Hydrophobe III -
3rd International Conference on Surface Technology with Water Repellent Agents,
Aedificatio Publishers, 171–178 (2001)

Water Transport—Liquid and Vapour—in Porous Materials: Understanding Physical Mechanisms and Effects from Hydrophobic Treatments

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Abstract

Rain penetration control by hydrophobic treatments should be regarded as a two-step measure. A hydrophobic treatment should first promote droplet beading and quick run-off of driving rain. Then, when rain droplets start to spread and to form liquid water films on the outer surface, it should sufficiently reduce capillary water uptake and prevent rain penetration through cracks. Faced with the risk of local water ingress through cracks reaching beyond the hydrophobic layer, hydrophobic treatments should be designed with a sufficient drying potential. Based on a detailed analysis of experimental results, the requirements needed to comply with these performance criteria are formulated for hydrophobic agents.

1 Introduction

The aim of a hydrophobic treatment is to prevent rain penetration through outer walls. Since rain penetration control is commonly conceived as a pressure imbibition problem, assessment methods for hydrophobic treatment, such as the Karsten pipe method, are based on controlling the reduction of the water uptake (under pressure).

However, recent monitoring of real driving rain has shown that phenomena such as droplet beading and run-off may significantly influence the real driving rain load on the wall [1]. It will be shown that droplets sticking on a hydrophobic surface with a contact angle greater than 90 degrees tend to spread and form a liquid water film in a given time span. The formation of this film allows both water uptake and water penetration through cracks, to occur. These findings indicate that considering driving rain loading on a hydrophobic material as a pressure imbibition problem oversimplifies the complexity of rain penetration control. In this perspective, rain penetration control by hydrophobic treatment should be regarded as a two-step measure. First, a hydrophobic treatment should promote droplet beading and quick run-off of driving rain, thus shortening the contact time of a droplet and hindering film formation, capillary absorption and possible rain penetration through cracks. Second, when rain droplets start to spread and to form liquid water films on the outer surface, a hydrophobic treatment should sufficiently reduce capillary water uptake and prevent rain penetration through cracks. Faced with the risk of local water ingress through cracks beyond the hydrophobic layer and for related moisture damage processes, hydrophobic treatments should be designed with sufficient drying potential: i.e. lowest possible increase in water vapour resistance.

In this paper, we try to explain the correlation between surface wetting, reduction of capillary absorption and increase in water vapour resistance by a hydrophobized porous material. The hydrophobic agent studied is an oligomeric alkyl-alkoxysilane ($R\text{-}Si\text{-}(OCH_3)_3$), which readily hydrolyses to silanol (-Si-OH). The silanol groups interreact to form a three dimensionally crosslinked polysiloxane (-Si-0-Si-) network chemically anchored to the porous surface. The active (R) groups, responsible for the hydrophobic effect, are octyl groups $(CH_2)_7\text{-}CH_3$.

Two porous building materials are studied: ceramic brick (CB) with a coarse pore structure and calcium silicate (CS), which is characterised by a broad pore system including fine pores [10^{-10}-10^{-8} m], mid-size pores [10^{-8}-10^{-6} m] and coarse pores [10^{-6}-10^{-4} m] (figure 1). Comparing the range of polymer lengths of the hydrophobic compound [10^{-8}-10^{-7} m] with the pore distribution, we expect the polysiloxane chains not to develop within the finer pore system [10^{-10}-10^{-8} m] leaving these untreated (see figure 2). Due to the statistical nature of the polymerisation process, the transition of untreated to treated pores is not abrupt at a given pore radius but gradually spreads out over a broader pore size range. In this transitional pore size range, the pore walls will

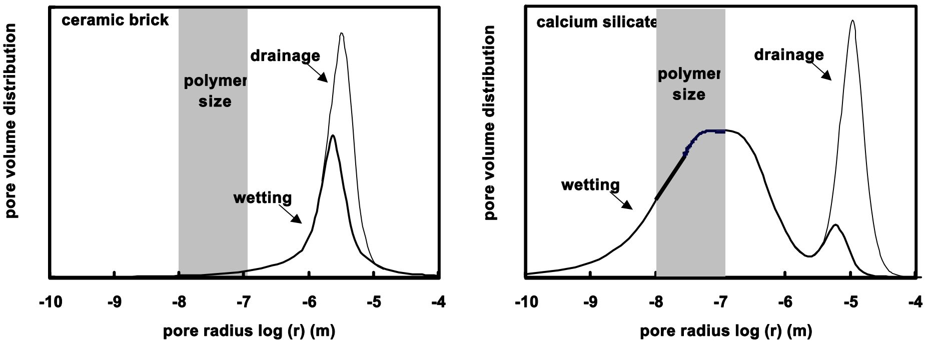

Figure 1: Pore volume distribution $f_V(r)$ for wetting and drying. The wetting curve represents the distribution of pores filled by liquid water during capillary absorption.
a) Ceramic brick. b) Calcium silicate.

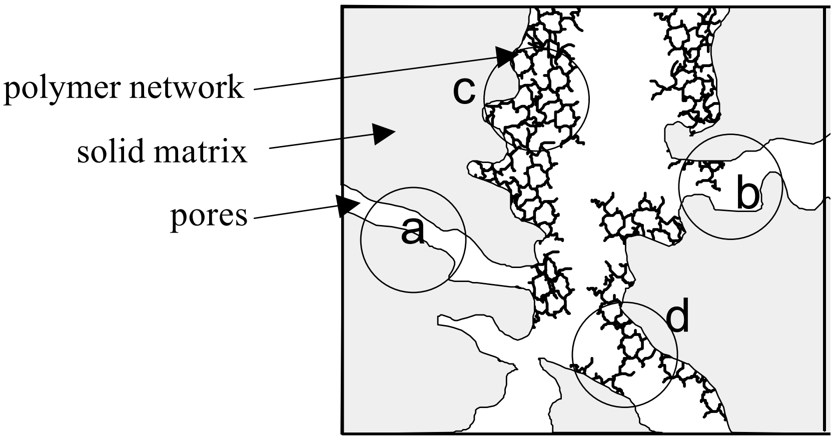

Figure 2: Schematic representation of a polymer network in the pore structure Polysiloxane chains cannot develop in the finer pore system leaving these pores untreated (a). In the coarse pores, the development of the chains on the pore walls results in a pore section reduction (c). In the intermediate pores partly covering (b) or clogging (d) may occur.

be partly covered by polymer. Since calcium silicate is characterised by an important fine and midsize pore system, a larger percentage of untreated or partly treated pores will be found. Ceramic brick with mainly a coarse pore system will be more easily accessible to the polymer chains. Therefore a more effective hydrophobic treatment of ceramic brick compared to calcium silicate is to be expected.

2 Contact angles, Wettability and Capillary Absorption

The wettability of porous material by liquid water is generally characterised in terms of the angle of contact that liquid water makes with the surface. The contact angle, γ, is defined by Young's equation

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

where σ_{lv}, σ_{ls} and σ_{sv} are the interfacial tensions at the boundaries between liquid (l), solid (s), and vapour (v). The contact is measured by optical inspection and issued as a measure of the hydrophobicity of the surface. Using Young's equation, we can predict wetting and adhesion properties of the porous material by calculating the solid-vapour surface tension. The surface is said to be non-wetting and hydrophobic when the contact angle of a water droplet with the surface is greater than 90°. Then, it is generally assumed that the water droplet is not absorbed by capillarity of the porous material and will easily run off the surface.

Young's equation is based on the (rapid) equilibrium of an axi-symmetric water droplet on a flat, horizontal, smooth, homogeneous, isotropic and rigid solid.

In practice, it was found that a whole range of contact angles is experimentally possible and that these will change over time leading to spreading of the liquid droplet (Figure 3). Both for ceramic brick and calcium silicate, it was observed that droplet spreading and surface wetting is attained in less than 800 seconds (Figure 4). The water of the droplet is finally absorbed by capillarity into the outer layer of the sample. Figure 4 also indicates that droplet spreading depends on the hydrophobic product used (CBs is a monomeric alkyl-alkoxysilane). From monitoring of real driving rain it was found that over 50 % of the total driving rain amount (on a five month measuring period) can remain on a hydrophobic surface [1]. Therefore, droplet spreading, surface wetting and capillary absorption are very likely to occur in practice.

To try to explain the droplet spreading, surface wetting and water uptake by the hydrophobic treated porous material the following scenario is proposed. First, because of statistical effects, water molecules escaping from the water droplet lead to a temporary adsorption on the hydrophobic surface, thereby changing the delicate balance between short-range and long-range forces. The long-range attractive forces become dominant leading to an increased adsorption and wetting of the hydrophobic surface. From a macroscopic point of view, if water vapour is adsorbed on the solid's surface, the surface tension solid-vapour decreases and according to Young's equation, the contact angle decreases leading to an increased wetting of the surface. In a second step, surface wetting subsequently promotes the adsorption of

t=61 s. γ=113° t=364 s. γ=86° t=482 s. γ=69° t=629 s. γ=26°

Figure 3: Droplet spreading and contact angle g as a function of time on hydrophobic treated calcium silicate

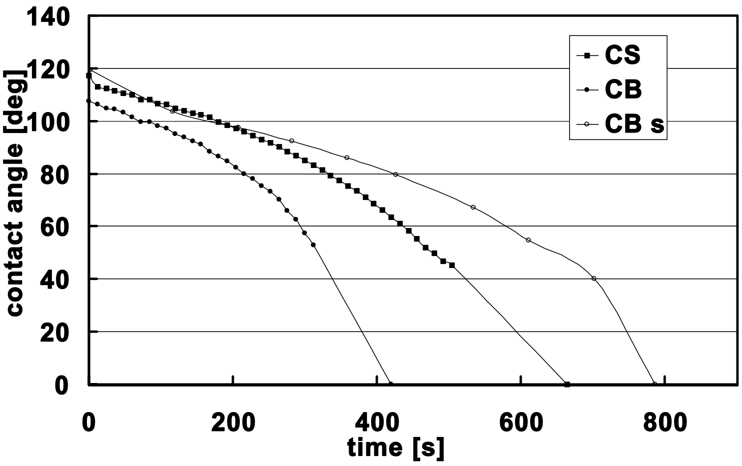

Figure 4: Contact angle γ as a function of time for hydrophobic Ceramic brick (CB), hydrophobic Calcium silicate (CS) and hydrophobic brick (product 2) CBs.

water vapour on pore walls inside the material. Experimental proof is given by the following: adsorption process leads to capillary condensation starting primarily in the fine and midsize pores, introducing capillary forces and microscopic liquid water transfer.

3 Adsorption, capillary absorption and water vapour resistance factor

The effectiveness of the hydrophobic treatment is evaluated by measuring the reduction of liquid water uptake in a capillary absorption experiment. The treated specimens have a hydrophobic zone at the bottom showing a height equal to the penetration depth d_p. Table 1 compares the capillary absorption coefficients A_{cap} for both the untreated and treated specimens. We observe that the hydrophobic treatment

A_{cap} ($kg/m^2s^{0.5}$)	untreated	treated	d_p (mm)
CB	0.18	0.000062	7
CS	0.043	0.0013	4

Table 1: Capillary water absorption coefficient

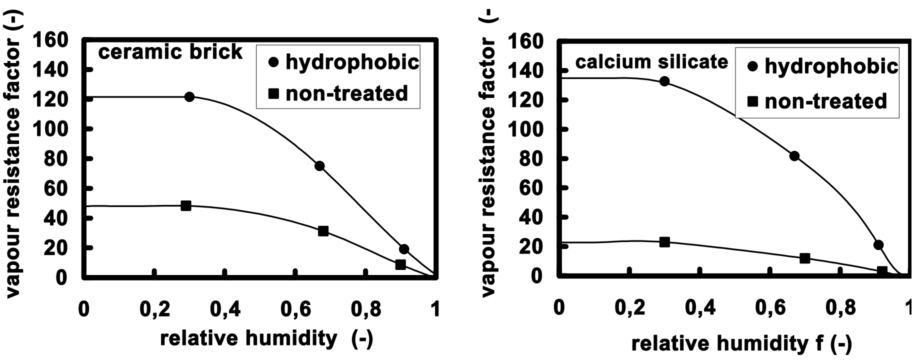

Figure 5: Water vapour resistance factor as a function of relative humidity for untreated and hydrophobic material

of ceramic brick works perfectly. For calcium silicate we observe a reduction of the capillary absorption coefficient by a factor of 40. This observation indicates that in calcium silicate finer pores remain capillary active after hydrophobic treatment, while for ceramic brick the capillary pores are blocked.

Water vapour resistance tests on treated and untreated ceramic brick and calcium silicate show that the water vapour resistance factor increases, with respect to the dry state, by a factor of 2 for ceramic brick, and by a factor of over 6 for calcium silicate (Figure 5). Possible explanations for this increase are:

- the reduction of available pore sections for diffusion because of the polymer network growth on pore walls (see Figure 1);
- the decrease of pore connectivity due to clogging of pore connective chambers;
- the shift towards less effective water vapour diffusion transfer mechanisms (e.g. from free diffusion to mixed or Knudsen diffusion).

We quantified these different effects using pore scale models [2] indicating that the decrease of connectivity due to clogging by polymer networks is the major source for the observed vapour resistance increase.

In Figure 5 a decrease of the water vapour resistance factor with increasing relative humidity for both untreated and hydrophobic material can be observed. The increase of the water vapour resistance factor in untreated materials is commonly attributed to microscopic liquid flow transport occurring in adsorbed liquid water sites and capillary condensed regions. The above observations suggest that adsorption and capillary condensation also occur on hydrophobic materials. To confirm this observation sorption isotherm experiments were performed on untreated and hydrophobized specimens [3]. The measurements confirmed that both untreated and hydrophobic materials adsorb water however, the hydrophobic treatment leads to a somewhat lower moisture contents. The S-shape of the curves indicates that capillary condensation most likely occurs in the pore space of the hydrophobic material.

These experiments lead to the conclusion that adsorption, capillary condensation and microscopic capillary absorption processes are still active in hydrophobic materials especially in fine pore systems. On the other hand, capillary absorption experiments showed the effective reduction of capillary uptake of liquid water. Combining the above observations, we conclude that an effective hydrophobic treatment should combine two mechanisms: (1) capillary condensation, capillary absorption, and liquid water transfer should be blocked in the coarser pores; (2) capillary condensation, capillary absorption, and liquid water transfer should still be active in the fine porous system, resulting in an enhancement of the unsaturated permeability. Enhancement of the water vapour permeability is favourable, since it promotes the drying out of water from the bulk material through the hydrophobic zone. This delicate balance between blocking and enhancing unsaturated moisture flow highly depends on the compatibility between pore structure and polymer size range of the hydrophobic product.

4 Conclusions

Rain penetration control by hydrophobic treatment should be regarded as a two-step measure. First, a hydrophobic treatment should promote droplet beading and quick run off of driving rain, in this way shortening the contact time of a droplet and impeding film forming, capillary absorption and possible rain penetration through cracks. Second, when rain droplets start to spread and to form liquid water films on the outer surface, a hydrophobic treatment should sufficiently reduce capillary water uptake and prevent rain penetration through cracks. We showed that an optimal hydrophobic product should: (1) show slow droplet spreading dynamics facilitating run-off of driving rain; (2) allow controlled water adsorption, capillary condensation and microscopic liquid water flow in a limited fine porous region facilitating the drying out of penetrated water; (3) delay water adsorption to such a level that capillary condensation and microscopic liquid water flow is blocked in the coarse pore region of porous material; (4) prevent the clogging of connective pore chambers by the polymer network since this leads to an important increase of the water vapour resistance.

5 References

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