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Effect of moisture content of concrete on water uptake

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ABSTRACT

The penetration of water and non-polar hexane in Portland cement mortar prisms with different initial moisture contents was investigated using nuclear magnetic resonance (^{1}H NMR). The amount of water in gel pores strongly affects the penetration of water in much larger capillary pores. Water penetration is reduced by the self-sealing effect as characterized by non-$\sqrt{t}$ dependence of capillary uptake and penetration depth. This is explained by the ongoing redistribution of water from capillaries into gel pores which results in internal swelling and loss of continuity of the capillary pore system; a correlation was observed between the amount of redistributed water and departure from $\sqrt{t}$ behaviour. A descriptive model is used to explain the dependence of water uptake and penetration on moisture content. For increasing initial moisture contents up to a critical value equivalent to equilibrium with a relative humidity between 65 and 80%, less penetrating water is able to redistribute. Thus more penetrating water is in larger capillaries with less viscous resistance; uptake and penetration depth increase. Above the critical initial moisture content, uptake and penetration depth decrease towards zero. This is explained by (a) an overall reduction in capillary pressure because transport takes places in fewer and larger pores and (b) an increase in viscous resistance due to the connection of penetrating capillary water with pores already containing water. Less capillary pore space is available for transport. The surface region of concrete placed in contact with water is not instantaneously saturated. Water content increases with time depending on the degree of surface saturation. A new transition coefficient for capillary suction γ is defined for the calculation of surface flux.

1. Introduction

The resistance of concrete to water penetration is an important property regarding the design of concrete structures in contact with water and requirements placed on concrete composition. The uptake of water by dry concrete surfaces depends on capillary suction due to the action of surface tension at the pore water meniscus and resistance to viscous flow of the penetrating water. This means that the depth of penetration x and, correspondingly, the water uptake by the concrete should increase with the square root of the contact time depending on surface tension σ, contact angle α and viscosity η.

$$x \propto \sqrt{\frac{\sigma \cos\alpha}{\eta} t} \tag{1}$$

However, it is well-known that the rate of water uptake by concrete over longer time periods does not exhibit $\sqrt{t}$ behaviour [1,2], but progressively tends towards lower values. This is generally attributed to the self-sealing effect. Recently, ^{1}H NMR was used by the present authors to study the self-sealing effect directly during water penetration in mortar [3].

Despite the practical importance of the self-sealing effect, the underlying mechanism is still poorly understood. The explanations of its causes are varied and include Bingham flow, dissolution and precipitation processes, physical clogging by loose particles etc. [4]. In absorption experiments with water and organic liquids, Hall et al. [1] observed (a) lower water uptake by dry cement-based materials than predicted by $(\sigma/\eta)^{0.5}$ in comparison with several organic liquids and (b) wetting expansion only for water uptake. They attributed this behaviour to the action of water on the unreacted and dehydrated components of the hardened cement paste matrix and associated hydration with swelling because such effects are chemically specific to water. Krus et al. [5] argued that the self-sealing effect is linked to the swelling of the cement gel in concrete which occurs when water enters gel pores. Their reasoning was based on the observation that, as opposed to polar water, the uptake of non-polar hexane is linear with $\sqrt{t}$ and hardened cement paste does not swell on hexane uptake. The main properties affecting water and hexane transport in porous materials are listed in Table 1.

Past investigations [6,7] have shown that penetration depth and uptake depend strongly on the initial moisture content of concrete. This is significant because concrete components exposed to water are not usually dry and the self-sealing process may be affected by the amount of gel pore water. In the present work, ^{1}H NMR was used to investigate the effect of the initial moisture content of concrete on water penetration and

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Table 1
Liquid properties affecting transport of water and hexane in porous materials.

Liquid	Density ρ[g/cm³]	Surface tension σ[mN/m]	Dynamic viscosity η[mPa s]	$(\sigma/\eta)^{0.5}$ $[\mathrm{m}^{0.5}/\mathrm{s}^{0.5}]$	Dipole moment [Debye]
Water	0.998	72.8	1.002	8.5	1.85
Hexane	0.659	18.43	0.326	7.5	0.00

self-sealing. Insight into the mechanisms governing water penetration was gained by comparing water and hexane uptake.

2. Experimental procedure

A mortar slab ($700\times150\times150$ mm^3) was prepared from local 0/4 mm Munich sand and Portland cement CEM I 42.5 R at 515 kg/m^3 and a w/c ratio of 0.60. The slab was demoulded after 24 h and immersed in water for three days after which prisms ($240\times45\times45$ mm^3) were sawn from the centre of the slab to minimize surface effects. Following a period of three months in water, the prisms were oven-dried for three months at 50 °C and then stored to constant weight over saturated salt solutions in desiccators at relative humidities of nominally 50, 65, 75 and 80% RH and a controlled temperature of 23 °C. The free saturation, i.e. the equilibrium water content of specimens on immersion, was also determined. A relative humidity of 50% was chosen for the driest storage environment because lower values are not usually relevant to practical conditions. According to the well-known Kelvin equation for the maximum pore size filled with condensed water vapour, the major capillary pores in mortar equilibrated at 50% RH are empty because the condensate only fills pores below 3 nm in size. A thin adsorbed water layer 0.45 nm in thickness is present in pores of all sizes [8].

A few weeks before measuring, the 240×45 mm^2 prism sides were coated with several layers of epoxy resin to minimize moisture exchange with the atmosphere and ensure a one dimensional transport process along the length of the prisms. The end surfaces were roughened with a wire brush and the specimens replaced in the desiccators until immediately before measuring. At this time the specimens were at least one year old.

The NMR investigations were performed by placing each prism on a carriage which moved it in 1 mm steps through the sensitive region of a 0.47 T magnetic field positioned across the width of the prism. In this manner, step-scans of ^{1}H signal strength along the length of each prism were recorded. A more detailed description of the equipment is available elsewhere [9].

Each prism was removed from its desiccator, the initial weight recorded and an initial NMR "dry" scan performed. Then the prism was placed with an end face in contact with water or hexane and removed after different times to record weight and perform an NMR scan — the total procedure requiring 10 min. In this manner data were recorded for a series of suction times totalling up to 509 and 411 h for water and hexane, respectively. The specimens were also weighed on completion of each scan. No discernible change in weight was observed between the beginning and end of each scan.

In order to calculate profiles of water content in L/m^3 as a function of depth from the NMR scans, the signal intensity recorded at each scan step was corrected by subtracting the appropriate value from the initial "dry" scan before water uptake and then multiplying by a calibration factor F. The factor F was determined by measuring NMR uptake profiles for prisms equilibrated at 80% RH after a suction time of one hour. F was calculated from the weight gain due to water uptake and the corresponding total NMR signal intensity found by integrating signal strength over prism length. The resulting value was used for the subsequent scans. It was assumed that mainly capillary pores were filled after this short suction time.

3. Water uptake

The water uptake determined gravimetrically after storage at relative humidities between 50 and 80% RH is shown in Fig. 1. Now, the uptake of water is expected to depend on the amount of empty pore space as defined by the water vapour sorption isotherm and thus the pore size distribution. Thus uptake should decrease with preconditioning relative humidity as observed in [6]. In view of this, the maximum uptake observed for a preconditioning relative humidity of 75% RH is surprising. The results of two separate measurements for 75% RH are included in the figure to illustrate the reproducibility of the measurements.

Fig. 2 shows the penetration profiles obtained from the NMR scans. The available pore space for water uptake in samples preconditioned at 50% RH is approximately 146 L/m^3 (see Table 2). It is denoted by the upper dotted line in the plots. The grey areas indicate the additional initial water content of specimens equilibrated at 65, 75 and 80% RH with respect to storage at 50% RH. Thus the space below the lower dotted line and above the profiles is available for water.

The effect of capillary pressure p_σ and viscous resistance p_η on flow may be illustrated by the uptake of water by a cylindrical capillary of radius R.

$$p_\sigma = \frac{2\sigma\cos\alpha}{R} \qquad p_\eta = \frac{8\eta}{R^2}x\frac{dx}{dt} \tag{2}$$

Neglecting the effect of gravity on suction, the penetration depth in the capillary is given by

$$x = \sqrt{\frac{\sigma\cos\alpha R}{2\eta}t}. \tag{3}$$

Thus capillary transport is faster in larger pores which exert less viscous resistance.

The change in intensity of the NMR signal during water uptake depends on the number of hydrogen nuclei in the water molecules entering the material together with the relaxation time of the hydrogen nuclei spins compared with the dead time between the excitation pulse and the beginning of signal acquisition in the RF coil. In the present equipment, the relaxation time for unbound water molecules in large pores, as in for example coarse structured materials such as sandstone, is longer than the dead time so signal strength is proportional to water content. Cementitious building materials, however, contain small gel pores in which water molecules are strongly bound by surface forces. In this case, the relaxation time for hydrogen nuclei in gel pore water falls within the dead time; this water is not registered.

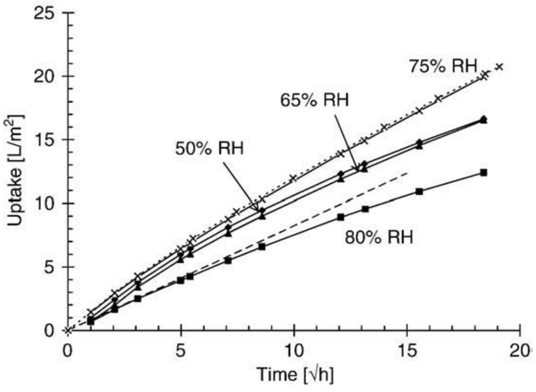

Fig. 1. Capillary suction of water by mortar prisms following storage at relative humidities between 50 and 80% RH. The dashed line fitted to the first three points of, for example, the 80% RH data is used to calculate the departure from $\sqrt{t}$ behaviour in Fig. 6.

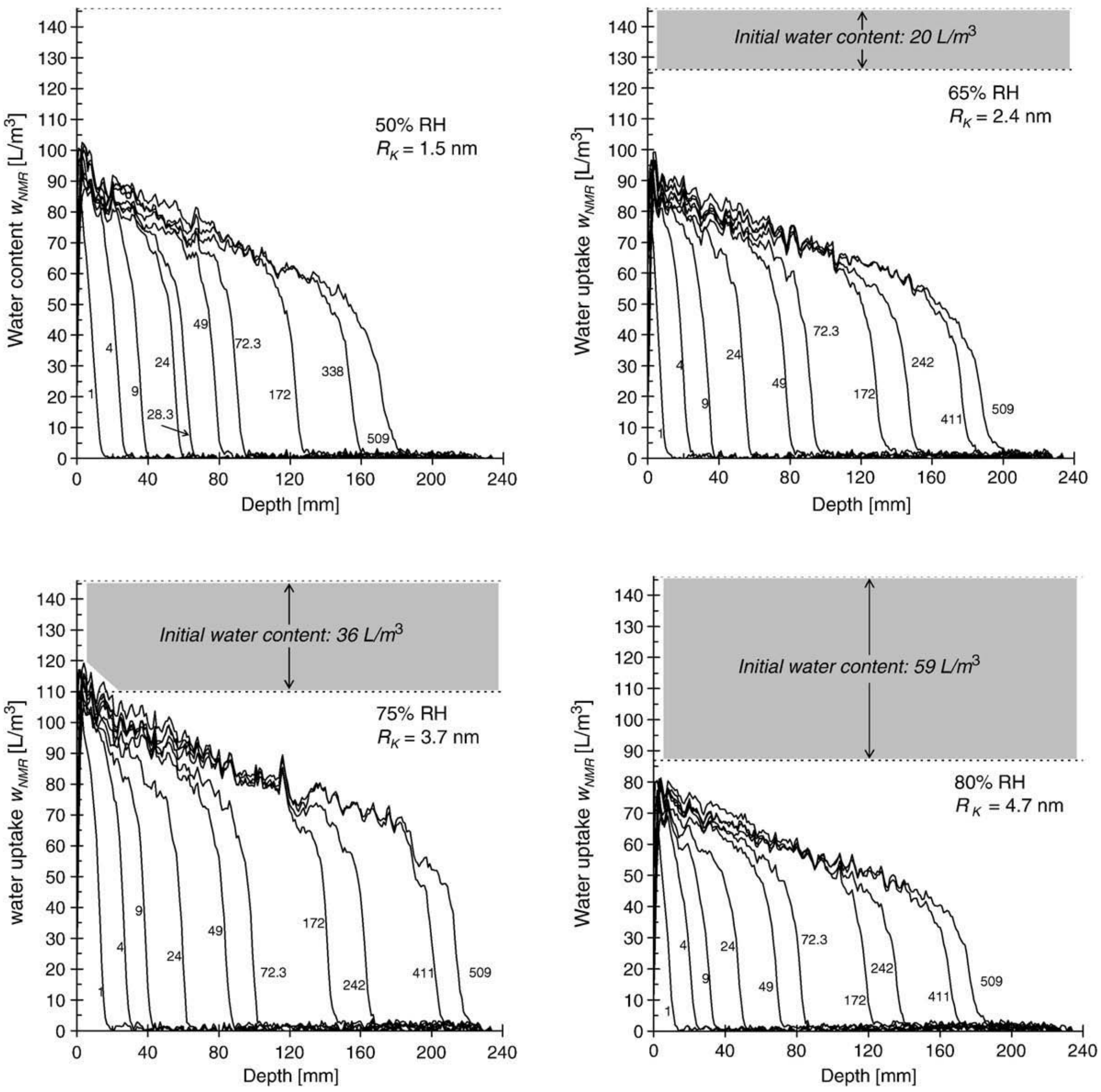

Fig. 2. Penetration profiles of water in mortar bars during capillary suction after storage at relative humidities between 50 and 80% RH. The suction time is in hours. The maximum value of the vertical axes corresponds to the suction capacity of the mortar after storage at 50% RH. The grey areas indicate the additional water content of specimens equilibrated at 65, 75 or 80% RH. The corresponding Kelvin radii are included.

In order to quantify the effect of pore size on signal intensity for the investigated mortar, an additional series of specimens ($45 \times 45 \times 15$ mm^3) was prepared as described above and stored at different relative humidities or saturated with water. Fig. 3 shows the NMR signal intensity integrated over specimen length (15 mm) as a function of gravimetric water content. To provide additional data over a range of water contents, signal intensity and water content were also recorded a number of times before constant specimen weight was reached.

The squares in the figure denote the equilibrium values where the corresponding Kelvin radii are included. At relative humidities above 80% RH, the NMR signal intensity increases in proportion to water content. At lower relative humidities, only pores with radii below approximately 5 nm are filled with water which is not completely registered by the equipment. Hence the water contents for the penetration profiles in Fig. 2 apply to water in pores with radii above roughly 5 nm.

Table 2
Water content of mortar equilibrated at different relative humidities and on free saturation.

Storage environment	65% RH	75% RH	80% RH	Free saturation
Water content [L/m^3]	20	36	59	146

The values were determined by weighing and are with respect to equilibrium at 50% RH ("zero" condition). The free saturation of oven-dried specimens was 188 L/m^3.

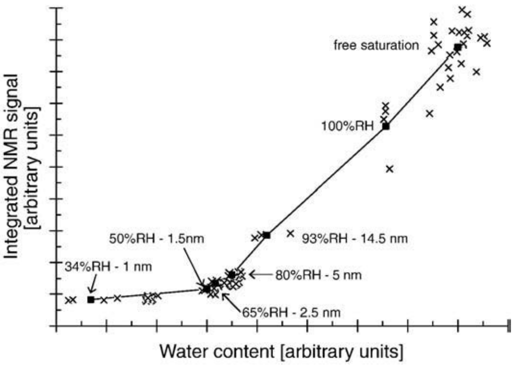

Fig. 3. Integrated NMR signal intensity and degree of saturation. ×: recorded during storage at different relative humidities. ■: at equilibrium with given relative humidity. The appropriate Kelvin radii are included.

The profiles in Fig. 2 were integrated over prism depth to determine the total amount of water registered by the NMR scan w_{NMR} which is plotted in Fig. 4 as a fraction of the increase in water content w determined by weighing.

It is apparent that the fraction of water registered by NMR diminishes in the course of uptake. This indicates that the amount of water which has moved from capillary pores into smaller gel pores ($1-w_{\mathrm{NMR}}/w$) increases with suction time. The rate at which w_{NMR}/w decreases is similar to the development of swelling stress observed in earlier investigations [10] following the immersion of dry thin-walled hardened cement paste cylinders in water.

The time dependence of penetration depth shown in Fig. 5 was estimated by extrapolating straight lines fitted to each leading penetration profile edge through the horizontal axes in Fig. 2.

Not only the amount of water absorbed (Fig. 1), but also the penetration depth clearly departs from linear $\sqrt{t}$ dependence. At the same time more water undergoes redistribution (Fig. 4). To examine this effect in more detail, each measured absorption value in Fig. 1 was subtracted from the corresponding point on a straight line fitted to the data for the first 9 h. The resulting values are plotted in Fig. 6 as a function of the weight fraction of redistributed water, i.e. the water no longer registered in the NMR scans.

It is apparent that a correlation exists between the departure of capillary uptake from $\sqrt{t}$ behaviour and the amount of redistributed water. This provides evidence that the self-sealing effect during capillary suction is caused by the redistribution of water from capillary pores into smaller gel pores.

4. Effect of initial moisture content on water uptake

The penetration profiles measured with NMR show that water in gel pores decisively affects the transport of water in much larger capillaries, as can be seen from the Kelvin radii in Fig. 2. As well as water uptake (Fig. 1), the depth of water penetration (Figs. 2 and 5) increases as the preconditioning relative humidity is raised from 50 to 75% RH. Preconditioning at 80% RH then leads to a reduction in capillary uptake and penetration depth.

Sosoro and Reinhardt [7] measured the absorption and penetration depth of heptane for a number of concrete compositions over a period of 24 h. The initial degree of water saturation was varied up to 90% by (a) exposure of the specimens to water and limitation of the uptake followed by (b) sealed storage for several weeks to ensure an even moisture distribution. Both penetration depth and uptake were observed to be approximately constant for concrete initially saturated up to about 20%. This effect was attributed to a reduction in liquid transport in capillaries owing to the uptake of liquid by gel pores. At higher degrees of saturation, penetration depth and uptake steadily decreased towards zero at about 90% saturation.

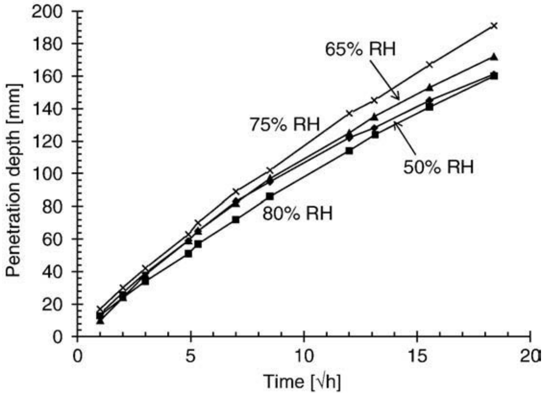

Fig. 5. NMR penetration front during capillary suction of water by mortar after storage at relative humidities between 50 and 80%.

Based on the present observations and the work in [7], the following descriptive model is proposed for the effect of the moisture content of concrete on water uptake, Fig. 7. The maximum uptake is defined as occurring at a critical degree of saturation ϕ_c.

4.1. Initial degree of saturation below ϕ_c

When dry concrete is placed in contact with water, water rapidly enters the capillaries and, at the same time, is partly redistributed into the empty gel pores where it is in effect rendered immobile. Thus less water is available for transport in large capillaries with a low viscous resistance, Eq. (3). At the same time, the ongoing redistribution of water into gel pores results in more and more internal swelling which reduces the connectivity of the capillary pore system slowing down the uptake below $\sqrt{t}$ dependence, [3,11].

In moist concrete the gel pores already contain water so less penetrating water moves from the capillaries into the gel pores; Fig. 4 shows that initial storage at higher relative humidities results in a lower proportion of water undergoing redistribution. Consequently, uptake is larger because more water in larger pores with less viscous resistance takes part in capillary transport.

Maximum uptake is reached at ϕ_c where insufficient space is available for redistribution. In the present investigations ϕ_c corresponds to moisture equilibrium in the region of 75% RH at which pores up to

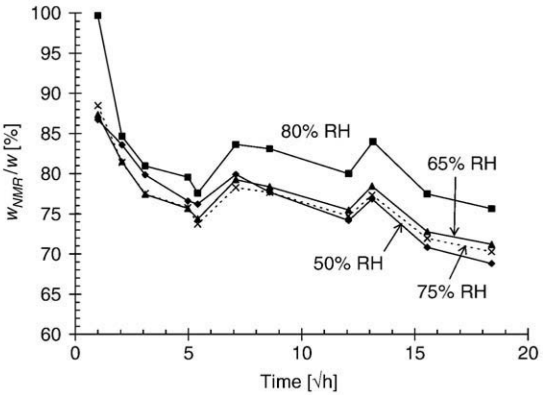

Fig. 4. Fraction of water measured by NMR during capillary suction by mortar prisms after storage at relative humidities between 50 and 80% RH.

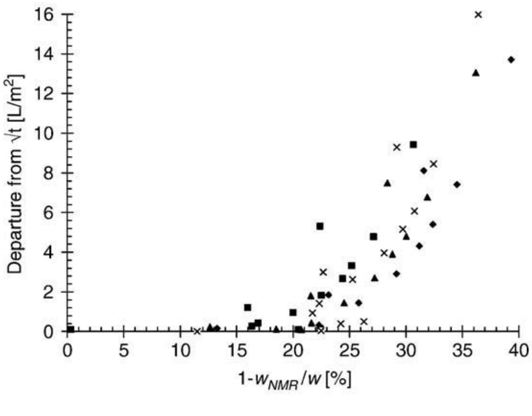

Fig. 6. Departure of capillary uptake from initial √t behaviour as a function of weight fraction of redistributed water. Symbols for relative humidity as in Fig. 1.

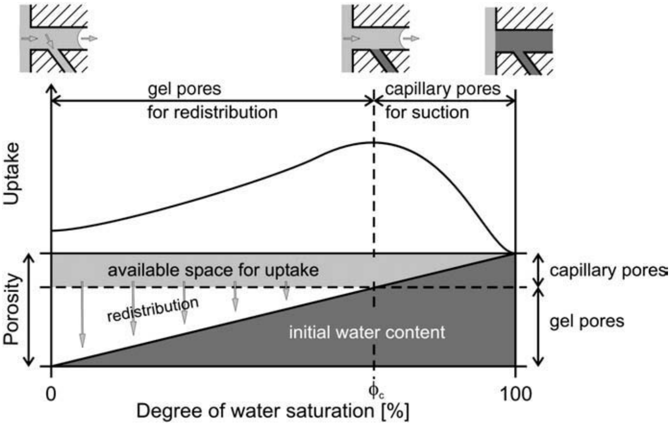

Fig. 7. Effect of initial degree of saturation on water uptake of concrete — a descriptive model.

Kelvin radii of 3.7 nm are filled with water, the much larger capillaries still being empty apart from the adsorbed layer.

4.2. Initial degree of saturation above ϕ_c

If the capillary pore system is empty then the menisci of water penetrating the system move through pores covering a large range of sizes. The suction rate and the spatial distribution of water content are determined by the capillary pressures exerted at the wetting front in different sized pores and viscous resistance. This depends on the interconnection of the different sized capillaries, their volumetric size distribution and the momentary depth of penetration.

If the capillary pore system is partially saturated, water will tend to be in smaller capillaries owing to their larger suction pressure p_σ which moves water from larger into smaller pores until equilibrium is reached, see [9]. Thus the menisci of external water penetrating the pore system will be confined to larger pores. Despite the lower viscous resistance in such pores, water uptake and penetration depth are reduced on the whole because the smaller (already) water filled pores (a) do not contribute significantly to capillary transport at the penetration front, but (b) contribute to viscous resistance when linked with larger pores newly filled behind the penetration front. Thus water uptake and penetration depth decrease with ϕ_c as observed in [7] for water and a number of organic liquids.

5. Uptake of hexane

The capillary uptake of hexane was investigated using prisms that had been stored to constant weight in atmospheres with 50 and 80% RH. In confirmation of earlier observations [5], the absorption of hexane obeys $\sqrt{t}$ dependence increasing until terminated when the opposite face of the prism is reached by the liquid, Fig. 8. Like water, the rate of uptake depends on the initial moisture content.

The hexane penetration profiles are presented in Fig. 9. Hexane obviously penetrates faster than water. Both hexane and water uptake by prisms stored at 80% RH lead to saturation of the empty pore volume in the surface mortar region. However in contrast to water uptake, hexane saturation also occurs following storage at 50% RH, cf. Figs. 2 and 9.

The penetration depths and total fractions of hexane were calculated in the same manner as for water. In Figs. 10 and 11, the resulting values are compared with the equivalent results obtained for water uptake.

The penetration front of hexane exhibits $\sqrt{t}$ behaviour for both storage humidities. According to the values of $(\sigma/\eta)^{0.5}$ in Table 1, hexane should penetrate the capillary pore system of concrete about 12% slower than water. The higher penetration rate observed for hexane may be explained by the much weaker van der Waals interaction of non-polar hexane with the internal pore surface compared with water and consequently the absence of the self-sealing effect due to internal swelling. This also explains why w_{NMR}/w for hexane in Fig. 11 does not, as opposed to water, decrease with time. The NMR relaxation time for hexane molecules in gel pores does not significantly decrease — because they are not affected by interactions with the gel pore surface. This behaviour is, as already mentioned, in agreement with the absence of swelling when dry concrete is saturated with hexane [5].

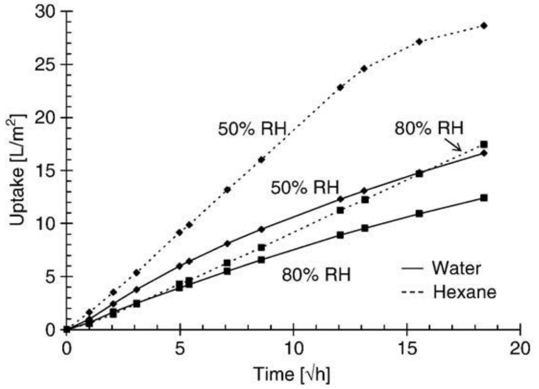

Fig. 8. Capillary suction of hexane and water by mortar prisms after storage at 50 or 80% RH.

The penetration rate of hexane decreases with initial moisture content owing to the reasons given for water ($\phi > \phi_c$) in Section 4. The miscibility of hexane and water is extremely low so that changes in the amount of gel pore water and thus internal shrinkage caused by solvent exchange are expected to be small.

6. A surface transition coefficient for capillary suction

The NMR measurements show that the amount of water or hexane in the mortar surface region increases during the first hours tending towards an upper limit after which, in the case of water, redistribution sets in. This indicates that the saturation of the surface mortar placed in contact with a liquid is not immediate, but a time dependent process. To examine this effect closer, the liquid content near the surface of the mortar (3 mm) was estimated from the penetration profiles, Fig. 12.

In the case of water, the surface liquid content increases during the first 5 h and levels off owing to redistribution. Hexane, which remains "visible" in all pores for the NMR equipment, steadily increases beyond this time.

The diffusion of water vapour from the external liquid into the empty pore space is too slow to explain the observed rate of increase — this was verified by calculations for capillary suction and water vapour diffusion.

In contemporary numerical simulations for capillary suction, either instantaneous water saturation of the porous material at the surface is assumed or material coefficients are adapted to the water/material boundary. The use of transition coefficients to describe the effect of surface boundaries on heat transport is standard engineering practice so, in analogy, a new transition coefficient γ for capillary suction is defined such that the liquid flux L/(m^{2}s) across the surface is given by

$$J_\gamma = \gamma \Delta w. \tag{5}$$

Here Δw is the empty surface volume available for uptake by capillary suction. Values of γ were estimated at around $2 \cdot 10^{-5}$ m/s for water and hexane uptake by the investigated mortar.

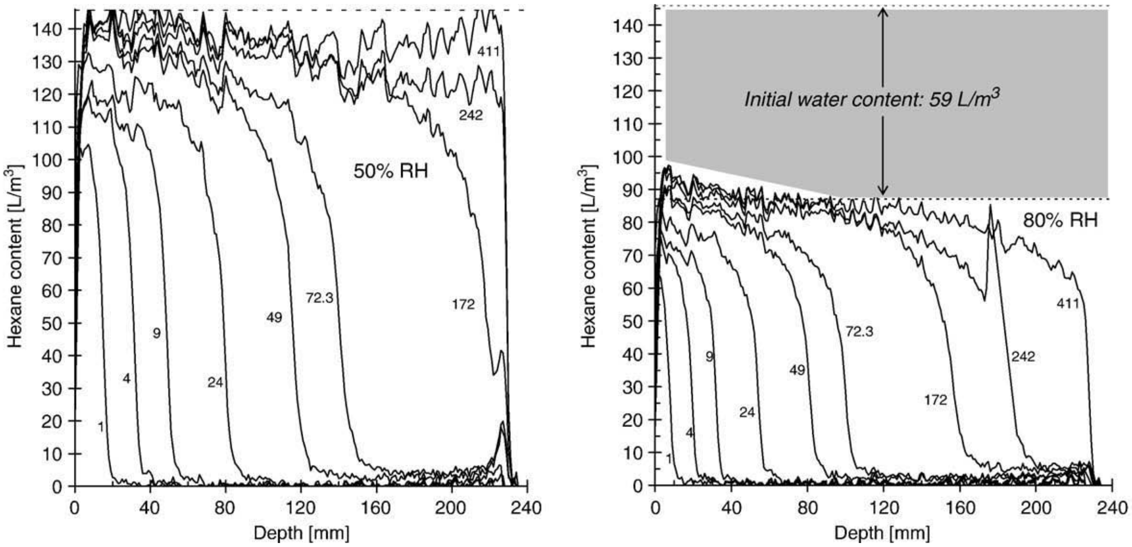

Fig. 9. Penetration profiles of hexane in mortar prisms during capillary suction after storage at 50 or 80% RH. The suction time is in hours.

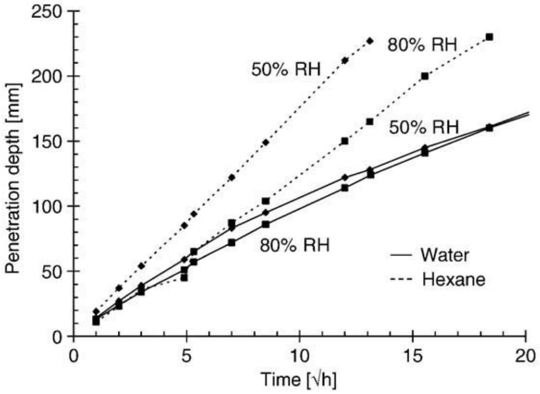

Fig. 10. Penetration depth of hexane and water measured by NMR in mortar prisms during capillary suction of water or hexane after storage at 50 or 80% RH.

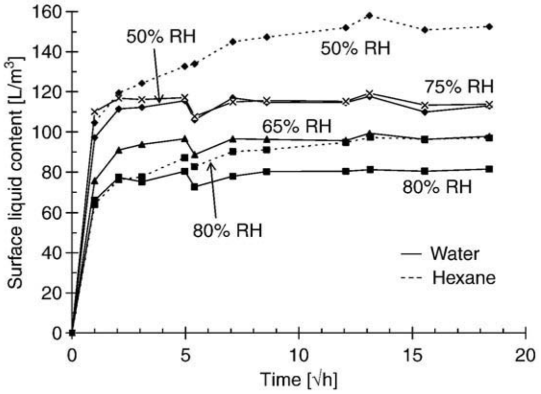

Fig. 12. Variation of liquid content of surface mortar (3 mm) during uptake of water and hexane in dependence of relative humidity of storage atmosphere.

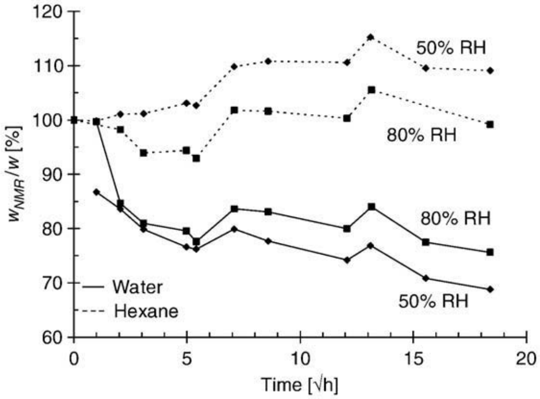

Fig. 11. Fraction of hexane and water measured by NMR during capillary suction by mortar prisms after storage at 50 or 80% RH.

7. Conclusions

The rate of uptake and depth of penetration of water in contact with cementitious building materials depends on the initial moisture content of the material. The penetration of water is limited by the self-sealing effect as characterised by non-$\sqrt{t}$ dependence of capillary uptake and penetration depth as observed for mortar equilibrated at relative humidities between 50 and 80% RH. The self-sealing effect is explained by the ongoing redistribution of water from capillary pores into smaller gel pores where it (a) no longer takes part in transport and (b) restricts capillary flow because swelling reduces the connectivity of the capillary pore system; a correlation was observed between the amount of redistributed water and departure from $\sqrt{t}$ behaviour.

Water in gel pores strongly affects the transport of liquids in much larger capillaries. Water uptake and penetration depth increase with the initial degree of saturation up to a maximum value equivalent to equilibrium with a relative humidity between 65 and 80% RH. Higher degrees of saturation then reduce uptake and penetration towards zero. This behaviour is explained using a descriptive model as follows. If water enters the dry concrete part of it is redistributed into gel pores and therefore does not contribute to capillary transport. For initial moisture contents up to a critical value, the gel pores already contain water so less penetrating water is able to redistribute. Thus more water flows in larger capillaries with less viscous resistance; uptake and penetration depth increase. If the initial moisture content is above the critical value redistribution does not take place. Uptake and penetration depth decrease with initial moisture content owing to (a) an overall reduction in capillary pressure (larger capillaries are involved in transport) and (b) an increase in viscous resistance of the penetrating water due to connection with capillary pores which already contain water. Less capillary pore space is available for transport.

The capillary uptake of non-polar hexane depends on initial moisture content in the same matter as water; apart from the absence of redistribution and internal swelling, the mechanisms are similar.

The surface region of concrete is not instantaneously saturated on water contact. Liquid saturation increases with time depending on the degree of surface saturation. A new surface transition coefficient for capillary suction γ is defined for the calculation of surface flux.

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