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Title

Is colour change a good measure of a water penetration front?

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Abstract

GARField nuclear magnetic resonance (NMR) profiling is used to demonstrate that the sharp colour change boundary commonly used to locate the water front in cement and concrete sorption tests is a poor indicator of the true depth of water penetration. Across a range of mortars and concretes, NMR invariably shows a smooth and often near zero gradient in the degree of saturation at this boundary. Any sharp front that does exist, as might arise from a strong dependence of the effective diffusivity on concentration and a multimodal pore size distribution on the nanoscale is always far beyond the colour change line.

Keywords

Sorption; NMR; Colour boundary;

List of notation

w/c	water to cement ratio
r_K	Kelvin-radius
ψ	relative humidity
T	temperature
M	molar mass
σ	surface tension
ρ	density
θ	contact angle between liquid and solid
R	gas constant
T_2	nuclear spin-spin relaxation time

1. Introduction

Visual observation of a colour change at a water ingress front in cementitious materials is a common method to determine water uptake in test methods such as the sorptivity and the water penetration under pressure test (BS EN 12390-8:2009).

Sorptivity is measured by capillary uptake and has units of distance per root time: m $s^{-1/2}$. Sorptivity was first introduced by (Philip 1957) in the field of hydrology. Hall (Hall 1977, Hall 1981) subsequently applied the term and test procedure to cementitious materials. The test comprises of placing a pre-dried sample above a water reservoir and watching the capillary uptake of water into the porous structure. Either the increasing mass of the sample is measured at intervals during the capillary uptake, or the sample is split and an internal surface inspected for a visual water front. In the latter case, a plot of depth of penetration against square root of time is expected to be a straight line for times sufficiently short that the front does not approach the other end of the sample. It has been noted before that the sorptivity derived from mass uptake and penetration depth analyses usually differ (Basheer 2001). Moreover, in the case of visual measurements, it has been suspected that some water ingresses beyond the colour change front (Hall, Hoff 2009).

The water penetration under pressure test as a measure of permeability was first introduced by (Murata 1965). Several mix designs, durations of test and applied pressure were investigated. It was concluded that the water penetration depth determined by visual observation was an appropriate method to measure permeability. RILEM Recommendations (RILEM TC 1994) specified the area where pressure is applied depending on sample size and also the applied pressure steps and duration. The test procedure became standardised in Germany in 1986 (DIN 1048:5 1991) and then used internationally (ISO/DIS 7031). These standards used a similar procedure to the technical recommendation. The German standard later became the base for the current EN 12390-8 European standard.

The purpose of this short report is to present nuclear magnetic resonance imaging (MRI) evidence that the colour change front can present a significantly

inaccurate measure of the actual water from position. Profiles of the water concentration profile in mortar cylinders after 1 day of sorption obtained using a laboratory GARField NMR system (Glover et al. 1999) are compared to photographic recording of the colour-change front. Data sets show that the water penetrated region extends well beyond that indicated by visual observation of the colour boundary. Parallel measurements using a Surface Garfield NMR system (McDonald et al. 2007) of the water sorption profile into the surface of concrete blocks show similar effects. The temporal development of the water concentration spatial profile, the water distribution within the open porosity, and evidence for C-S-H swelling in the same materials are reported elsewhere (Fischer et al 2014, Fischer 2014).

2. Materials and Methods

2.1. Materials.

Standard mortar(BS EN 196-1:2005) samples were mixed and cast into cubic moulds of 150 mm side length. The mortar mix had a ratio of 0.5 : 1 : 3 by mass for water : binder : aggregate. Two different binders were investigated, Portland cement and Portland cement with 10 % silica fume by mass added at mixing. One day after casting, the cubes were removed from the moulds and further cured at 20°C for a minimum of 3 months either sealed in a double layer of plastic sheet or underwater in lime water. One cube was prepared for each mixture and curing method.

Cylinders of 18 mm diameter and 150 mm length were wet cored from the cured cubes. The paste skin that forms on the surface of the sample at casting was not removed from the end of the cylinders. The mortar cylinders were dried to constant mass at 60°C, and under light vacuum to minimise carbonation, over a period of about 2 weeks. After drying, the samples were wrapped with PTFE tape with the two ends open.

The cylindrical samples were then exposed to liquid tap water from one end. To do this, the cylinders were suspended above a shallow pool of water with

the lower end 1-2 mm below the water surface. The water level was kept constant. The PTFE wrapping prevented drying from the sides and encouraged one-dimensional water transport along the length of the cylinders. Other common sealants and tapes, such as epoxy coating could not be used as they give a significant ^{1}H background signal in NMR.

Concrete slabs were also investigated with the same binders and w/b ratio. An example of a sealed cured OPC concrete and an OPC with 10% silica fume are included in this report. The concrete slabs were cut from the centre of the 150 mm cubes. Similarly to the mortars, the samples were dried to constant mass at 60°C. After drying, the cut surface was stood in water for the uptake test. The sides of the slabs where the colour-change water-front line was observed had a thin paste skin originating from casting / curing. To ensure that this did not significantly affect the results, a slab was split in half to observe the internal water-front. It was found to be in good agreement with the surface.

2.2. Methods

Capillary water sorption was assessed in three ways: gravimetrically, by observation (photographic recording) of the colour-change front and by ^{1}H spatially localised NMR relaxometry. The sample mass was measured after 1, 2, 4, 8 and 24 hours of sorption. The purpose was to ensure that we remained in the region of linear dependence of uptake on the square root of time. A photograph of the sample with the same reference white background and scale was taken after 24 hours of sorption. An NMR profile was also acquired after 24 hours of capillary sorption. In general, more frequent periodic recording was not done, as this would have required overly exposing the sides of the sample to the atmosphere. For NMR profiling, mortar cylinders were stepped through the resonant plane of a laboratory GARField magnet. The step size was normally 1 mm. At each step, a Carl-Purcell-Meiboom-Gill (CPMG) echo train was recorded (Meiboom, Gill 1958). The 1H NMR frequency was 23.4 MHz and the $\pi/2$ pulse length was 6.5 μs. A total of 64 echoes with 64 μs echo spacing and 2048 averages were recorded at each step.

A simple profile of the water content was constructed by summing the echo intensities at each location. This yields a profile with a relatively good signal-to-noise ratio. However, the echo-sum intensity is not linearly proportional to water content. A better measure is provided by fitting the echo train data to multi-exponential decays. It is well established that water in more mobile environments / larger pores exhibits a longer decay time. To that end, the first 2 echoes (that contain a significant contribution from the hydrate gel interlayer water and that can suffer from artefact) were disregarded at each location and the remainder fit to a two component exponential decay plus baseline representing water in gel pores, interhydrate spaces and capillary pores respectively (Muller et al 2013). The sum of these three amplitudes is thus a measure of the evaporable water content. The baseline was used since the maximum echo time (4.1 ms) was less than the expected decay time of capillary water. Chemically combined water (in, e.g. Portlandite) has a decay time too short for even the first echo.

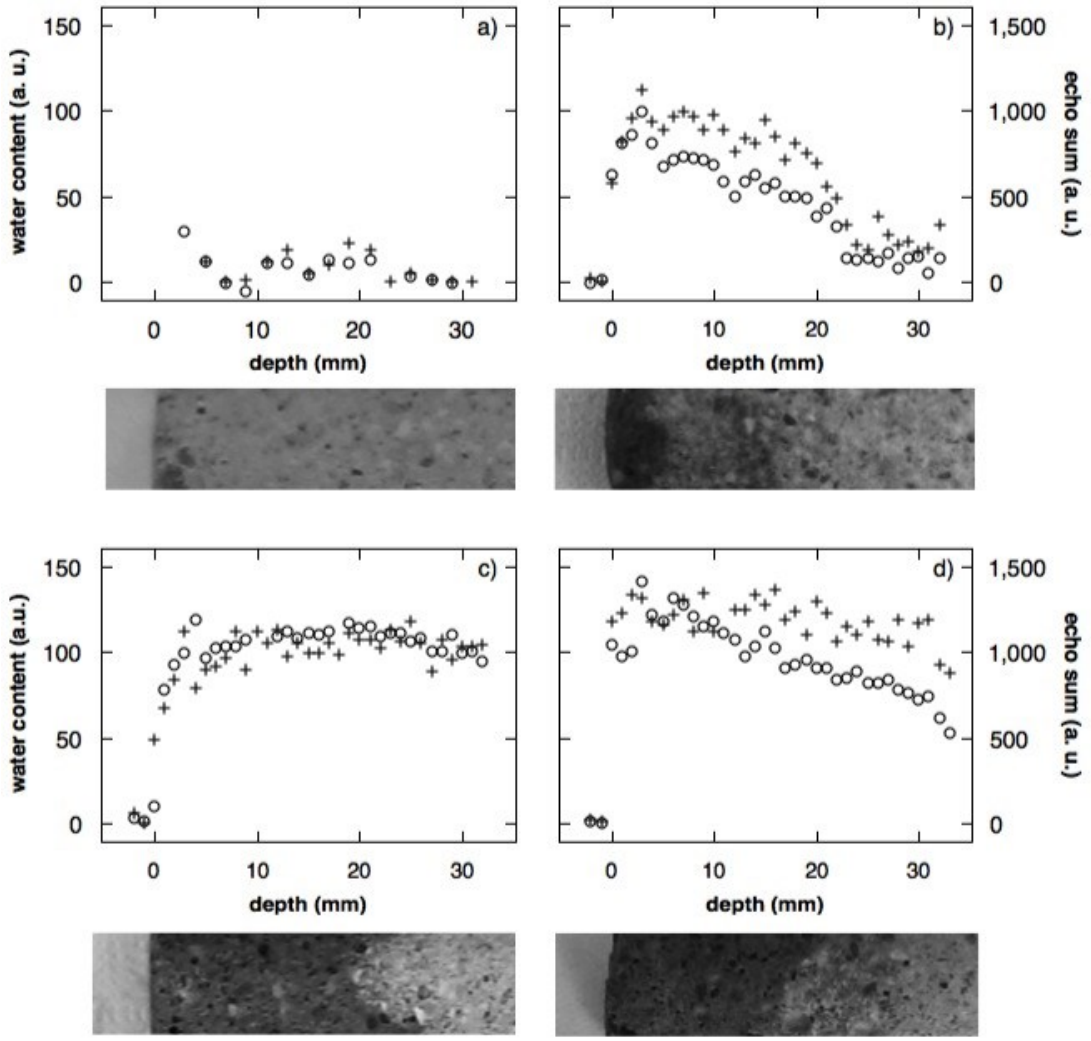
3. Results and analysis

Figure 1a and 1b show NMR profiles of water in the first 32 mm of sealed-cured OPC-mortar cylinders after drying and again after 1 day of sorption respectively. The exposed surface is at 0 mm on the scale. The profiles are constructed in two ways: as echo sum data (right hand access) and from the total amplitude of the exponential fits to the echo train data (left hand access). Typically for the parameters used most of the signal occurs in the first 10-12 echoes. Hence the echo sum is about ten times the initial amplitude, though both are of course in arbitrary units. The profiles show water invading about 22 mm into the sample, with a sharp front at about 22 mm on the scale. The fact that the pre-sorption intensity is close to baseline supports the claim that evaporable water is being monitored. According to the echo sum data, there is a significant gradient in concentration across the invaded region after 1 day of sorption. However, this is much less evident in the intensity derived from the echo-train fitting analysis. The difference likely reflects a redistribution of the water in the

nanoscale porosity due to C-S-H swelling that is discussed elsewhere (Fischer et al 2014).

Photographs of the same section of the cylinder before and after sorption are shown immediately below the profile plots. The photographs are all greyscale and slightly enhanced for brightness. All photographs were taken with the same white background. Before sorption, the dry sample is uniformly light coloured. After 1 day of sorption there is a clear darkening of the wetted surface layers with a clear colour boundary at about 5 mm. Beyond this the sample is slightly darker and there is an indication a weaker colour change at about 14 mm. However, whichever boundary is taken as the water front, neither extends as far as the NMR shows water to penetrate.

Figure 1c and 1d repeat figure 1b for two further samples of the same mortar. In these samples, the water travels much further in one day by both measures. The visual interface is much more evident in these samples and so the results are even less ambiguous. The NMR profile shows greater ingress than the optical measurement in each case. Indeed, in the case of 1b water extends beyond 32 mm. The water concentration measured by NMR is relatively smooth across the visual interface. However, careful observation suggests that there is a slight change in gradient at the colour change, notably for the echo sum data. Echo sum has the effect of magnifying the contribution of water content in larger capillary pores relative to smaller gel pores. A key question is why the sorption in figure 1b is substantially less than in figure 1c or 1d. The answer lies in the sample history. The sample used for figure 1b was cast in May, cured sealed, cored and dried in August and used for sorptivity in January. Those for figures 1c and 1d were cast in May (same cube) cored and dried in January and used for sorptivity in February.



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208 Fig 1. NMR profiles and photographs of a sealed cured OPC mortar
209 cylinder use in sorption experiments: (a) dry and (b) after 1 day of capillary
210 sorption. The profiles are constructed from echo sums (circles, right hand axes)
211 and exponential fitting intensities (crosses, left hand axes). (c) and (d) are
212 profiles and photographs of 2 further samples after 1 day of sorption. All
213 cylinders were cored from the same cube of mortar. The cylinder used in (a and
214 b) was dried 4 months before use. The cylinders in (c and d) were not dried until
215 needed.

216 Figure 2 shows examples of an underwater cured OPC mortar and a
217 sealed cured OPC mortar with silica fume after 1 day of capillary sorption. In
218 case of the underwater cured sample, the wet region is less marked in the
219 photographs. Notwithstanding, a weak colour change boundary can be discerned

at about 22 mm on the scale. The NMR profile constructed from the echo sum shows a gradual water concentration gradient right across this boundary. The profile constructed from the fitted echo amplitude is more constant around 22 mm with a more marked interface nearer 30 mm. In the case of the sample with silica fume, the water front is much more marked, both optically and by NMR. However, the former is at about 6 mm depth, whereas the latter is at about 18 mm.

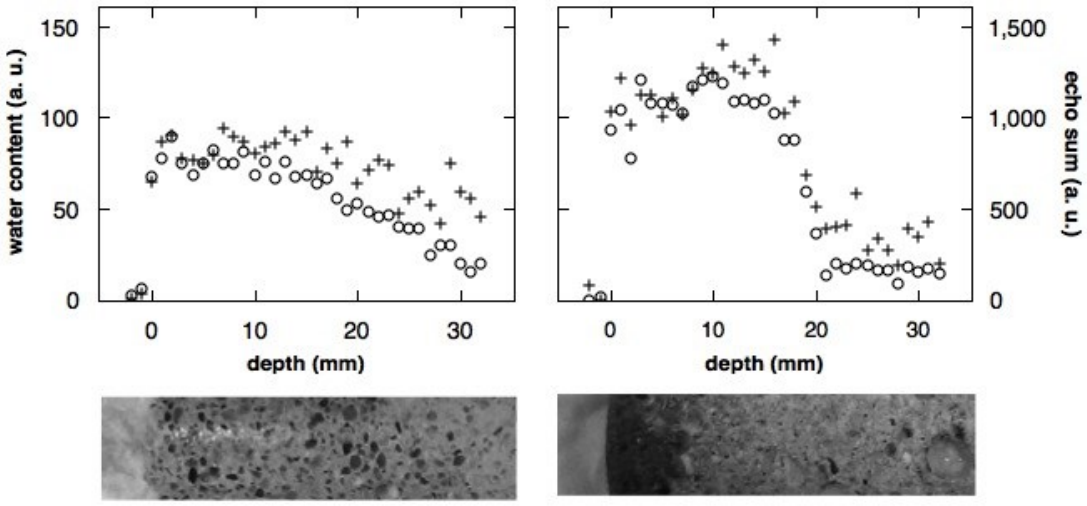

Fig 2. Under water cured OPC mortar (left) and sealed cured OPC with silica fume mortar (right) sample after 1 day of sorption. NMR profile of gel+capillary water (crosses, left axes) and echo sum (circles, right axes). Photographs of the same area are below the NMR data

In total, 4 sealed and 2 underwater cured OPC mortars and 3 sealed cured OPC mortars with silica fume were investigated. In every case the water ingress as measured by NMR profiling extended significantly beyond the water front indicated by the colour change boundary. In no case, was there an unambiguous sharp feature in the NMR data at the colour change boundary.

Figure 3 shows two concrete samples measured by the surface GARField. The signal to noise ratio decreases with depth with surface GARField. The profiles shown are constructed from measurements from both sides of the

sample. Hence the signal to noise ratio of the data is worst in the profile centre. The profiles are shown as echo sums only as the signal to noise ratio in these measurements did not permit exponential fitting. The surface in contact with water is at 0 mm. The photographs of the cross section of the samples are below the NMR profiles. In case of the OPC concrete, the sample was wet all the way through as measured by NMR. However, the photograph shows a gradual colour change boundary nearer 15 mm. The first 15 mm from the left side is darker than the rest of the sample. In the case of the OPC concrete with silica fume there is an even more clear water line, about 10 mm from the wet surface. However, the NMR profile shows water extending well beyond this dark region, down to about 30 mm from the wet surface.

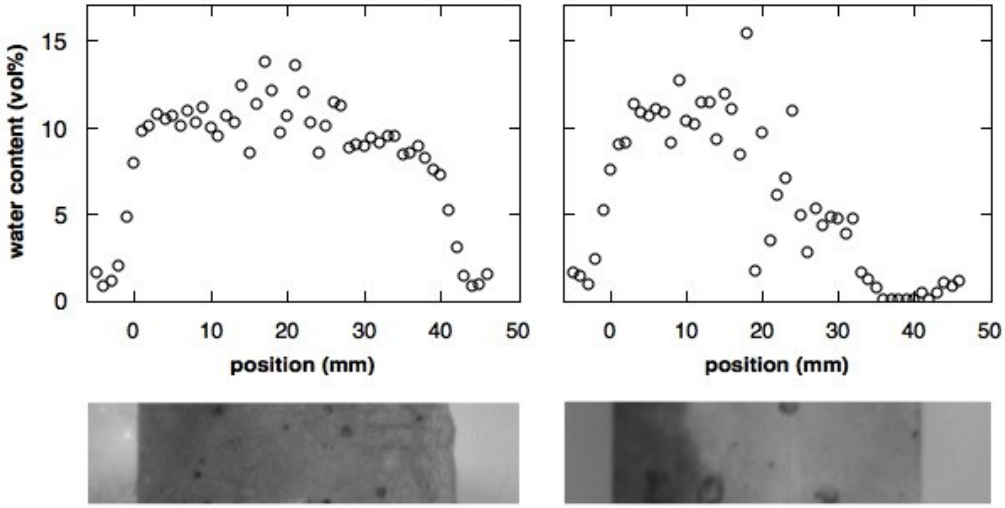

Fig 3. Echo sum NMR profiles concrete samples after 1 day of sorption with photographic cross-sections below. The samples are sealed cured OPC concrete (left) and OPC concrete with silica fume (right).

4. Discussion

In a capillary uptake experiment, there is a gradient of internal relative humidity in the sample from 100% where the sample is in contact with liquid water down to the ambient value at the exposed end. Capillary uptake of water at the lower end, evaporation at the water front, and a detailed liquid and vapour mass flow

rate balance though pore network lead to a non-uniform water content profile as has been discussed by Hall and Hoff (Hall, Hoff 2009).

Theoretical understanding of the colour change of wetted porous ceramic bricks has been discussed previously (Hall, Hoff 2009). It is a complex problem. Not withstanding, it is reasonable to assume that the colour change is associated with the wetting of pores of size comparable to the wavelength of light, circa 400-700 nm. The Kelvin equation

$$r_K = -\frac{2\sigma M \cos\theta}{RT\rho \ln\psi}$$

gives the critical radius, r_K, of a pore that is filled with water at a relative humidity, ψ, and temperature, T. In this equation M is the molar mass, σ the surface tension, ρ the density and θ the contact angle of the liquid in the pore and R is the gas constant. For optical wavelengths, and using parameters for water and assuming that water wets cement, this suggests that the colour change occurs at relative humidities exceeding 99.7 %.

The NMR signal lifetime, (the nuclear spin-spin relaxation time, T_2) of ^{1}H in water in small pores is proportional to the pore size (D'Orazio et al. 1990). The NMR measurements made in this work are sensitive to water in gel pores (a few nanometres), inter-hydrate pores (a few tens of nm) and larger capillary pores (100 nm to mm) resultant from chemical shrinkage and air voids in the original mix (Muller et al. 2013). By the Kelvin equation, and taking representative sizes of 3, 30, 300 and 3000 nm, these different pore sizes fill at relative humidities of 70, 96, 99.6% and >99.9%. There is inevitably a (non-constant) gradient in vapour pressure across the sample during sorption: the upper face of the sample is in equilibrium with the atmosphere. Given that the NMR senses water across a very wide range of pore sizes, and hence relative humidities, it is therefore reasonable to expect that water is seen over a great spatial range. One does not then expect to see a sharp feature in the NMR water profile at the colour change boundary. Such sharp boundaries as do occur are beyond this line and could well be associated with the multi-modal pore size distribution on the nano-scale as revealed by NMR (Muller et al. 2013).

5. Conclusions

A colour change boundary line is often used to determine the penetration waterfront in cement and concrete water transport test procedures. The results should be treated with caution. NMR profiling yields clear evidence that there is significant amount of water beyond the colour change line in sorptivity tests. In most cases, the degree of saturation of the sample is only marginally less beyond the darkened region and there is, in general, no marked change in the degree of saturation gradient as this boundary is crossed. Notwithstanding, in many instances there is a sharp water front as predicted by several numerical models on the basis of a strong dependence of the effective diffusivity on pore size and vapour pressure and hence saturation. However, as shown by NMR, it occurs significantly beyond the optical boundary.

The results in this paper focused on water ingress into dried material. The water penetration under pressure test focuses on water ingress into already wet material. This test also relies on visual observation. Other experiments to be reported elsewhere (Fischer 2014) show that NMR does not detect a strong front under those conditions either.

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