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Anomalous diffusion in unsaturated flow: Fact or fiction?

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Abstract

The standard model of unsaturated flow widely used in building materials is essentially the extended Darcy law and the Richards equation of soil physics and hydrology. Much of the evidence for its validity comes from the measurement of water absorption (imbibition) kinetics and the analysis of water content distributions. While this model clearly captures the essential features of unsaturated water transport in some materials, several anomalies are known. In cement-based materials, strong deviations are sometimes observed. These are reviewed and assessed in relation to the wider interest in anomalous diffusion phenomena.

Keywords: Diffusion; Permeability; Transport properties

1. Introduction

It is just over 25 years since the evolution of the water distribution in building materials during capillary absorption was first measured with any sort of accuracy [1]. This was done by means of the then new technique of magnetic resonance imaging, MRI. The experiments established that the unsaturated flow of water in several inorganic building materials was broadly similar to that in soils. As a result the standard diffusive model of soil physics, embodied in the extended Darcy law and the Richards equation, was slowly adopted for building materials. The parameters of the Richards theory started to be measured systematically for brick, stone and concrete.

The modelling of transport and the characterisation of transport properties remains of great practical interest even after all this time. However it is a sign of the maturity of the standard theory that there is now real interest in deviations from it and of anomalies in transport behaviour. Much of this turns on experimental data on cementitious materials. In this paper, I ask: what is the strength of experimental evidence for deviations from the standard model in well conducted tests? And if there are such deviations, how large are they and of what nature are they?

2. Unsaturated flow

2.1. Capillary absorption and moisture distributions

The first MRI water content profiles were measured because at that time there was an increasing interest in *unsaturated flow* in construction materials [2–6]. The saturated permeability does not tell the whole story of water transport, and the common situation in which there are gradients of moisture within a structure called for an understanding of the spontaneous wetting and spreading processes which occur in the interior. Broadly speaking these are porous media capillarity phenomena. Experimentally what was needed was a method which allowed us to observe how the internal moisture distributions evolve with time in well controlled experiments.

These first profiles (one set of which is shown in Fig. 1a), and many that have been obtained since, showed that for a number of porous inorganic materials (clay brick, building stones, plasters and mortars) in unidirectional water absorption into a long bar the profiles advance roughly as the square root of time and maintain constant shape. That is to say, replotting the moisture content profile $\theta(x,t)$ against $\phi = x/t^{1/2}$ produces a

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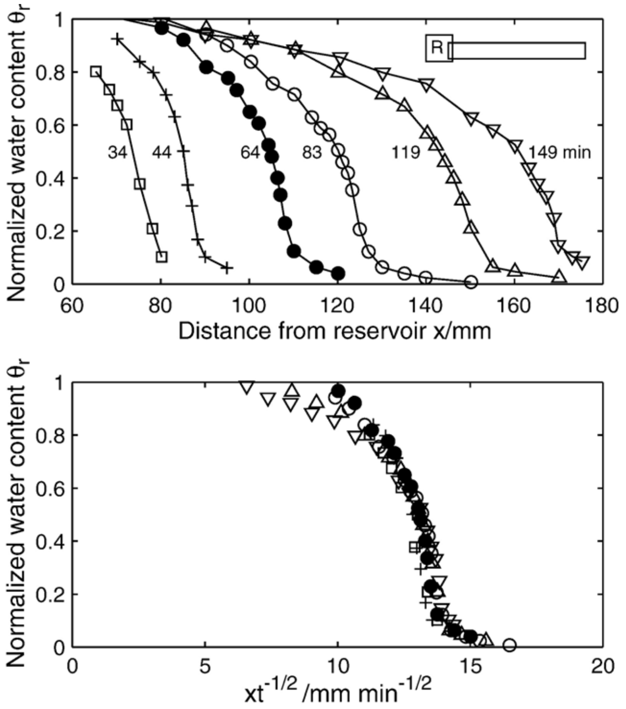

Fig. 1. (a): Water content profiles obtained by NMR during capillary absorption of water by a plaster bar. Elapsed times t are shown. (b): Profiles plotted against the Boltzmann variable $x/t^{1/2}$. The bar ($235\times33\times33$ mm) was cast from a mix (1:2 by volume) of a commercial hydrated lime and a commercial retarded hemihydrate plaster (class B, type b2 gypsum building plaster). After setting and drying, all side faces were sealed with an epoxy coating. Inset sketch in a shows bar with attached reservoir R to supply water to the inflow face during the experiment. Signal amplitude is scaled to the range 0–1.Volume fraction porosity f 0.45. Redrawn from [1].

master profile $\theta(\phi)$ which does not vary with time (Fig. 1b). This result can be modelled using a non-linear diffusion equation,

$$\frac{\partial\theta}{\partial t}=\frac{\partial}{\partial x}\left(D(\theta)\frac{\partial\theta}{\partial x}\right) \tag{1}$$

in which the quantity $D(\theta)$ is a material property, generally now called the capillary diffusivity. Subject to a free reservoir boundary condition at $x=0$ and uniform initial water content throughout, Eq. (1) has the solution

$$x(\theta,t)=\phi(\theta)t^{1/2} \tag{2}$$

as found experimentally.

Insofar as it is true, the empirical result and its non-linear diffusion description are valuable as the basis for modelling unsaturated flow in more complicated geometries and with different boundary conditions [6]. The diffusivity property $D(\theta)$ can be obtained by analysis of the $\theta(\phi)$ profile by Matano's method, first used in metallurgy [7]. Calling D a diffusivity of course simply reflects the fact that Eq. (1) is a parabolic non-linear PDE of the diffusion type, but it connotes nothing about the transport physics and certainly does not imply Brownian processes.

Subsequently, water content profiles of this kind have been measured many times, using a variety of techniques and on many more materials [6]. MRI and X-ray attenuation methods have proved themselves to be the best methods for laboratory tests [8,9]. The simple sample configuration shown in Fig. 1 has been widely used. In the work reported there has been broad acceptance that the $t^{1/2}$ scaling is valid for brick, stone and many cement-based materials (for example [10]). In only a few cases has anomalous behaviour been reported in work in which moisture profiles have been measured, and none on cementitious materials.

2.2. The underlying physics and the Richards equation

In soil physics, a similar diffusive description of unsaturated flow was already established [11]. This was based on the Buckingham law of capillary flow: $\boldsymbol{u}=-K\nabla\Psi$ (sometimes called the extended Darcy equation). The local vector flow velocity $\boldsymbol{u}$ is taken to be controlled by the local gradient of the capillary (pressure) potential Ψ. K is a generalized permeability, called in the soils literature the hydraulic conductivity. Both K and Ψ depend strongly on the local moisture content θ. When combined with a continuity equation we obtain the Richards equation,

$$\frac{\partial\theta}{\mathrm{d}t}=\nabla(K\nabla\Psi). \tag{3}$$

If $\Psi(\theta)$ is known, we can use θ as the sole dependent variable, so that we have

$$\frac{\partial\theta}{\mathrm{d}t}=\nabla(D(\theta)\nabla\theta) \tag{4}$$

where

$$D(\theta)=K\mathrm{d}\Psi/\mathrm{d}\theta. \tag{5}$$

Thus for the 1-D case we recover Eq. (1). It was therefore natural to adopt the Richards equation to describe capillarity-driven unsaturated flow in porous construction materials which showed $t^{1/2}$ water absorption behaviour; and furthermore to at least tacitly interpret the measured diffusivity in terms of K and Ψ. In fact, because K is difficult to measure directly, Eq. 5 has rarely been tested experimentally for materials such as brick, stone and concrete.

2.3. The sorptivity

It follows directly from Eq. (2) (and is obvious from Fig. 1) that the total volume of water absorbed in a one-dimensional imbibition increases as $t^{1/2}$. This is the basis of the *sorptivity* S, a material property which we generally define by means of

$$i=A+St^{1/2}. \tag{6}$$

Here i is the cumulative volume of absorbed liquid per unit area of inflow surface at elapsed time t, and A is a small constant which bundles together minor surface effects. In sharp

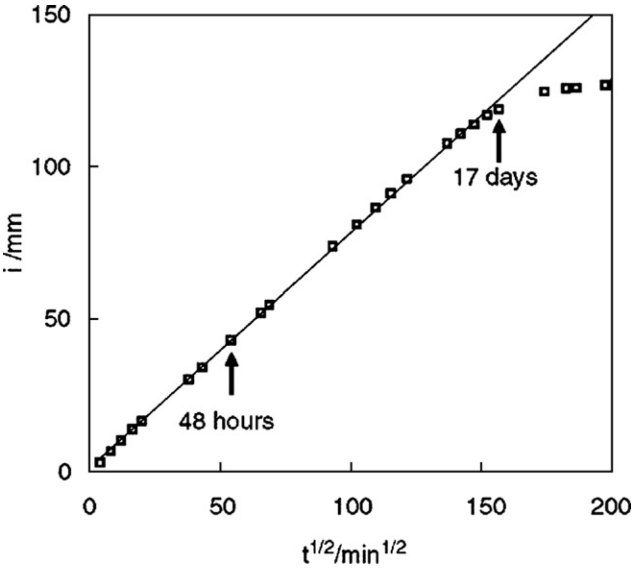

Fig. 2. Long-term cumulative capillary absorption $i(t^{1/2})$ of water into a Lépine limestone bar 630 mm high [13,6].

contrast to the diffusivity, the sorptivity is easy to measure, since little more than a laboratory balance is needed.

If we accept also the validity of the Buckingham equation, tantamount to assuming that capillarity is the dominant process at work, we find that for different completely wetting liquids the sorptivity scales as $(\sigma/\eta)^{1/2}$ where σ is the liquid surface tension and η the liquid viscosity.

The sorptivity has the status of a poor man's diffusivity and sorptivity data have been reported in hundreds of research and technical publications. It should go without saying [12] that the sorptivity of Eq. (6) can only be defined if the test data are indeed well represented by a $t^{1/2}$ straight line, but this is found for many materials. It is also true that many investigators assume it to be true and do not look for small deviations.

Nonetheless for many materials in well conducted tests, the $t^{1/2}$ dependence of the cumulative water absorption is strikingly confirmed. Fig. 2 shows a markable dataset obtained on a limestone specimen in an experiment lasting more than two weeks [13]. Undoubtedly the simple sorptivity equation and the non-linear diffusion equation that lies beneath it capture an essential truth about the kinetics of imbibition for many porous building materials.

However capillary absorption data do not always conform to Eq. (6). Even if they do, careful analysis may reveal anomalies of other kinds.

2.4. The HAMSTAD project

The recently completed EU-funded HAMSTAD project [14] has provided further results on the measurement and interpretation of water absorption profiles. HAMSTAD was a consortium project to support the development of new standards in heat, air and moisture transfer, primarily for building design. It included a round-robin exercise on test procedures for measuring moisture transfer properties of building materials. Three materials were selected for the round-robin: a fired clay brick ceramic, a hydrated calcium silicate [CS] board material, and an autoclaved aerated concrete. The properties measured included the sorptivity and the moisture diffusivity by the profile method. The CS material is notable among commercial building materials for its extremely low bulk density (in this case 268 kg/m^3), high porosity (0.90 volume fraction) and high sorptivity (9.50 mm/min$^{1/2}$) [15]. The main inorganic component of the material is the calcium silicate hydrate mineral xonotlite. An SEM microstructure is shown in Fig. 3. The high porosity is a consequence of the needle-shaped particles which prevent compact packing. The porosity is fine-grained with a mean MIP equivalent pore radius of about 0.5 μm. Moisture content profiles during water absorption were determined by several laboratories. Fig. 4 shows capillary absorption profiles obtained by MRI and the excellent master profile obtained by $t^{1/2}$ scaling. Almost identical results were obtained by an X-ray attenuation method [9]. Capillary absorption measured gravimetrically increased as $t^{1/2}$ and well defined sorptivities were obtained. For this calcium silicate hydrate with a large capillary porosity but little or no nanoscale porosity, the $t^{1/2}$ scaling looks secure.

3. Recognized complications in $t^{1/2}$ scaling

Departures from the diffusion equation must appear as failures of the $t^{1/2}$ scaling in 1-D water absorption profiles or, more accessibly, as failures of linearity in $t^{1/2}$ sorptivity plots. In fact simple capillary absorption data have been a rich source of information on unsaturated flow in construction materials and have revealed anomalies of several kinds. However by way of preamble it is important to be alert to the effects which have nothing to do with imbibition physics or interactions between liquid and material.

3.1. Geometry and homogeneity

Even for ideal capillary porous materials, diffusive $t^{1/2}$-behaviour is only to be expected if certain conditions are met

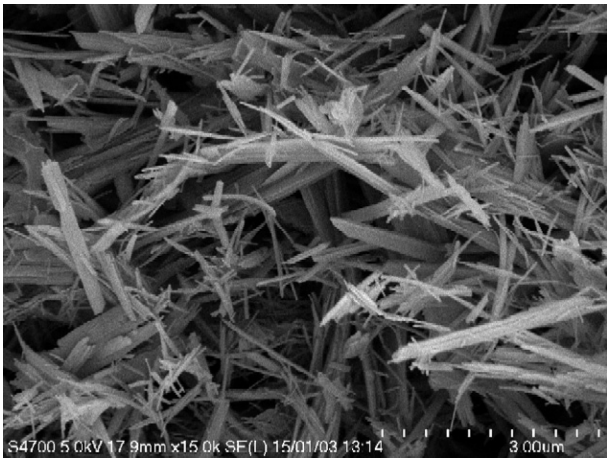

Fig. 3. High magnification SEM image of a fracture surface of a CS sample showing a porous microstructure formed from a loosely packed mass of acicular xonotlite particles. Scale bar 3 μm. Reproduced from [15].

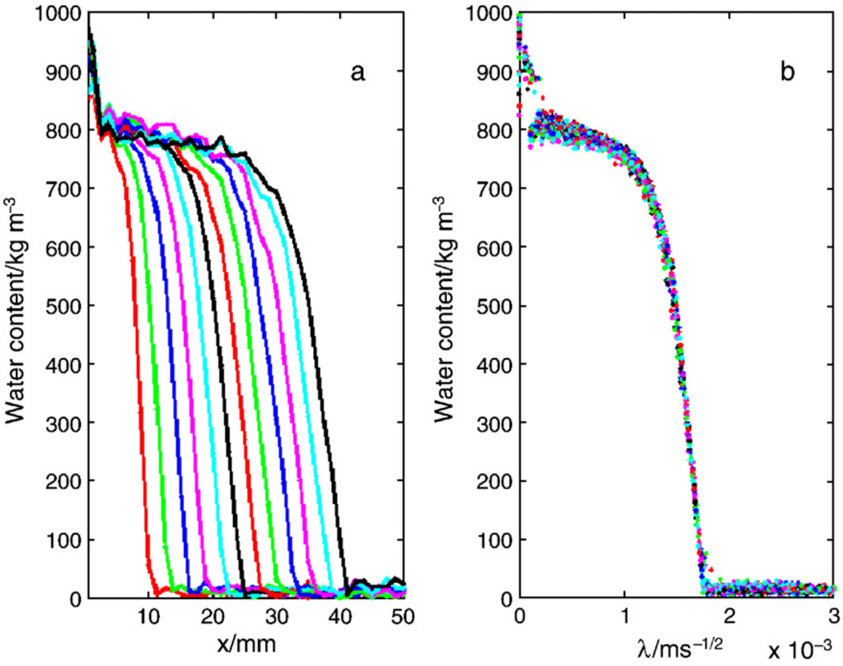

Fig. 4. Water absorption into a cylindrical calcium silicate plug: MRI SPRITE image data.(a):Water content density profiles at selected elapsed times 40, 60, 90, 120, 160, 200, 250, 300, 360, 420, 490 and 560 s. (b): Boltzmann-transformed profiles. Unpublished data, C. Hall and B. J. Balcom (MRI Center, University of New Brunswick).

[12,6]. The $t^{1/2}$-scaling holds strictly only for one-dimensional absorption into a semi-infinite homogeneous material with a constant concentration boundary condition. In 2-D or 3-D configurations, the flow may be divergent or convergent and $t^{1/2}$-behaviour is neither expected nor found. For cementitious materials, the homogeneity requirement is particularly exacting. Homogeneity is required both in the transport properties (and therefore in the structure of the matrix) and in the initial moisture content. Even for cement pastes and mortars, cast specimens tend to have variations of property near the surface (the "skin" of concrete to use P. Krieger term [16]). In concrete, the cast in-situ concrete has a cement-rich surface as coarse aggregate is excluded; and of course the continuum description can only hold over representative volumes much larger than the size of the coarse aggregate.

Even if the porous matrix is homogeneous, the initial moisture content may not be. In laboratory experiments on robust and relatively inert materials such as clay brick and building stones, aggressive oven drying can be used to establish a uniform state of dryness in a test specimen. With cementitious materials, this is likely to create damage, but gentler conditioning may leave the specimen with appreciable gradients of pore moisture. There is some evidence that spontaneous redistribution is hard to achieve in concrete; in any case careful tests of the initial moisture state of the material are rarely carried out and even more rarely reported (or vice versa).

Finally, in some tests gravitational effects may be observed. In many capillary porous building materials, capillary forces are much stronger than gravitational forces, which can then be neglected. Heuristically, this means that the kinetics of capillary rise are indistinguishable from horizontal capillary absorption on the time and length scales commonly used in laboratory tests. However this is not invariably true. In poorly compacted concrete, the capillary forces which act in the filling of the largest pores are weak and lead to marked deviations from $t^{1/2}$ behaviour in capillary rise tests [17]. Similar effects are observed in cellular concrete and AAC, where there is a strongly bimodal pore size distribution. The coarse aeration pores remain empty at heights above a few mm and strong curvature is seen in the initial capillary rise kinetics $i(t^{1/2})$.

It follows that non-linear sorptivity plots may not be due to any fundamental failure of the diffusion equation or the Richards equation. Where inhomogeneity of material is the cause, it may be possible to represent the material or building element as a layered composite with each layer having an appropriate sorptivity or diffusivity [6].

3.2. Air-trapping

More problematic is the behaviour of air in unsaturated flow. In the Richards model, the displaced air plays no role. The model is a pseudo-single phase representation of an immiscible gas–liquid displacement. It is implicit that the air is at the boundary pressure throughout the pore system and at all times. Consequently there are no pressure gradients in the gas phase and viscous resistance of the air plays no part in the imbibition fluid mechanics. While this may often be an acceptable approximation for soils, the role of displaced and trapped air in unsaturated flow deserves more attention in construction materials. Capillary rise into laboratory specimens produces initial "satiation" water contents which are generally only 60–90% of the vacuum saturation values. The remarkable Gummerson experiment [5,6] showed that during water absorption trapped air is distributed throughout the sample, is

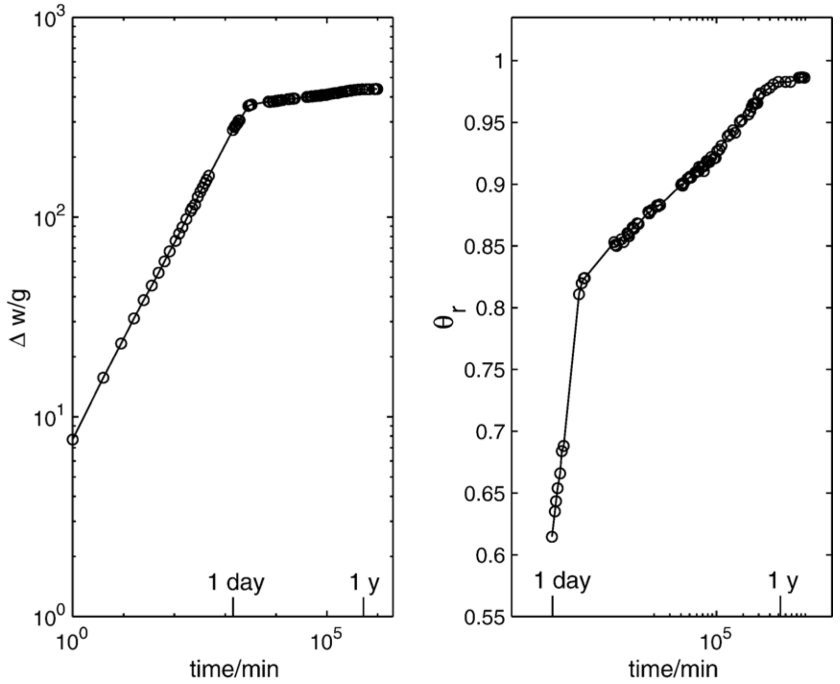

Fig. 5. Gummerson's experiment: long-term capillary rise water absorption in a single common clay brick. The brick used had dry mass 2.737 kg, dry bulk density 1910 kg/m^3 and volume fraction open porosity 0.31 determined by vacuum saturation. Δw, the gain in mass, is plotted against elapsed time t. Reproduced from [6].

pressurized and diffuses only extremely slowly to the boundary. Fig. 5 shows the entire two-year history of water absorption into a clay brick, in which the initial capillary absorption (with immaculate $t^{1/2}$ kinetics) is followed by further water uptake as air is lost by molecular diffusion to the exposed surfaces. Recent direct measurement of the pressure of trapped air in clay brick ceramic [18] shows that it is about 1 bar above the external atmospheric pressure.

Processes associated with trapped air can often be seen clearly in water content profiles, for example in Fig. 4. It is evident that the water content near the inflow surface ($x=0$) approaches the volume fraction porosity of the material, but falls quite rapidly in the interior to a lower value which is close to the capillary moisture content. Air is not trapped in the surface pores but air trapped near the surface is progressively released by diffusion of dissolved gas. Since this air diffusion process itself has $t^{1/2}$ kinetics, it is incorporated into the master curve. It is however a secondary phenomenon. The HAMSTAD protocol [7] for deriving a moisture diffusivity excludes the part of the profile where the water content is greater than the capillary moisture content.

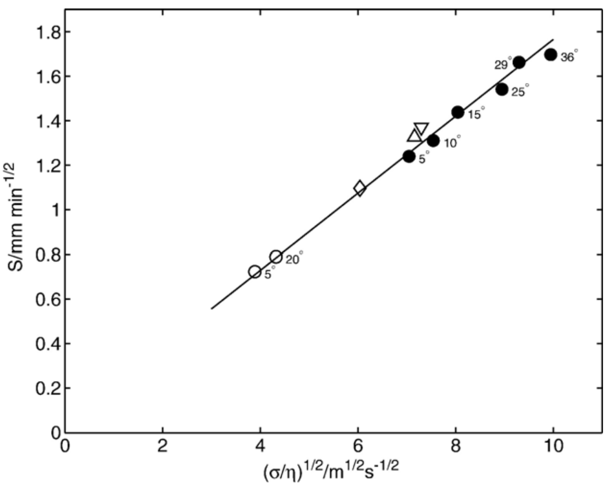

Fig. 6. Capillary absorption of water and organic liquids by clay brick ceramic. ● water, ○ ethanol, (temperature/°C as shown); ◇ methanol (13.5 °C); Δ n-heptane (26 °C); ∇ ethyl acetate (24 °C). The measured sorptivity S is plotted against the quantity $(\sigma/\eta)^{1/2}$, where σ is the surface tension and η is the viscosity. For this material, the intrinsic sorptivity $\mathcal{S}$ is $2.2\times10^{-5}\mathrm{m}^{1/2}$. Reproduced from [6].

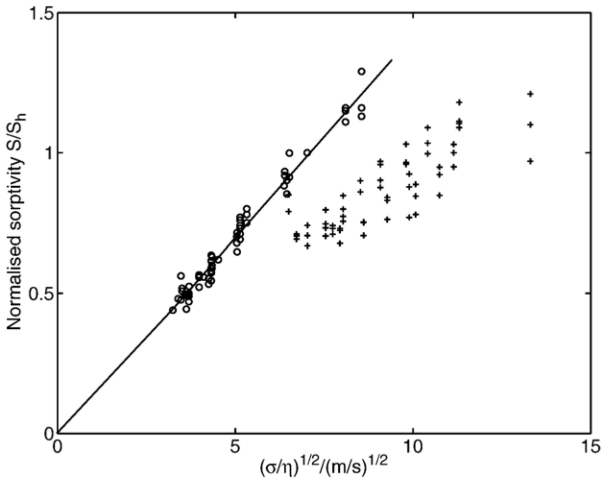

Fig. 7. Sorptivity S of a variety of cement-based materials (mortars and concretes) measured with organic liquids. S is plotted as the normalized sorptivity $S_n=S/S_h$ where S_h is the sorptivity measured with n-heptane at 20 °C for the same material. + are water sorptivities, ○ are sorptivities measured with organic liquids. Reproduced from [19].

3.3. Wettability

A powerful way to investigate capillary phenomena is to make comparative measurements using different liquids. For capillary processes, the only liquid phase properties which come into play are the surface tension σ and the viscosity η. For different liquids which completely wet the porous solid, we expect simple scaling relations for transport properties such as sorptivity and diffusivity. For fired clay brick, Fig. 6 experimental data show that the sorptivity scales as $(\sigma/\eta)^{1/2}$ and confirm that water absorption is a pure capillarity process. There is no evidence of partial wettability for any of the liquids including water on this high-energy surface. As a bonus, this result allows us to predict the temperature dependence of the sorptivity and diffusivity directly from the temperature dependence of the surface tension and viscosity.

3.4. Water-sensitivity in cement-based materials

For a number of cement mortars and concretes [19,20], the situation is dramatically different, as Fig. 7 shows. Here organic liquids are well behaved and conform to the expected capillarity scaling, but water is markedly different, the water sorptivities being lower than expected by as much as a factor of two. It should be emphasized that the water absorption in a standard test procedure is well behaved and increases as $t^{1/2}$, so that a liable sorptivity can be measured. However for water (but not organic liquids) a synchronous wetting expansion is observed, so that it is reasonable to interpret the sorptivity anomaly of water as the result of microstructural changes in the material, for which indeed there is ESEM evidence in the rewetting of dried material [19]. These are clearly rapid on the timescale of the water absorption test and not rate-determining.

On a longer timescale, changes can occur in cement-based materials which produce strong failures of the $t^{1/2}$ law. The best evidence (Fig. 8) comes from Taylor *et al*. [21]. A 1:2 OPC: sand mortar shows exemplary behaviour over more than two weeks when tested with the organic liquid *n*-decane but strikingly different behaviour with water. Since the water absorption falls progressively below the $t^{1/2}$ line, this behaviour may be described as subdiffusive.

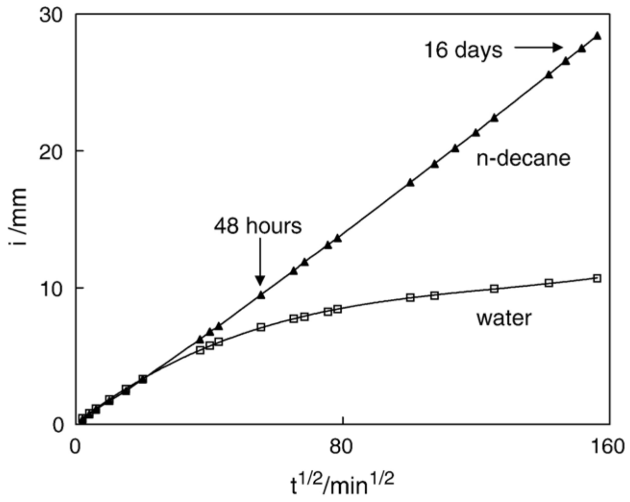

Fig. 8. Long-term cumulative capillary absorption i versus $t^{1/2}$ for water and *n*-decane into a mortar 1:2 Portland cement:sand by weight, 0.4 water:cement ratio by weight, cured under water for 28 days, dried at 40 °C for 24 h and at 105 °C to constant weight. Reproduced from [21].

Such effects in unsaturated flow in cement-based materials may be regarded as an example of *water sensitivity*, arising from a strong physicochemical interaction between the pore fluid and the porous solid. Similar effects are well known in sedimentary rocks, frequently caused by the presence of swelling clays. The sorptivity anomaly observed in unsaturated flow in some cement-based materials is presumably closely related to time-dependence often reported in the (saturated) water permeability of concretes [22]. This too is known to be absent when the test liquid is changed to an alcohol.

4. Status of the Richards equation

Why does the Richards equation work, at least for some materials? The obvious answer is that it is based on a simple linear transport law and as such is as uncontentious as Ohm's law; or more appropriately Darcy's law. But the important difference lies in the strong dependence of the transport coefficient on the water content. From the microphysical point of view, it is troubling that the capillary potential is an equilibrium quantity, yet it is applied in the vicinity of the wet front where the local water content is changing rapidly. Worse still, in a $t^{1/2}$ process, the initial behaviour is associated inevitably with fast kinetics (as in the Washburn equation where inertial effects at early time have been investigated endlessly for many decades). Putting it crudely, the Richards equation places the water at the leading edge of the advancing wet front in the finest of the pores, yet one might expect that the larger pores would fill more rapidly. In the Richards model, local equilibrium is maintained throughout. On the other hand, Barenblatt and Gilman [23] showed, for the case of countercurrent immiscible imbibition, how a non-equilibrium model can be set up. Indeed Le Guen and Kovscek [24] have recently presented X-ray profile data on water and *n*-decane absorption into a diatomaceous rock which show weakly superdiffusive behaviour as an experimental confirmation of non-equilibrium effects.

In fact there is evidence from several directions that the filling of small connected pores intimately connected to large ones may be surprisingly efficient [25,26] and it may be that the distribution of liquid near the wetting front is indeed close to equilibrium for timescales and flow rates of interest.

5. Anomalous diffusion: recent contributions

There is clear evidence for unsaturated flow anomalies in cementitious materials, of which perhaps the clearest is that shown in Fig. 8. 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. Of course, the evidence is limited to a single case. However the consequences for modelling are significant. Lockington and Parlange [27] in analysing the Taylor data have proposed that the moisture diffusivity D can be regarded as a slowly varying function of time. They further propose that the time dependence and water content dependence are separable, $\gamma(t)D(\theta)$, and are thus able to define a generalized sorptivity. This suggests a reworking of the continuum theory of unsaturated flow to incorporate time dependence in the material properties. Other approaches are also described [28,29].

The Taylor anomaly is a strong one and needs to be fully understood. It tells us that long-term (days+) water transfer by unsaturated flow is likely to be slower than predicted from material property values obtained in short term experiments. (Nothing is known yet about the situation at even greater ages). This result however needs to be seen in the context of several other claims for much weaker manifestations of anomalous diffusion in construction materials. Thus El Abd and Milczarek [30] find weak effects (both subdiffusive and superdiffusive) in fired clay brick and sandlime brick from profiles obtained by neutron radiography; and Küntz and Lavallée [31] similarly weak superdiffusive behaviour in re-analyzing the MRI data of Pel on fired clay brick. Küntz and Lavallée have proposed further [32] that such superdiffusive behaviour is general for systems in which the diffusivity D is an increasing function of θ. However Pachepsky *et al.* [33] in an extensive reanalysis of published data on soils find mostly weak subdiffusive deviations.

6. Some conclusions

It is fairly clear that for many inorganic building materials (notably clay brick, limestones and sandstones), the extended Darcy model and the Richards equation provide a satisfactory engineering macro-description of unsaturated flow. Experiments with non-aqueous liquids show evidence of partial wetting in some cases, but this does not in any way invalidate the Richards equation. There is evidence of weak anomalies, but it is inconsistent.

For cement-based materials, the situation for organic liquids is arguably much the same as for brick and stone, but for water transport there is good suggestive evidence of anomalous behaviour. Therefore the summary conclusions are:

1. The non-linear diffusion equation provides a good description of capillary transport in water-stable inorganic building materials.
2. It is not likely to replaced for engineering characterisation and design purposes in the near future.
3. It is not yet established that the hydraulic diffusivity is given by the Richards equation.
4. There is clear evidence of water sorptivity anomalies in cementitious materials.
5. For some purposes, the behaviour of organic liquids in experimental liquid transport experiments provides a revealing counterpoint to that of water.

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