

Hall's Notes and Queries

NQ11

Reactive transport in cement-based materials

In 2012 in [1], Hoff and I wrote (p151, n19):

'The water sensitivity of cementitious materials which is evident in both permeability and sorptivity properties (particularly on dried materials) carries an important message. It indicates that all water transport in cement-based materials is *reactive*, and that appropriate reactive transport models are required ... In addition to rehydration in dried cements, there is the leaching of soluble components, notably portlandite, with microstructural consequences.'^a

^aThis was repeated more or less unchanged in the third edition [2] (p177, n26). In both editions, we cited [3] as a pathfinder paper.

Today, even after long years of investigation in many laboratories, the water-sensitivity of cement-based materials continues to generate interest and sometimes confusion, especially in the context of transport properties (and of sorptivity in particular). The purpose of this NQ is to try to provide a clear if brief status report.

1970s, 1980s

First, a little history. When Hoff and I started our work on water transport in inorganic construction materials in the mid 1970s, we were well aware that investigations of cement-based materials were likely to be complicated by the chemical action of water on the microstructure. This was not a profound insight. From the outset we had seen water transport as a stepping-stone to understanding degradation and decay, which as we often said,¹ were “mediated by water”. With that in mind, we started our work on capillarity and unsaturated flow by looking first at fired-clay brick, believing that it was reasonably inert. We hoped thereby to establish the basic phenomena in the absence of chemical complications.

In our earliest publications [5, 6], the first sorptivity measurements were obtained on English production bricks. They showed that the linear $i-t^{1/2}$ relation² predicted from the simplest theory and tested using the simplest equipment was preternaturally exact. Later, much work was done on French and English limestones, chosen also because of their relative insensitivity to contact with water. These stones too show imbibition kinetics that closely obey the paradigm $t^{1/2}$ law. In Fig 1 are three exemplary datasets, acquired in three different decades of research.

In the early work on brick we experimented with the imbibition of organic liquids. This allowed us to establish that the sorptivity scales

¹This point was made in the second sentence of the Preface of the first edition [4].

²This is the square-root of time t relation that is the “diffusive” result of elementary capillarity theory for one-dimensional imbibition (Lucas-Washburn for porous media), with i the cumulative absorption (imbibed volume per unit inflow area), dimension L. In early papers, we called this *absorption* rather than *imbibition*, following established usage in soil physics (see [2], p32, n1). For brick, stone and concrete, it took many years to reach consensus that the $t^{1/2}$ law was even empirically valid (see [2, 7]). But once that happened, deviations from $t^{1/2}$ were regarded as anomalies.

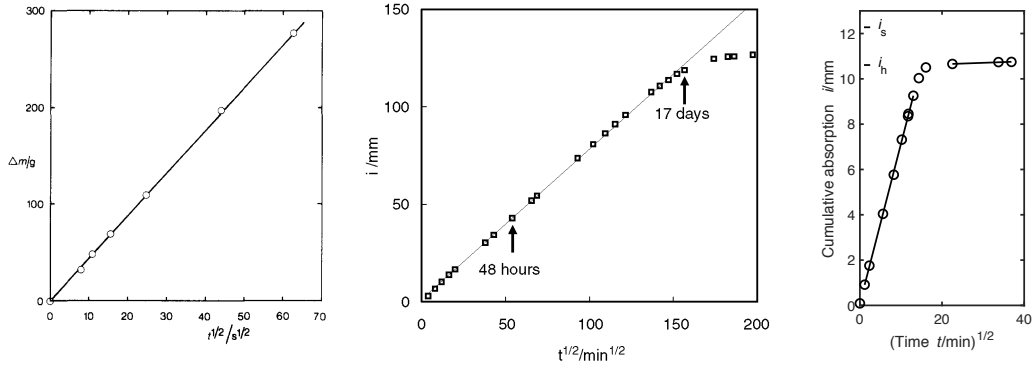


Figure 1: Sorptivity through the ages. Left: 1980, English fired-clay "common" brick, porosity f 0.309, sorptivity S 1.547 mm/min^{1/2}, imbibition through bed-face of whole brick, weight gain Δw [6]; centre: 1998, Lépine limestone bar, 630 mm long, f 0.21, S 0.782 mm/min^{1/2} (recalculated), Hirschwald state reached after 17 days, cumulative absorbed volume i , data from [8], reproduced in [1, 2, 4]; right: 2021, Bath limestone, 50 mm cube, f 0.248, S 0.704 mm/min^{1/2}, subscripts s , h denote saturation and the Hirschwald state [2]. Graphs as originally published.

with the surface tension σ and the viscosity η as $(\sigma/\eta)^{1/2}$, and thence to understand how S varies with temperature [6, 9]. Comparing the imbibition of water and organic liquids has proved to be extremely informative.

We did also dip toes into the shark-infested waters of cement-based materials at this time. In 1976 I developed a model of leaching for flow-column experiments intended for concretes. This had the support of Witold Gutt at the UK Building Research Establishment, but the project lapsed for want of a research student (without which...). The model was never published. More fruitfully, around 1980, there were two exploratory undergraduate projects on the sorptivity of cement mortars (by Thomas Kam Ming Tse) and of concretes (by Raymond M H Yau). These formed the basis of later publications [10, 11].

The data of Tse on various cement-lime-sand mortar mixes showed impeccable linearity in $i-t^{1/2}$ plots. Tests, lasting not more than 1 h,

were carried out on 250×50×50 mm bars, only about 14 days age, with water absorption through a 250×50 mm face. The sorptivity was unchanged over four wetting and drying cycles.

However, some other mortars, made from masonry cement and plasticizer but without lime, did show some slight (downward) concavity in $i-t^{1/2}$ plots. We had previously seen some early-time nonlinearity in AAC [5], and noted the low suction of the large aeration pores. We therefore tentatively ascribed the curvature in some mortars to gravity effects in coarse pores. Yau's data on concrete mixes also showed excellent linearity in some materials but rather pronounced curvature in others. Again, we attributed the curvature to the effects of gravity drainage in coarse pores. The explanation was speculative, but not unreasonable, although not supported by any confirmatory arguments. AAC was later one of the materials used in the HAMSTAD round-robin project. The gravity-drainage origin of the non-linearity in AAC was later established through a detailed study [12]. This included a comparison of the imbibition of water and the hydrocarbon *n*-decane. Both showed the same early-time nonlinearity, and this ruled out any alternative chemical explanation peculiar to water.

A terse summary of our view in the late 1980s was included in [10]. We wrote:

'It would be unsurprising if cements and concretes were to show deviations from [the $i-t^{1/2}$ law] because of changes in pore structure and possible pore-blocking effects accompanying the passage of water. Our results, however, do not show evidence of major effects of this kind in the mortars we examined, at least in the short term.'

By that time, we had expected that we might find some clear evidence of water-sensitivity³ in cement-based materials, but had not done so.

The 1990s

Eventually evidence of water-sensitivity in cement-based materials did appear, initially from the work described in three fine PhD investigations.

The first came in the experimental data of Nataliya Hearn, and concerned the water *permeability* of concretes and mortars [14]. Hoff and I [4] later summarised Hearn's findings:

'[I]t appears that specimens which have been wet-cured and not subjected to drying before a measurement is made have a constant permeability. The intrinsic permeability is much the same whether water or isopropyl alcohol is used. Concretes which have been dried show a progressive decline in permeability measured with water over a number of hours (typically by a factor of 10), but with isopropyl alcohol the permeability changes little. Intrinsic permeabilities measured with isopropyl alcohol on dried samples match well with the early time values measured with water.'^b

^bThese words were repeated in [1, 2] little changed, apart only from the addition of new citations to other work that had confirmed the same conclusion.

³The term water-sensitivity comes from petrophysics, where it was long known that the permeability of some rocks tended to fall during testing, usually as a result of the dispersion and movement of clay particles [13]. Water-sensitivity is found mainly in argillaceous sandstones, but occasionally it is found in limestones.

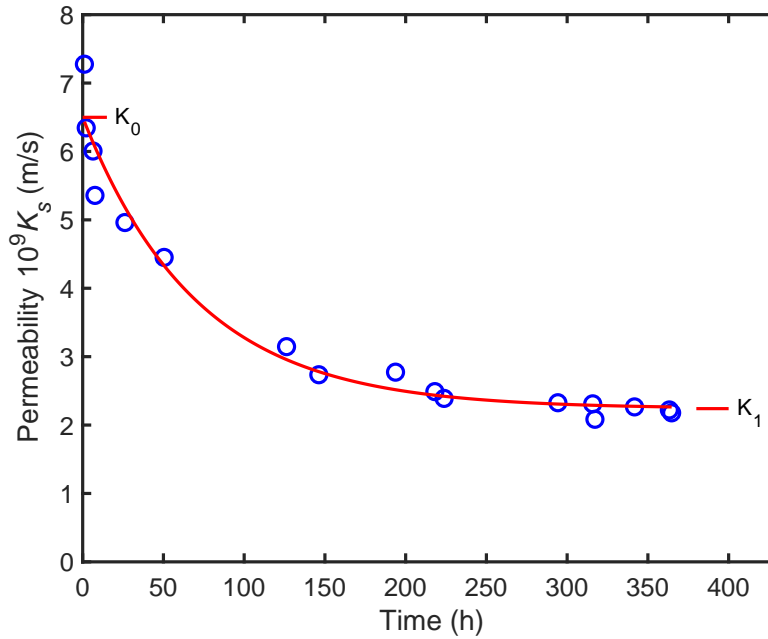


Figure 2: Saturated water permeability K_s of 1:3 cement:sand mortar, aged 3 months, measured at laboratory temperature in a Hassler-type cell [16] after drying and vacuum saturating; data from [15] replotted; K_s decays exponentially from initial value K_0 to long-term value K_1 ; line is least-squares fit to $K = K_1 + (K_0 - K_1) \exp(-t/\tau_c)$, with $K_0 = 6.50 \times 10^{-9}$ m/s, $K_1 = 2.24 \times 10^{-9}$ m/s, $\tau_c = 70.9$ h.

We might usefully have been explicit about how long it takes for the permeability of a dried material to decrease and stabilise when tested with water. Hearn [14] tested concretes that were 26 years old, and mortars 18 months old. Permeabilities, measured with water at times up to 7 days, suggested that the transition occurred over about 40–100 h, apparently much the same or concretes of greatly different ages.⁴

Hearn’s findings were confirmed by Kim Green who, in another excellent PhD project, reported [15] the decrease in saturated water permeability of a 1:3 cement:sand mortar, see Fig 2. Here the decay

⁴Hearn used the regression equation $k' = at^b$, with k' the intrinsic permeability, a, b fit parameters. The equation is a useful empirical equation over the limited duration of the tests, but does not have defined values of early-time and late-time permeability.

constant τ_c is about three days. Later, in [17], the decay of the water permeability was measured in another cement:sand mortar (1:2.15 by wt, w/c 0.40); treated as an exponential decay, the decay time is 44 h. There is every reason to expect that the decay time varies somewhat from material to material, but all available data suggest that the transition from 'dry-state' to 'wet-state' water permeability in mortars and concretes of all kinds made with portland cement occurs slowly over several days, not less, not more.

The second line of evidence was provided by Sarah Taylor who in her PhD [8] measured the *sorptivity* of some concretes and mortars in imbibition tests with water and organic liquids. While most sorptivity tests were made on small specimens, Taylor worked also with an unusually long bar of mortar. Its length was 250 mm, and the correspondingly long duration of the imbibition tests was about 18 days. Fig 3 shows in dramatic comparison the imbibition of water and *n*-decane by this long mortar bar.⁵ Taylor sought evidence of material alteration by measuring the expansion of samples during imbibition, finding nonzero wetting strain with water but none with organic liquids [8]. ESEM observations showed that new CSH cement gel was formed during the rewetting of crack surfaces [25].

An important difference between a saturated permeability test and a capillary imbibition test concerns the *contact* between the matrix and the water. In a permeability measurement the sample is saturated before it is mounted in the apparatus. Therefore, the entire sample is in contact with water from the beginning of the test. In contrast, in imbibition, the contact time varies with position throughout the wetted region as the imbibition proceeds. Any alteration of the material must depend on the contact time at each location in the sample, not

⁵This striking figure has been reproduced many times [1, 2, 4, 18–23]. It first appeared in print in [24], although captioned incorrectly to refer to a concrete mix rather than to a mortar.

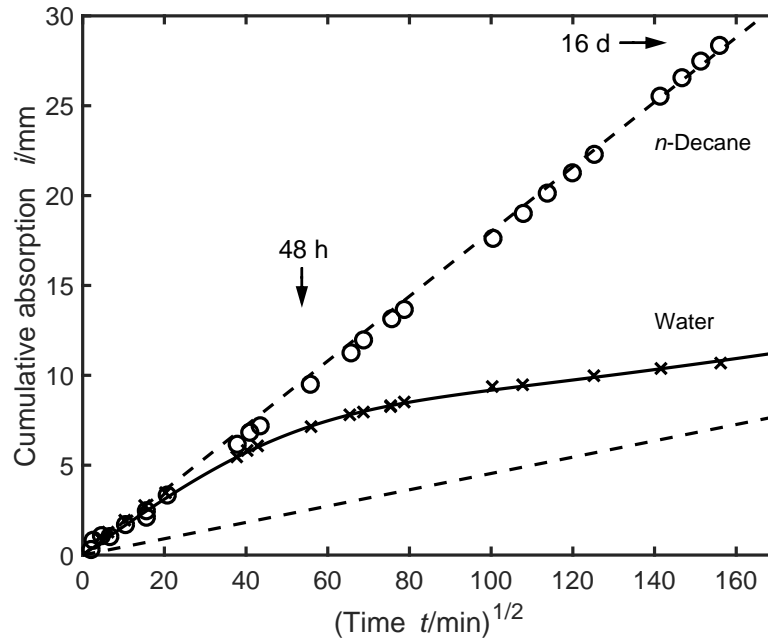


Figure 3: Long-term cumulative capillary absorption i versus $t^{1/2}$ for water and n -decane into a mortar, 1:2 Portland cement:sand by weight, 0.4 water:cement ratio by weight, cured under water for 28 d, dried at 40 °C for 24 h and at 105 °C to constant weight. Data from [18], figure from [19]; solid line is a fit to water data points using the time-dependent permeability model of [19] with $S_0 = 0.16 \text{ mm min}^{-1/2}$, $K_0/K_1 = 12.4$, $\tau = 2090 \text{ min}$; dashed lines calculated for constant permeability, $S = 0.18 \text{ mm min}^{-1/2}$ (upper line), and $S = 0.045 \text{ mm min}^{-1/2}$ (lower line).

on the elapsed time since the start of the test. The contact time was introduced and discussed in [19].

The 2000s and since

In 2005, I gave a talk at Centro Monte Verita⁶ that I called 'Anomalous diffusion: Fact or fiction?'. There were many things to discuss besides water-sensitivity, but the following passage encapsulates the state of understanding of that in the early 2000s.

⁶The talk, later published [26], contributed to a workshop on *Cementitious materials as model porous media: Nanostructure and transport processes*.

'There is clear evidence for unsaturated flow anomalies in cementitious materials, of which perhaps the clearest is that shown in [Fig 3 here]. The long-term behaviour of water shows a strong subdiffusive character. Since *n*-decane does not show this behaviour, we can regard it as a consequence of the water-sensitivity of the cement-based material, provisionally as evidence of chemomechanical interactions between matrix and pore fluid. ... The Taylor anomaly is a strong one and needs to be fully understood.'^c

^cFrom [26].

Two words stand out: first, we had started to use the term *chemomechanical*⁷ to bring together the chemistry and the mechanics, disparate disciplines that are often hard to merge but pave the golden road to understanding in cement science. Second, the term *subdiffusive* was used simply to describe a concave deviation from the $i-t^{1/2}$ law of capillary imbibition. It did not imply a mechanism, and it was perhaps unfortunate in unintentionally suggesting a simple power-law of anomalous imbibition.

Accepting that water-sensitivity was a real phenomenon, the next step was to find a model description of it, applicable to both water permeability and water sorptivity.

An early attempt [20] to model the anomalous sorptivity introduced a time-dependent hydraulic diffusivity into the Buckingham-Richards unsaturated flow equation. Lockington and Parlange suggested that D is function of both θ and t , and in such a way that the variables are separable, so that $D(\theta, t) = \gamma(t)\delta(\theta)$. However as noted

⁷First used in print by us I believe in [25].

in [19]:

'... there is the objection that any formulation which describes the diffusivity as a function of the imbibition time t implies that the diffusivity varies simultaneously throughout the material for all $t > 0$, and at all positions, whether wet or dry. Lockington and Parlange further suggest (but "For simplicity and purposes of illustration only") that $\gamma(t)$ is a simple power of time, so that $\gamma(t) = at^b$, and find from analysis of limited data that $b \approx -0.14$. This weak power-law with negative exponent raises three further difficulties: it implies (1) that the diffusivity is infinite at zero time; (2) that the diffusivity continues to fall continuously and does not reach a long-time limiting value; and (3) that the decrease in diffusivity has no natural timescale or rate. These features are largely unphysical, or at least hard to reconcile with known material behaviour.'

A later model [3] (already mentioned) also uses the unsaturated flow equation (with a Brutsaert diffusivity function D_0), but now relates changes with time directly to changes in the porosity f caused by dissolution and pore-clogging, so that $D = f^{19/6} D_0$. The model has had some impact in the nuclear-waste field. Its otherwise limited take-up is probably due to the complexity of the chemical underpinning of the $f(t)$ relation, which lacks experimental support.

A model that eliminates the four deficiencies listed above was published in 2019 [19]. This has two parts. First, the permeability is represented as an exponential decay, with $K_s = K_1 + (K_0 - K_1) \exp(-t/\tau)$. This describes well the admittedly sparse experimental data that show how the saturated permeability transitions from an initial dry-state value K_0 to a later wet-state value K_1 over a time τ , the de-

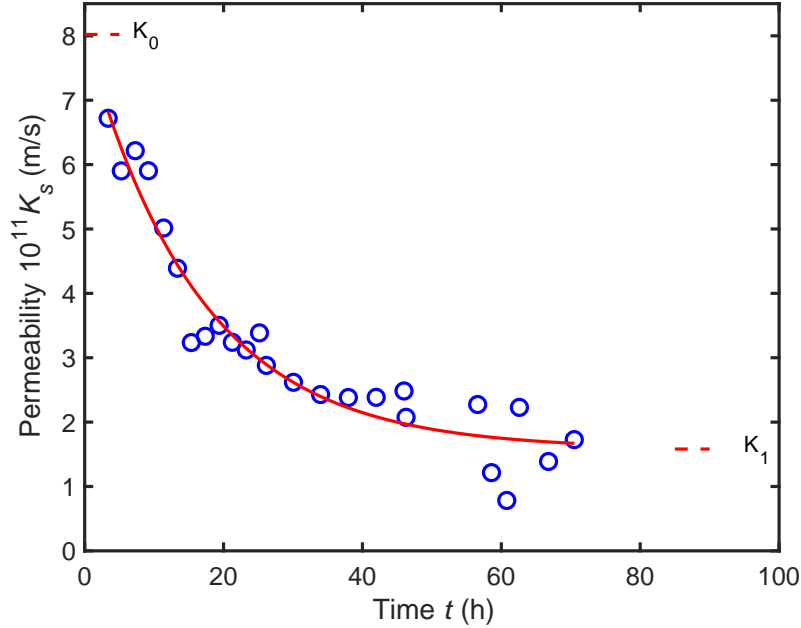


Figure 4: Saturated water permeability K_s of 26-year old concrete (1:2:5 cement/sand/aggregate, w/c 0.9) after drying and vacuum saturating; data from [14] replotted; K_s decays exponentially from initial value K_0 to long-term value K_1 ; line is least-squares fit to $K = K_1 + (K_0 - K_1) \exp(-t/\tau_c)$, with $K_0 = 8.0 \times 10^{-11}$ m/s, $K_1 = 1.6 \times 10^{-11}$ m/s, $\tau_c = 16.5$ h.

cay time. One dataset has already been shown in Fig 2. A second is shown in Fig 4: it is the only set of data shown graphically in Hearn [14]. In both these cases, and also in others in [17, 27], it is clear that the permeability falls rapidly at first on contact with water and then more slowly before eventually stabilising at a lower value. Both the time constant τ and the ratio K_1/K_0 vary with the material, but the available data are too meagre to allow any detailed conclusions to be drawn about the causes of this variation.

To apply a time-dependent saturated permeability function to capillary imbibition (and hence to the standard sorptivity test) requires any model to incorporate a contact time: in other words, any such model must allow for the fact that the length of time that the material has been in contact with water must vary with position through the advancing wetted region. The concept of contact time was in-

roduced in [19], described more fully in [2], and used most recently in [28]. The most straightforward way to link the permeability decay to the imbibition process is through a Sharp-Front model [2, 19], in which the permeability of the wetted region appears explicitly. Such a model was used in [19] to represent the Taylor dataset shown in Fig 3. The agreement between model and data suggests that at early times the imbibition follows a dry-state linear $i-t^{1/2}$ relation; that there is a transition stage during in which the $i(t^{1/2})$ shows some concavity; and that eventually the $i-t^{1/2}$ once again becomes linear (the wet-state sorptivity). In the long-time data, the effective permeability of the wetted region has stabilised at K_1 . The mean contact time \bar{t}_c of the wetted region is $2t/3$, so at long times the short contact times locally near the wetting front have little or no effect on the effective permeability of the wetted region as a whole.

Another approach that has been developed in a series of publications [29, 30] is to represent the imbibition $i(t)$ as a simple power law $i = S't^\beta$, with $\beta = 0.25$. This representation suffers from two of the four deficiencies already noted: namely, it implies that the change in permeability occurs uniformly and simultaneously throughout the material irrespective of the local wetting history; and also it does not incorporate any characteristic time-scale for the permeability transition. In addition, there appears to be no strong theoretical basis for the choice of the value 0.25 for β . In any case, the $i = S't^{0.25}$ relation does not does not convincingly describe the available data (Fig 5). For example, when this equation is applied to the data shown in Fig 3, the structure of the residuals plot, Fig 5 (inset), strongly suggests some systematic deviation from linearity in $t^{0.25}$.

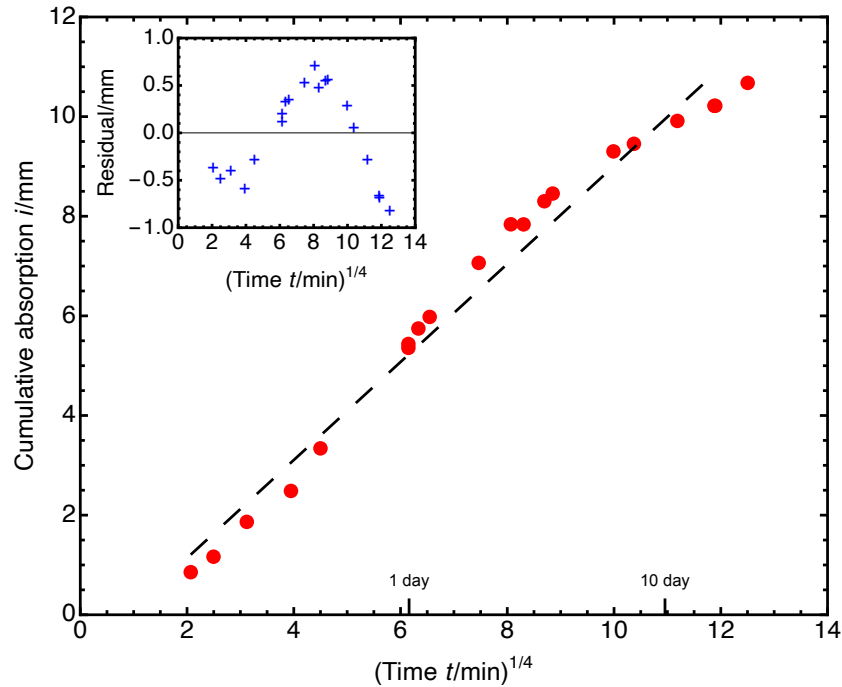


Figure 5: Water imbibition data from [8] (see Fig 3 here) replotted and fitted to $i = a + S't^{0.25}$, as in [29]. The dotted line is the least-squares fit with $a = -0.829$ mm, and $S' = 0.984$ mm min $^{-1/4}$. Inset shows residuals.

Status 2025

My summary ...

- It is now established that cement-based materials exhibit water-sensitivity in permeability and sorptivity tests when the material has been dried (or is dry) before testing. (Drying in some form is of course unavoidable in sorptivity/imbibition testing). The data are sparse, but this water-sensitivity appears to occur irrespective of the age of the material. Both permeability and sorptivity decrease from initial dry-state values to long-term wet-state values over a transition period of tens of hours, say roughly 50–150 h. In imbibition tests of short duration, say

lasting not more than 3 h, the $i-t^{1/2}$ law is obeyed, and a "dry-state" sorptivity can be measured.⁸ In imbibition with organic liquids, the $i-t^{1/2}$ law is obeyed in tests of long duration and no anomaly is observed.

- Although evidence is limited, the water permeability appears to decrease at least approximately as an exponential decay, from an initial value K_0 to a final value K_1 that appears to be stable in the long-term.
- The changes in transport properties during wetting are accompanied by expansion of the material (wetting strain). Some microstructural changes are also observed in ESEM. These support the explanation that the water-sensitivity in permeability and sorptivity is due to some combination of dissolution, rehydration, pore-blocking, and healing of microfractures. It is not yet clear which of these occur or are dominant.
- The development of descriptive or explanatory models has far to go. The simple exponential-decay model may provide a workable description of the permeability transition, although the decay constant derived from data-fitting is entirely empirical. To incorporate this into a model of imbibition kinetics appears to require a robust account of a contact time.

The topic of water-sensitivity in the transport properties of cement-based materials is complex and much remains to be fully understood. This somewhat personal summary is no more than a sketch. A more complete survey [21] covered activity up to 2020. A fully comprehensive review is now overdue and would be welcome.

⁸One recalls that Powers and Brownyard [31] in their massive study of hardened portland cement pastes reported in 1947 that water absorption into small mortar samples is linear in $t^{1/2}$ "for about the first 60 minutes". What happens after that they do not say.

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To cite this NQ: C Hall, Reactive transport in cement-based materials, *Hall's Notes and Queries* [NQ11](#)

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