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Dynamic Contact Angles, Wettability and Capillary Suction of Hydrophobic Porous Materials

G. Houvenaghel and J. Carmeliet
Laboratory of Building Physics, Dept. of Civil Engineering, Faculty of Applied Science, Leuven, Belgium

Abstract

The wettability of a porous material by liquid water is generally characterized in terms of the contact angle that the liquid makes with the surface. Young’s equation is used to predict wetting and adhesion properties of the porous material by calculating the solid vapor surface tension. It was found that in practice a range of contact angles - rather than a single one - is experimentally possible, and that these change over time. In this paper the experimentally observed droplet dynamics, linked to linked effectiveness of the hydrophobic treatment as expressed by the reduction of the capillary sorption coefficient, are explained. The compatibility of a hydrophobic agent with the pore structure of the porous material is found to be of major importance: a monomer hydrophobic agent is found to be more effective on a porous material with a broad pore range as calcium silicate than an oligomer one. Formulating the findings in the perspective of practical application, a hydrophobic treatment should promote droplet beading and quick run-off of driving rain shortening droplet contact time. In this way microscopic spreading phenomena and film forming are reduced, and capillary suction and possible rain penetration through cracks are impeded.

1 Introduction

The wettability of a porous material by liquid water is generally characterized in terms of the contact angle that the liquid makes with the material surface. Using Young's equation, wetting and adhesion properties of the porous material can be predicted by calculating the solid-vapor surface tension. The contact angle is considered as a measure of hydrophobicity of the surface. A surface is said to be non-wetting and hydrophobic when the contact angle between a water droplet and the surface exceeds 90°. It is generally assumed that in case of a hydrophobic surface the water droplet is not capillary absorbed by the porous material and that it will easily run off the surface.

In practice we found that a whole range of contact angles - rather than a single one - is experimentally possible and that they change over time, although the wetted surface area remains constant. It was observed that the droplet dynamics are related to the effectiveness of the hydrophobic treatment as determined by the reduction of the capillary sorption coefficient. In this paper, we try to explain the above relation between contact angle, droplet dynamics and the effectiveness of the hydrophobic treatment of the porous material.

Finally, we formulate the findings in the perspective of practical application. A hydrophobic treatment should promote droplet beading and quick run off of driving rain. A good compatibility between the pore structure of the porous material and the polymer chain length of the hydrophobic agent is of major importance.

2 Contact Angle, Wettability and Young's Equation

The wettability of a porous material by liquid water is generally characterized in terms of the contact angle formed at the solid-liquid interface. The equation of state of these phenomena is described by Young's equation, which relates the surface and interfacial tensions of the liquid and the solid to the contact angle (Figure 1):

$$\sigma_{ls} + \sigma_{lv} \cdot \cos\gamma = \sigma_{sv} \tag{1}$$

with σ_{ls}, σ_{lv} and σ_{sv} the interfacial tensions at the boundaries between the liquid (l), the solid (s) and the vapor phase (v). Here σ represents the energy required to create a unit surface area of a given interface, provided that - in the case of σ_{sv} - mechanical distortion and strains are negligible.

Using Young's equation, we can predict wetting and adhesion properties of the porous material by calculating the solid-vapor surface tension σ_{sv} or the water adhesion tension τ_{lv} which is defined as:

$$\tau_{lv} = \sigma_{lv} \cdot \cos\gamma \tag{2}$$

with σ_{lv} the water interfacial tension = 0.0725N/m at 20°C.

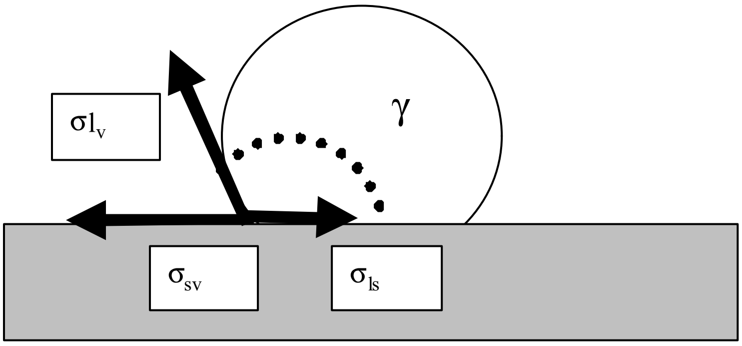


Figure 1: Definition of contact angle

Despite the success in offering insight into the wettability and spreading phenomena, Young's equation has been subject of considerable controversy and discussion. [1] Young's equation gives a unique equilibrium contact angle γ, supposing the absence of external fields (e.g. gravitational fields) and of substrate deformation due to the solid-fluid interaction forces (e.g. capillary forces and the equilibrium force compensating $\sigma_{lv}\sin\gamma$). Young's equation only yields for ideal surfaces that are perfectly smooth, homogenous, insoluble and devoid of all chemical and structural inhomogeneities. In many solid-liquid systems, a thin precursor film due to local intermolecular interactions spearheads the liquid front. As the liquid film becomes thinner a sharp distinction between solid, liquid and vapor phase can no longer be assumed and the microscopic contact angle no longer obeys Young's equation since the continuum concept of surface energies to represent the local molecular interactions becomes increasingly tenuous for precursor films approaching molecular thickness.

Wettability is related to the self-association of water. Self-association of water molecules in the liquid phase results from the polar interaction between the water molecules, causing a more-or-less ordered three-dimensional hydrogen-bonded network. The importance of this last property is that localized perturbations in water chemical potential (e.g., at the boundaries of a droplet) may induce compensating changes in water properties over considerable distances from the point of origin of the perturbation. Surface hydrophobicity results predominately from the state of water self-association in contact with a non-polar surface. Churaev [2] finds that water structure at modestly-wettable surfaces, within the range of $15° < \gamma < 40°$, corresponds approximately to bulk water structure, while it increases with decreasing water wettability, and thus increasing partial molar volume.

The key measure of water structure, and hence of wettability, is the contact angle and its expression in terms of water adhesion tension rather than parameters computed from various theories, such as surface free energy γ_s and Zinsman's critical surface energy γ_c. [3]

The contact angle as given by Young's equation is a static equilibrium angle. However, we observed that a liquid droplet on a hydrophobic surface shows a broad range of contact angles changing in time. The contact angles measured are apparently dynamic contact angles. [4]

3 Materials

Two hydrophobic agents are analyzed: an oligomer alkyl-alkoxysilane (OA) and a monomer alkyl-alkoxysilane (MA). The active ingredient of the momomer agent is isobutyl-tri-ethoxysilane. The active groups of the oligomer agent are octyl groups. The alkyl-alkoxysilane (R-Si-$(OCH_3)_3$) readily hydrolyses to silanol (-Si-OH). The silanol groups react mutually forming a three dimensionally cross-linked polysiloxane (-Si-O-Si-) network chemically anchored to the porous surface. The oligomer is supposed to have a higher crosslinking ratio than the monomer.

Two porous building materials are studied: ceramic brick (CB) and sand-lime brick, i.e., calcium silicate (CS). The ceramic brick is a Belgian red fired pressed clay brick. The sand-lime brick is made with sand (SiO_2) as an active granulate and hydrated lime ($Ca(OH)_2$) as a binder. By autoclave hardening at elevated temperature θ ($110<\theta<225°$) and saturated vapor pressure p_{sat} ($1.43\ 10^5<p_{sat}<25.8\ 10^5$ Pa), a CaO-SiO_2-H_2O system is built which gives the material its strength. Figure 2 gives the pore volume distributions for both materials. The ceramic brick shows a primary coarse pore system and a less important secondary fine-texture pore system in the hygroscopic range. The pore volume distribution of calcium silicate is characterized by a broad pore system including fine (10^{-10} to 10^{-8}m) and mid-size (10^{-8} to 10^{-6}m) pores in the hygroscopic and capillary range and an important coarse pore system (10^{-6}-10^{-4}m) in the capillary range.

Comparing the range of the polymer lengths (OA 10^{-8} to 10^{-7}m, MA 10^{-10} to 10^{-9}m) to the pore size distribution, we expect the polysiloxane chains not to develop in the total pore space but leaving the finer pore system (10^{-10} to 10^{-8} m) untreated. Due to the statistical nature of the polymerization process the transition from treated to untreated pores is not abrupt at a fixed pore radius but gradually spread out over a broader pore range.

Calcium silicate shows an important fine and mid-size pore system; hence a higher percentage of untreated and partially treated pores will be found. Since the monomer alkyl-alkoxysilane has a shorter polymer length than the oligomer alkyl-alkoxysilane, the latter one is expected to be less effective for this material. As shown in the next section, droplets disappeared in less than 500 seconds for calcium silicate treated with silane but after 800 seconds if treated with a siloxane. On cera-

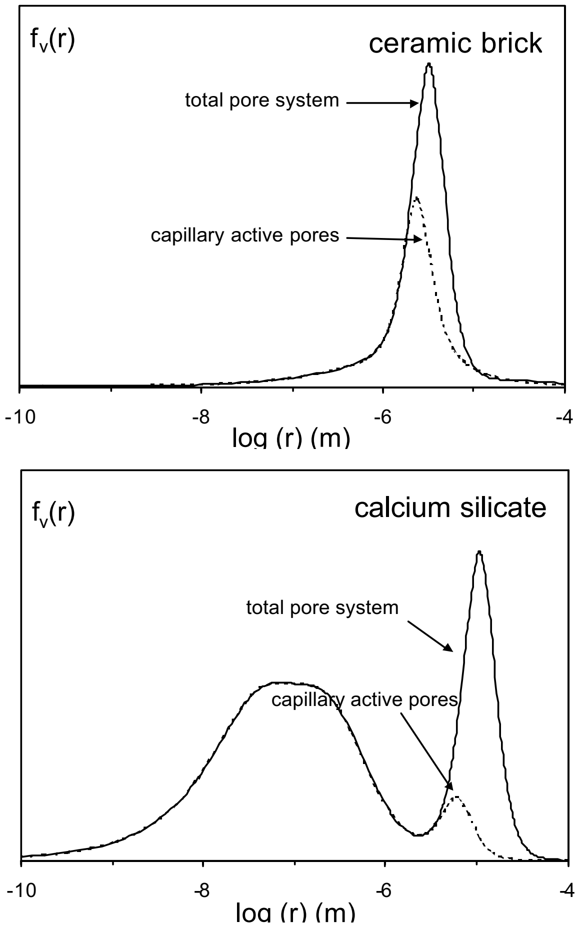


Figure 2: Pore size distribution of calcium silicate and brick

mic brick having mainly a coarse pore system, a hydrophobic treatment is expected to be more effective since nearly all pores are accessible for the polymers. Experimental verification of the effectiveness of the hydrophobic treatment expressed by the reduction of the capillary sorption coefficient is given by Carmeliet et al. [5, 7].

Prior to the hydrophobic treatment, thin samples (95x45x5mm) are conditioned during two weeks at 25°C and 75% RH to an average moisture content which corresponds to actual moisture contents found in practice (0.75kg/m^3 for CB and 18.1 kg/m^3 for CS). The hydrophobic agent is applied by capillary suction. After the hydrophobic treatment, the specimens are conditioned during two weeks at laboratory conditions (25°C and 65% RH) in order to obtain full polymerization.

4 Measurement Data

The contact angles are measured using the optical sessile drop method. Droplets of 1µl ultra-pure water (18MΩcm^{-1}) are placed on the treated surface. The contact angle is determined from photovisual images. The shape of the drop is fitted to an ellipse and both left and right contact angle are calculated as the angle between the baseline droplet-surface and the tangent to the ellipse. Ellipse fitting is preferred to circular fitting since it gives better results for irregular drop shapes and for drops over a wide range of contact angles and it is much faster than Laplace fitting.

In practice, a whole range of contact angles is found starting at about 110 to 130° for calcium silicate and at about 110 to 120° for ceramic brick. The contact angles are found to vary with time and for both materials it was observed that the droplet disappeared in less than 850 seconds. Figure 3 gives the contact angle as a function of time for ceramic brick and calcium silicate treated with the two hydrophobic agents. Table 1 summarizes the contact angle measured at t = 5 sec for both brick and calcium silicate.

Visual observation showed that the initially wetted contact area between droplet and porous material stays constant in time. This indicates that there is no droplet spreading, as can be seen in the photographic series of a droplet as a function of time (Figure 4). In the beginning, the base radius of the droplet stays constant with declining contact angle, while afterwards both the base radius and the contact angle decrease as a function of time.

For non-hydrophobic brick a very steep increase of the contact angle as a function of time is recorded. The base radius of the droplet increases as a function of time, corresponding to the spreading out of the droplet. The contact angle on brick treated with the monomer agent (MA) shows a quick decrease during the first seconds, thereafter the decrease is comparable to that on brick treated with the oligomer agent (OA).

Table 1: Initial contact angles, mean and (standard deviation)

	Silane (MA)	Siloxane (OA)
Ceramic brick	112.1° (7.4°)	114.2° (6.8°)
Calcium silicate	117.6° (7.6°)	134.7° (13.7°)

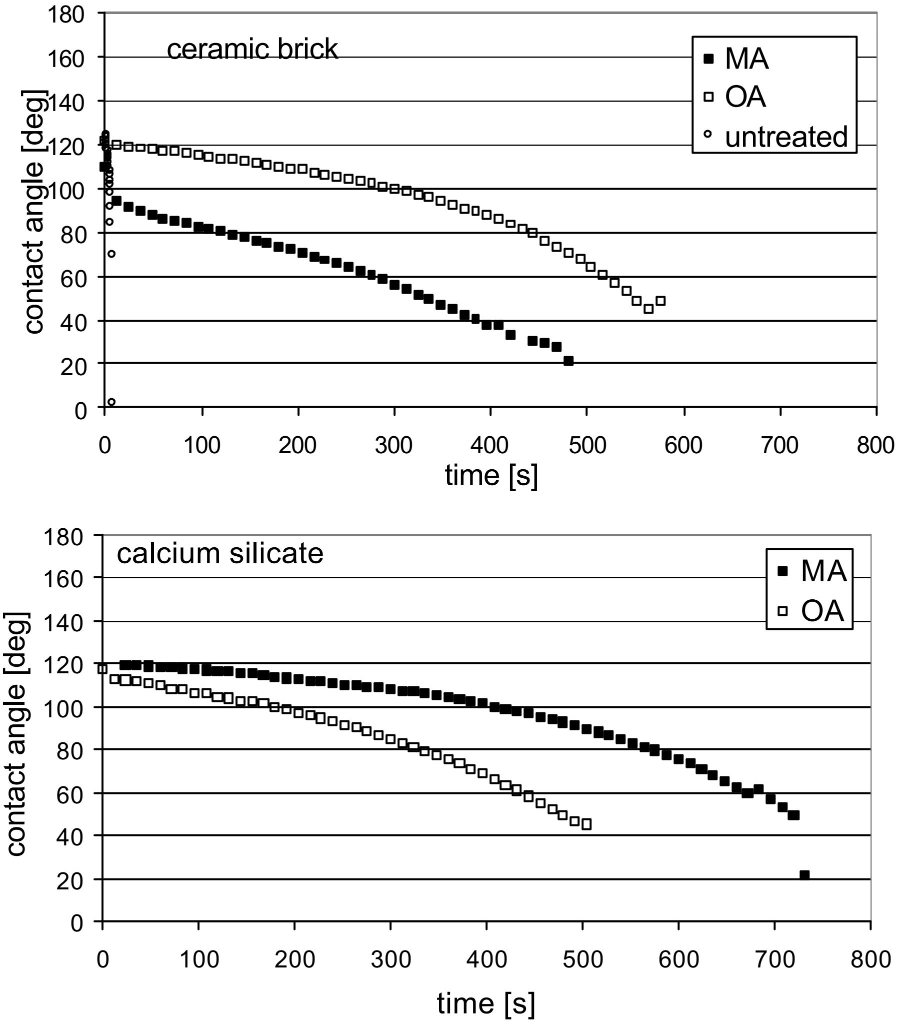
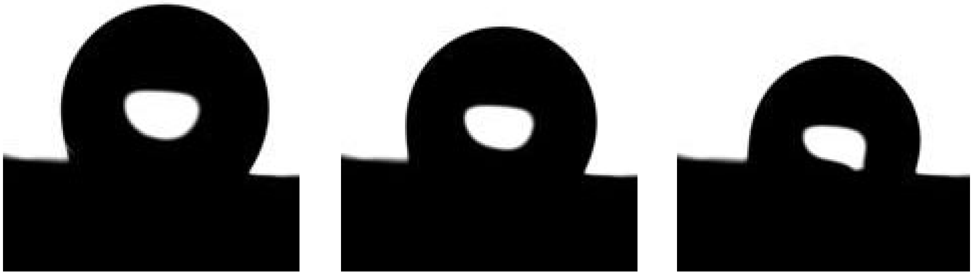


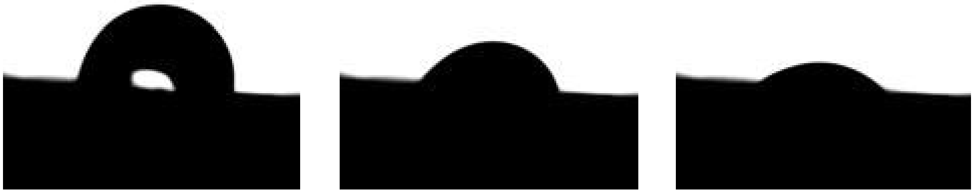
Figure 3: Contact angle as a function of time for ceramic brick and calcium silicate treated with an oligomer (OA) and a monomer (MA) alkyl-alkoxysilane

5 Discussion

The large standard deviation obtained for the initial contact angles (Table 1) is due to heterogeneities both in the surface smoothness and the local effectiveness of the hydrophobic treatment. The initial contact angle is not an unambiguous indication of the effectiveness of the hydrophobic treatment. Calcium silicate treated with siloxane (OA) has a higher capillary absorption coefficient and higher adsorption



t = 2 sec γ = 120.8° t = 114 sec γ = 114.1° t = 244 sec γ = 103.5°



t = 357 sec γ = 91.0° t = 467 sec γ = 63.2° t = 526 sec

Figure 4: Droplet as a function of time, calcium silicate treated with silane (MA)

rates than calcium silicate treated with silane (MA). [5, 7] So a siloxane treatment is less effective than a silane one, although the latter shows smaller contact angles at t=0 sec.

The decrease in contact angle is related to the decrease of the droplet volume as a function of time. The decrease of the droplet volume is caused by several mechanisms, such as droplet evaporation and capillary absorption into the porous material. Using macroscopic properties to model the capillary absorption of liquid water from the droplet into the pore system [6] and taking into account the evaporation of the droplet, a droplet lifetime much higher than 850 seconds is attained. This indicates that other microscopic phenomena occur, for which we propose the following scenario. Due to statistical effects water molecules escape from the droplet leading to a temporary adsorption on the hydrophobic surface, thereby changing the delicate balance between short- and long-range forces. The long-range attraction forces cause an increased adsorption on the hydrophobic surface resulting in droplet spreading and surface wetting. From a macroscopic point of view, adsorbed water vapor on the solid's surface favors a decrease of the solid-vapor surface tension and, according to Young's equation, decreased contact angles. In a second step surface wetting promotes the adsorption of water vapor on the pore walls in the inner material. Experimental proof of capillary adsorption in hydrophobic materials and of the adsorption process leading to capillary condensation starting primarily in the finer and midsize pores, introducing capillary forces and microscopic liquid transfer, is given by Carmeliet et al. [5, 6, 7]. The decrease of the droplet volume, and hence of the contact angle, results from the delicate balance between evaporation, capillary absorption and microscopic phenomena which are controlled by the equilibrium between short- and long-range forces.

When a droplet is placed next to an area that has been wetted by a previous droplet, it was observed that the base of the new droplet also spreaded out over the previously wetted zone. This is due to the changed balance between short- and long-range forces and the enhanced adsorption capacity of the previously wetted zone. On a macroscopic scale this phenomenon favors the formation of a water film on the hydrophobic surface. From this water film capillary water uptake and water penetration through cracks can take place.

Figure 3 indicates that the change of contact angle as a function of time depends on the hydrophobic product used. The time evolution of the contact angle on calcium silicate with a silane treatment is slower than that on calcium silicate with a siloxane treatment, resulting in a longer droplet lifetime. On calcium silicate a silane (MA) treatment is found to be more water repellent then a siloxane (OA) treatment, due to the poorer compatibility between the pore structure and the polymer size range of the hydrophobic, which was also found by Carmeliet et al. [5, 7]. The siloxane (OA) is not able to penetrate into the finer pores, so these stay active for capillary absorption. In the case of ceramic bricks, the silane was found to be slightly less effective than the siloxane. Figure 3 shows that the contact angle of a droplet on a silane (MA) treated brick changes quickly during the first seconds in order to reach a new equilibrium state and from then on the change of the contact angle is parallel to that of a droplet on a siloxane (OA) treated brick. These findings confirm that the silane is slightly less effective than the siloxane.

Monitoring of real driving rain has shown that more than 50% of the total driving rain amount on a hydrophobic surface can get left on the surface [8]. The results obtained in this study show that considering driving rain loading on a hydrophobic material to be a pressure imbibition problem oversimplifies the complexity of rain penetration control. Experimental set-ups, such as the Karsten pipe, only consider pressure imbibition and do not allow for droplet beading and related effects. Therefore these tests do not reflect real driving rain solicitation and should be interpreted with care.

From the above measurements, we can conclude that a rain penetration control by hydrophobic treatment should promote droplet beading and a quick run-off of the driving rain. In this way the contact time of a droplet is shortened, the microscopic spreading phenomena, film forming, capillary suction and possible rain penetration through cracks are impeded. When rain droplets start to spread forming a liquid water film on the outer surface, a hydrophobic treatment should sufficiently reduce the capillary water absorption and prevent rain penetration through cracks.

6 Conclusions

A monomeric hydrophobic agent gives better results on calcium silicate than an oligomer one. On brick the oligomer hydrophobic agent performs slightly better. The proposed scenario of droplet dynamics explains the experimentally observed effectiveness of hydrophobic treatments. It also allowed to explain the differences between ceramic brick and calcium silicate, highlighting the important issue of compatibility of a hydrophobic agent with the pore structure of a porous material.

Rain penetration control by hydrophobic treatment should promote droplet beading and a quick run-off of the driving rain thus shortening droplet contact time. In this way microscopic spreading phenomena and film forming are reduced, and capillary suction and possible rain penetration through cracks are impeded.

7 References

1. Asthana, R./Sobczak, N. (2000): *Wettability, spreading, and interfacial phenomena in high-temperature coatings*, JOM-e **52**.
2. Churaev, N.V. (1995): Adv. Colloid Interface Sci. 58, p. 87.
3. Vogler, E.A. (1998): *Structure and reactivity of water at biomaterial surfaces*. In: Advances in Colloid and Interface Science **74**, pp. 69-117.
4. Marmur, A (1992): *Contact angle equilibrium: the intrinsic contact angle*. In: J. Adhesion Sci Technology **6**, pp. 689-701.
5. Carmeliet, J./Houvenaghel, G./Roels, S. (2001): *Moisture phenomena in hydrophobic porous materials*. Baskaran, A., ed., Proceedings of International Conference on Building Envelope Systems and Technologies, NRC, Canada.
6. Carmeliet, J./Roels, S. (2000): *On the physics of adsorption, capillary condensation and drying of hydrophobic porous building materials*. Wittmann, F.H. and Verhoef, L.G.W., eds. Proceedings of the International Workshop on Urban Heritage and Building Maintenance IV, Maintenance and Restrenghtening of Materials and Structures, Freiburg.
7. Carmeliet, J. (2001): *Moisture phenomena in hydrophobic porous materials*. Proceedings of Hydrophobe III - Third International Conference on Surface Technology with Water Repellent Agents, Hannover, to appear.
8. Blocken, B./van Mook, F.J.R./Hagentoft, C.-E./Carmeliet, J. (2001): *A status report of numerical-experimental driving rain studies on 3 full-scale buildings*. Wisse, J./Kleinman, K./Gerrits, C. and de Wit, M., eds., Proceedings of the Third European & African Conference on Wind Engineering, Eindhoven University of Technology.