary pore water only and to add
536 back in the residual surface water layer that appears NMR solid-like as mobile
537 pore water is removed. The data is shown both in terms of filled porosity of the
538 paste and paste saturation. The solid line is a smooth cubic spline fit to the data
539 over the region of interest defined by the profile; the dashed line is a fit using
540 equation 9. The fit parameters are given in the text.

541 Figure 3. The water concentration profile in the as prepared paste (28 days,
542 squares) and after equilibration in the relative humidity gradient (609 days,
543 circles). The RH gradient is from 98 down to 15% (right to left). The profile is
544 constructed from the total integrated signal (echo-sum) so that long T_2
545 components are over weighted.

546 Figure 4: The equilibration of sample mass with time shown as grams water per
547 gram anhydrous cement (squares, right hand axis) and water flux through the
548 sample (circles, left hand axis). Inset: the equilibration of the integrated NMR
549 signal intensity. The solid lines are guides to the eye.

550 Figure 5: Exemplar log-linear T_2 echo intensity decays, these recorded at 5
551 (squares), 12.5 (circles) and 20 mm (triangles) across the sample after
552 equilibration in the RH gradient together with multi-component exponential fits
553 to the data as described in the text. The inset shows the same data in linear-
554 linear fashion.

555 Figure 6: Closed circles: The dynamic equilibrium water saturation profile
556 calculated from T_2 fits to the echo decays. The solid line is a smooth cubic spline

fit to the profile. The open circles, squares and triangles show separate contributions from the interlayer, gel pore and capillary pore water respectively.

Figure 7: The RH dependence of the effective water permeability calculated using equation 2. The broad minimum centred on 50% RH is stable to small variations in the data analysis, whereas the detail below about 25% RH (the decrease on the left of the plot) depends critically on the echo train fitting. The dashed lines show the calculated permeability derived from alternate fits of the echo train data in which the T_2 values are varied by 20% as described in the text.

Figure 8: The profile data from figure 6, this time shown with the overall best fit (solid line) according to equations 3 to 9, the coupled liquid water – vapour transport model, obtained by simulated annealing. Fit parameters are given in the text. The remaining curves illustrate the sensitivity of the best fit to these parameters. The dashed line that is lower than the best fit on the right hand side of the plot is obtained by increasing m by 20%. The other dashed line is obtained by decreasing K by 20%. The dotted line, almost obscured by the best fit, is the result of fixing K at the “best” value, increasing the parameter x by 10% and re-fitting for y only.

Figure 9: The liquid water and vapour relative permeability calculated using Equations 5 and 6 respectively with best fit experimental parameters as given in the text and $p = 5.5$.

Figure 10. The correlation between the fit parameters x and y for different “best fits” to the data found by the simulated annealing algorithm. The overall best fit has $x = 5.1$ and $y = 0.84$ in Equation 4.

Figure 11. The correlation of the hindrance parameter, f , with permeability for high ($S = 0.9$, squares), intermediate ($S = 0.5$, circles) and low ($S = 0.25$, triangles) saturation for different “best fits” to the data found by the simulated annealing algorithm. The overall best fit has $K = 2.3 \times 10^{-21} \text{ m}^2$.