

## Effect of wetting properties on the kinetics of drying of porous media

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2007 J. Phys.: Condens. Matter 19 112101

(<http://iopscience.iop.org/0953-8984/19/11/112101>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 16:35

Please note that [terms and conditions apply](#).

## FAST TRACK COMMUNICATION

## Effect of wetting properties on the kinetics of drying of porous media

N Shahidzadeh-Bonn, A Azouni and P Coussot

Institut Navier, Laboratoire des Matériaux et Structures du Génie Civil (UMR LCPC-ENPC-CNRS), 2 allée Kepler, 77420 Champs sur Marne, France

Received 12 January 2007

Published 27 February 2007

Online at [stacks.iop.org/JPhysCM/19/112101](http://stacks.iop.org/JPhysCM/19/112101)

### Abstract

The influence of the wetting properties of a model porous medium on the evaporation rate of water contained in the sample is studied experimentally. For a hydrophilic porous medium, drying is mainly controlled by the liquid film covering the solid grains and capillary rise inside the pores, leading to a constant drying rate and a homogeneous desaturation of the whole sample in time. For a hydrophobic porous medium, a drying front penetrates into the sample in the early stages of evaporation and the drying rate is found to strongly depend on the boundary conditions and wetting heterogeneities. In the presence of an air flow along the free surface of the sample, the drying rate varies as the square root of time, indicating a diffusive transport mechanism. Without air flow, a power law behaviour for the drying rate as a function of time is observed with an exponent of  $0.75 \pm 0.03$ . This is likely to be due to competition between diffusion through the vapour phase and local capillary rise of the liquid due to wetting heterogeneities. A surprising consequence is that for the late stages of drying, the total evaporated mass may become larger without air flow than with air flow.

Porous materials such as rocks, bricks, concrete, cement and wood when in contact with the atmosphere are continuously subjected to imbibition–drying cycles which seriously affect their durability, in particular because particle or ion transport may lead to chemical alterations of the structure. Drying is also one of the most energy-consuming industrial processes, and in addition the limitation of evaporation from soils is becoming a major challenge in the context of a possible global temperature increase. The use of wide range of hydrophobic surface treatments ‘*water-repellent products*’ in civil engineering and the building conservation industry underlines the importance of wetting properties of the matrix on water transfer through porous media. Mostly, the aim of such water-repellent treatments is to create a protective layer and prevent water from imbibing the porous medium, thus limiting the damage that can result [1, 2]. Pertinent examples of such damage are salt weathering during drying (displacement of ions to the surface and crystallisation) or frost damage due to the freezing of

water within the porous medium. However, the effect of wettability on water transport within porous media is far from being well understood from a physical point of view.

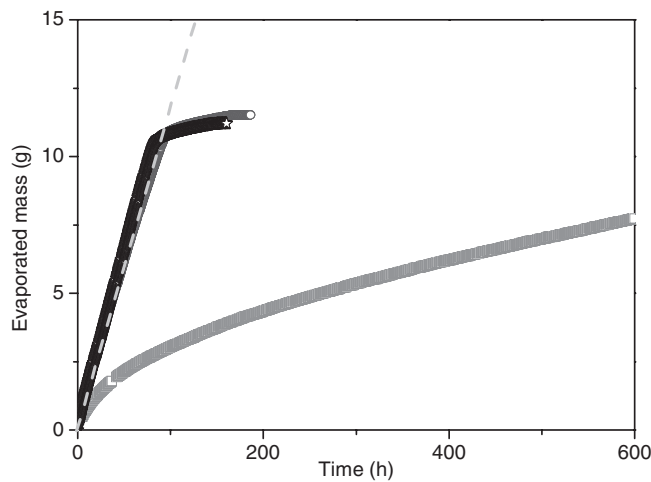
From an experimental point of view, for most types of porous materials drying of water takes place at an almost constant rate during a first stage (often down to a very low liquid content); this is the so-called constant-rate period (CRP). Subsequently the drying rate continuously decreases in time [3, 4]. However, these experiments were almost exclusively carried out in porous media that were perfectly wetting to water. The effect of the wettability properties of the solid phase was not studied systematically; van Brakel [5] simply remarked that a ‘contamination’ of the sample surface could affect the drying rate.

From a theoretical point of view, most existing approaches for describing drying characteristics rely on a description of the porous material as a continuum at some scale much larger than the pore size, so that specific, local, physical effects are included in some phenomenological parameters of the model [6]. In parallel the physics of (isothermal) drying has mainly been dealt with using pore network models [7]. However, strong discrepancies with experimental drying rates [8, 9] were observed, leading to the conclusion that drying could not be considered strictly as an invasion percolation phenomenon because liquid counterflow via continuous films plays a critical role [10, 11]. The potentially critical role of liquid films in drying was recognized in several recent publications [8, 12–14] and the possibility of non-trivial drying mechanisms including viscous effects was studied [11]. Finally, predicting the evaporation rate and the internal distribution of liquid during drying as well as assessing the effect of pore geometry remain a great challenge [5, 14–16].

All these considerations call for a better understanding of the effect of the wetting characteristics of the liquid on the porous medium on the speed with which the material dries. In this communication we report drying experiments on model porous media with well controlled wettability properties of the solid. In addition, we varied the boundary conditions by allowing the presence or absence of an air flow at the evaporating surface. The particular problem we want to address here is the relative importance of different transport mechanisms in the liquid and vapour phases during the drying process. To assess the role of capillarity on the transport of the liquid phase, the wettability properties of the porous media were modified. To investigate the role of the transport mechanism in the vapour phase, slow and fast drying experiments were done on the systems mentioned above by either avoiding or having an air flow over the surface. The results show a large impact of the wettability, with an additional important role for wetting heterogeneities for the hydrophobic case. Perhaps the most surprising finding is that under some circumstances at late times the total evaporated mass becomes larger without an air flow over the surface than in presence of an air flow.

The drying experiments were performed in unconsolidated model porous media consisting of hydrophilic or hydrophobic glass beads ((1) 240–320  $\mu\text{m}$  or (2) 104–128  $\mu\text{m}$ ). In their initial form the beads were hydrophilic. Hydrophobic beads were obtained by silanization with fluorinated silane solution (Degussa). The contact angles (advancing and receding) of water, determined from micro-photographs of the bead in contact with a droplet over a flat surface, were  $\theta_a = 11 \pm 5^\circ$  and  $\theta_r \sim 0^\circ$  for hydrophilic beads and  $\theta_a = 88 \pm 5^\circ$  and  $\theta_r = 84 \pm 5^\circ$  for hydrophobic ones [17].

The porous media were obtained by filling a glass column (porosity,  $p \approx 35\%$ ) with an automated packing system (diameter 3 cm, height 3 cm). Two kinds of packing were used: (a) hydrophilic or hydrophobic beads with a single diameter range (type 1); (b) hydrophilic beads with a two-layer structure of two diameter ranges: type 1 beads over 2 cm at the bottom and type 2 beads over 1 cm on the top. Since the liquid is retracting itself from the porous medium during drying, the receding contact angle is considered in the following. As a direct consequence, we anticipate that a hydrodynamic film remains present at all times in the case of hydrophilic

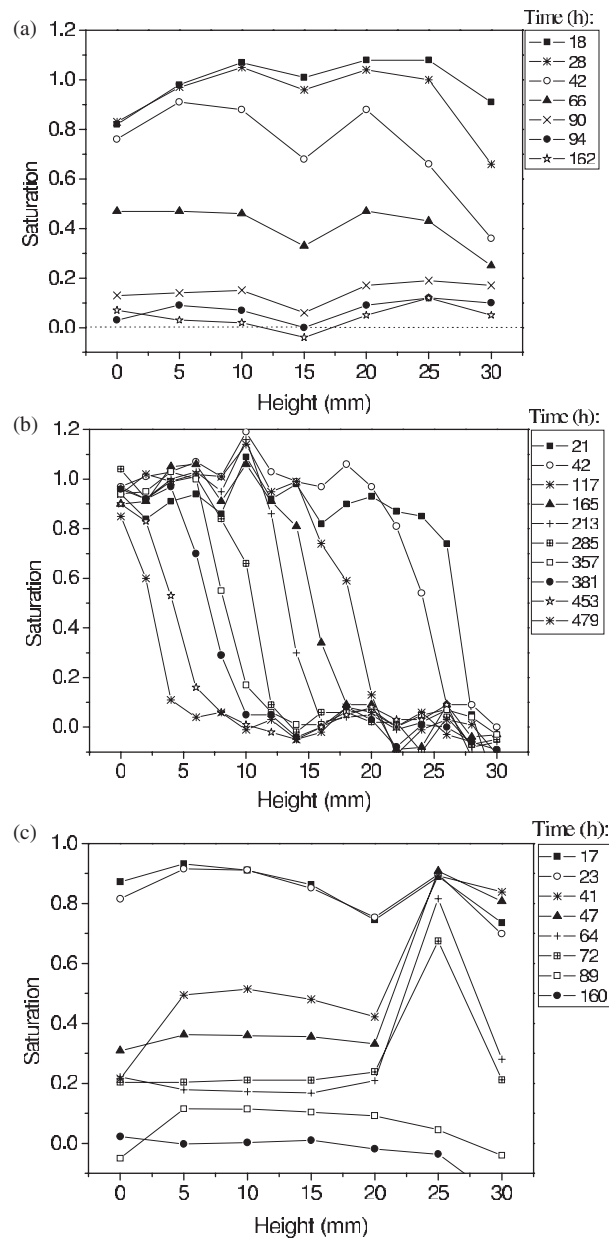


**Figure 1.** Evaporated mass of liquid as a function of time for homogeneous hydrophilic (circles), hydrophobic (squares/grey) and two-layer hydrophilic (stars) beads in the presence of an air flow on the top surface ( $0.2 \text{ m s}^{-1}$ ). The dotted line shows the linear trend in the CRP.

packing. Distilled water with a surface tension of  $\gamma = 71.9 \text{ mN m}^{-1}$  was used as the liquid phase and air as the gas phase. The water saturated porous media were dried from the top surface and in a controlled atmosphere chamber (relative humidity (RH)  $46 \pm 2\%$ , temperature ( $T$ )  $21 \text{ }^\circ\text{C}$ ) in the absence or in the presence of an air flow ( $0.2 \text{ m s}^{-1}$ ) at the top surface with the same water content and temperature. The weight of the sample with time was measured in time on an automated balance with a precision of ( $\pm 0.001 \text{ g}$ ). The saturation profiles during drying were obtained by measuring the absorption of gamma-ray radiation by the water in the sample. This is achieved by passing the sample through a gamma-ray densitometer consisting of a  $11.1 \text{ GBq}$  caesium-137 source and a NaI detector, and comparing the measured absorption at different heights in the sample with that of the fully saturated sample before drying. The uncertainty on saturation measurement is  $\pm 5\%$  of the measured value.

For hydrophilic beads the typical behaviour is that of drying at a constant rate ( $0.12 \text{ g h}^{-1}$ ) followed by a much slower drying that sets in at a very late stage, at almost complete desaturation (figure 1). The absence of an air stream also gives a constant rate of drying (CRP), but with a much slower evaporation rate ( $0.037 \text{ g h}^{-1}$ ). The critical saturation at which the CRP ends turns out to be independent of the boundary conditions (about 7%). The CRP is clearly associated with a homogeneous desaturation of the sample, i.e. there is no drying front down to very low liquid content, although there may be a slight decrease of the liquid saturation very close to the free surface of the sample (figure 2(a)). This result is similar to that obtained by Guillot *et al* [18] from MRI measurements on a drying porous rock. Moreover this result is in agreement with the simulations of Yiotis *et al* [10–12] showing that a CRP period is associated with the existence of a continuous liquid film in contact with the free surface of the sample. The spatial resolution of the measurements of the liquid distributions in the sample does not make it possible to observe how the saturation profiles evolve during the second stage of drying.

The rate of drying in the CRP for two-layer packing is similar to that for a homogeneous sample (see figure 1) [19, 20], which suggests that in the CRP some of the drying characteristics are independent of the sample structure. For hydrophilic beads, the capillary rise ensures a homogeneous distribution of the water throughout the sample. This also agrees with our data for a two-layer structure: it is observed that the capillary effects are stronger in the region of



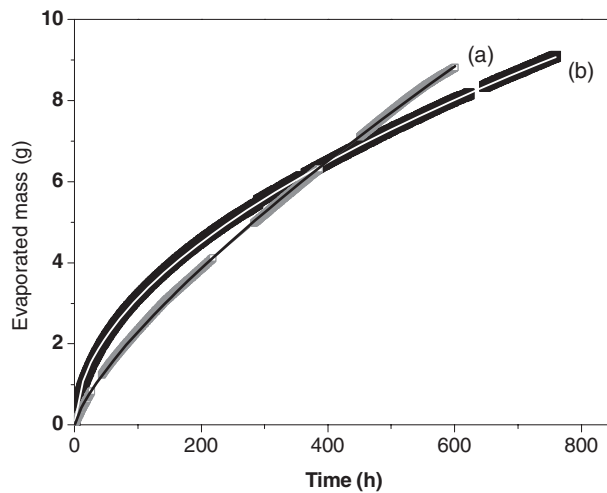
**Figure 2.** Saturation profile within the sample at different times during drying for (homogeneous) hydrophilic (a), hydrophobic (b) and two-layer hydrophilic (c) beads.

small pores, which leads to the desaturation of the bottom layer with the larger pores even if it is far from the free surface of the sample (see figure 2(c)). Thus, as long as some continuous liquid network exists throughout the porous sample drying mainly results from the liquid transport through the porous network towards the free surface of the sample. The air progressively penetrates into the sample via the formation of steady or transient continuous air networks which tend to keep the homogeneity of capillary effects throughout the sample.

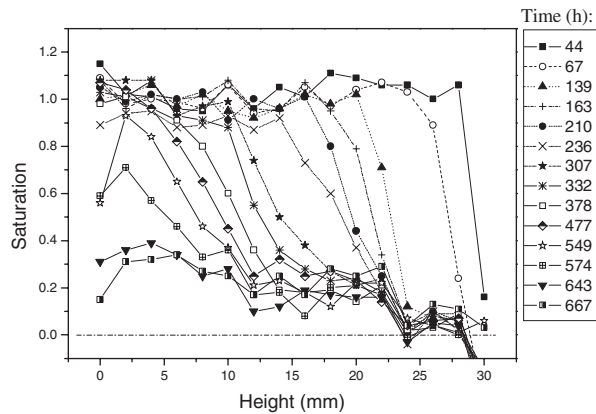
Some authors [11] identified that this period effectively corresponds to the CRP, but could not give a definite explanation for the fact that the rate of drying remains constant whereas the saturation decreases on average. It was basically suggested that the evaporation from a partially saturated porous material could be similar to that from a sample with a fully wetted free surface. This explanation relies on the theoretical work of Suzuki and Maeda [21] which showed that the evaporation from a dispersion of liquid patches on a planar solid surface is almost constant as long as the fraction of liquid–gas interface is larger than 10%. However, in a porous material the evaporation from liquid patches below the free surface of the sample must *a priori* also be taken into account. In this context it was suggested that rapidly below this surface the vapour density reaches a value close to its maximum, thus limiting evaporation [20]. The models [10–14, 16], which describe in detail the drying rate from one pore of specific shape, provide some explanation of the basic physical process at the origin of some of our observations: at this local scale there is a regime for which the film flows along particular solid surfaces making it possible to maintain a CRP while vapour transport due to diffusion from the interior remains negligible.

The results for the hydrophobic porous medium are completely different. When an air stream is blowing over the sample, the evaporation shows a much smaller drying rate for hydrophobic beads; the time to reach a saturation of approximately 25% is about ten times longer for hydrophobic than for hydrophilic beads (figure 1). The saturation profiles (figure 2(b)) also differ from those for the hydrophilic porous medium: the saturation decreases to zero close to the free surface, leading to a clear drying front that subsequently propagates into the material, and the drying rate decreases as the square root of time ( $0.52 \pm 0.02$ ). It follows that for the hydrophobic porous medium the capillary forces are not strong enough to ensure liquid transport to the surface at a rate that is comparable to the evaporation rate. The capillary rise  $2\gamma \cos \theta_a / \rho g r$ , in which  $\rho$  is the water density,  $g$  the gravity and  $r$  the typical pore radius ( $\sim 40 \mu\text{m}$ ), is only  $\sim 3.5 \text{ cm}$  in the hydrophobic medium while it is  $\sim 35 \text{ cm}$  in the hydrophilic one. Moreover, performing the classical Washburn experiments on the rate of capillary rise [22] in our water-wet and water-repellent porous media reveals that the rate of capillary rise for hydrophobic packing can be 5000 times smaller than that for hydrophilic ones. Consequently, the observation that the drying front starts at the free surface and subsequently penetrates into the porous medium suggests that it is the speed of capillary transport that is insufficient in hydrophobic media to ensure a saturation of the evaporating surface. The evaporation therefore takes place within the porous medium, and the evaporated molecules subsequently diffuse out of the porous material.

In the absence of air flow the dynamics significantly change for the hydrophobic matrix. The evaporated mass as a function of time may now be fitted by a power law behaviour with an exponent  $0.75 \pm 0.02$ , intermediate between that for the hydrophilic beads (CRP, exponent 1) and hydrophobic beads in the presence of air flow at the surface (exponent 0.5) (figure 3). This result suggests that, due to the absence of air flow and due to wetting heterogeneities, there subsists some slow locally capillary draining from the deeper regions to the top of the sample, while the rest of sample dries as usual by simple diffusion. Over long times, when the saturation becomes low the evaporation via this local capillary rise would become predominant, thus explaining the surprising fact that the total evaporated mass becomes larger without the air flow than with it. Although the resolution of our gamma-ray measurement is not sufficient to reach a definitive conclusion, our data concerning the saturation profiles in time seem to confirm this interpretation (figure 4): for most of the drying period the porous medium just below the surface remains saturated between 10 and 30% even over long times, in contrast with the result with air flow for which the saturation is zero as soon as the drying front has passed.



**Figure 3.** Evaporated mass of liquid as a function of time for a hydrophobic porous medium (a) without air flow and (b) in the presence of an air flow on the top surface ( $0.2 \text{ m s}^{-1}$ ).



**Figure 4.** Saturation profile within a sample at different times during drying of a hydrophobic porous medium in the absence of air flow at the surface.

These results show the major role played by both the wetting properties of the porous matrix and the boundary conditions (presence or absence of an air flow) on the drying process. The rate of evaporation reduces significantly between a hydrophilic porous medium and a hydrophobically treated identical porous structure. The evaporation kinetics of a hydrophobic porous medium is slower because of the small capillary rise related to the wetting heterogeneities (partially wetted surface). If the evaporated surface is no longer wetted by the liquid (corresponding to a receding drying front), the evaporated molecules have to be transported by a diffusion process. A surprising result of the competition between localized capillary rise and diffusion is that over long times the evaporation rate can become smaller with air flow than without. Due to air flow the initial drying rate at the surface is large and capillary transport remains insufficient to maintain liquid at the evaporating surface and hence ensure a partially wetted medium. Consequently, drying becomes governed by diffusion only associated with a receding (dry) front.

The authors are indebted to S Bichon and P Vié for their precious technical support and to X Chateau for fruitful discussions.

## References

- [1] Cardiano P *et al* 2005 *Polymer* **46** 1857–64
- [2] Ballester M A D and Gonzalez R F 2001 *Prog. Org. Coat.* **43** 258–66
- [3] Keey R B 1972 *Drying Principles and Practice* (Oxford: Pergamon)
- [4] Suleiman A A and Ritchie J T 2003 *Soil Sci. Soc. Am. J.* **67** 377
- [5] Van Brakel J 1980 *Adv. Drying* **1** 217–67
- [6] Coumans W J 2000 *Chem. Eng. Process.* **39** 53–68
- [7] Le Bray Y and Prat M 1999 *Int. J. Heat Mass Transfer* **42** 4207
- [8] Shaw T M 1987 *Phys. Rev. Lett.* **59** 1671
- [9] Laurindo J B and Prat M 1996 *Chem. Eng. Sci.* **51** 5171
- [10] Yiotis A G *et al* 2003 *Phys. Rev. E* **68** 037303
- [11] Yiotis A G, Boudouvis A G and Stubos A K 2004 *AIChE J.* **50** 2724–37
- [12] Yiotis A G *et al* 2005 *Transp. Porous Media* **58** 63–86
- [13] Eijkel J C T *et al* 2005 *Phys. Rev. Lett.* **95** 256107
- [14] Prat M and Bouleux F 1999 *Phys. Rev. E* **60** 5647
- [15] Coussot P 2000 *Eur. Phys. J. B* **15** 557–66
- [16] Van Brakel J and Heertjes P M 1977 *Powder Technol.* **16** 75–81
- [17] Shahidzadeh-Bonn N *et al* 2004 *Transp. Porous Media* **56** 209
- [18] Guillot G *et al* 1989 *J. Phys. D: Appl. Phys.* **22** 1646
- [19] Coussot P *et al* 1999 *C.R. Acad. Sci. Paris* **327** 1101–6
- [20] Petkovic J *et al* 2005 *Restoration of Building Monuments* **11** 97
- [21] Suzuki M and Maeda S 1968 *J. Chem. Eng. Japan* **1** 26–31
- [22] Washburn E W 1921 *Phys. Rev.* **17** 374