A. Elena Charola* and Eberhard Wendler

An Overview of the Water-Porous Building Materials Interactions

Abstract: Water is one of the key deterioration factors for porous building materials and has the capability of enhancing the deleterious effect of other factors such as air pollution and biocolonization, among others. The focus of the paper is the interaction of water with the porous inorganic materials: how does water enter the pore system, and how does it leave it? How does the presence of clays or soluble salts in porous materials affect these mechanisms? Pairwise examples are provided to illustrate the varying behavior of water in different materials. Also addressed is the importance of the pore size distribution on the behavior of water and its transport mechanisms. The aim of the paper is to synthesize the key points required to understand why water enters a porous system, in what way it is distributed within it, and the slow manner in which it departs, since time of wetness is fundamental in enhancing the effect of co-factors.

Keywords: absorption, adsorption, drying mechanisms, hygroscopicity, presence of clays, porous inorganic materials, soluble salts, water in pores, wetting mechanisms

1 Introduction

It is well known that water is one of the key deterioration factors for porous building materials [1–4]. What makes it such an effective deterioration factor is that it can act in various ways, by itself as a corrosive agent for calcareous materials; inducing mechanical stresses upon freeze-thaw; inducing swelling of clay containing stones; serving as transport medium to soluble salts, or providing

*Corresponding author: A. Elena Charola, Research Scientist, Smithsonian Institution, Museum Conservation Institute, 4210 Silver Hill Road, Suitland, MD 20746-2863, USA, E-mail: charola_ae@yahoo.com
Eberhard Wendler, Director, Fachlabor für Konservierungsfragen in der Denkmalpflege, Mühlangerstraße 50/1, 81247 Munich, Germany, E-mail: e.wendler@t-online.de

the moisture required for biocolonization, as summarized in Table 1.

Therefore, understanding how water enters and moves through the pore spaces of building materials is essential to develop preventive methods to avoid as much as possible its negative action. Water can enter porous materials both as a vapor and in its liquid state. The aim of the paper is to explore the behavior of water in porous inorganic building materials as illustrated by specific stones and the consequences this has for their deterioration.

2 Liquid water

Liquid water can enter the pore system of a building's construction material through different paths, such as rising damp, infiltrations from the top of the building if water pools on the roof; leaks in gutters or pipes within the building; driving rain wetting the building surface; condensation if the building surface is cooler than the temperature of the air at a given relative humidity, i.e. when the dew point temperature of the air is reached. Furthermore, liquid water can be generated by capillary condensation in the smaller pores even if the ambient relative humidity is below 99%.

The pore system of a material in contact with liquid water exerts an "attraction" on it so that the liquid will enter the capillaries and even rise against gravity. This occurs because the *surface energy* at the water-pore interface is higher than that at the air–pore interface. Therefore, capillary action (capillary rise or capillary suction) is the result of the combination of cohesive forces within the liquid, i.e. surface tension, and the adhesive forces of the pore material, so that the liquid "wets" the solid resulting in the initial uptake of water by a porous material. The eventual migration within the porous body is a result of local differences in water content, since the normal situation in building material corresponds to what is called unsaturated flow, as building materials rarely will be saturated in water.

The height to which capillary water can rise in a straight pore can be easily calculated (see Appendix for relevant equations corresponding to the theoretical

Table 1: Possible interaction of water with materials and the consequent deterioration mechanism.

Water action	Mechanism
Flowing water, either liquid or solid, over minerals	Physical/mechanical erosion.
Freezing of liquid water.	Ice crystal formation (new phase) induces mechanical stresses.
Sorption/desorption of water	Swelling/shrinking Hydration or dehydration of unstable minerals, e.g. gypsum, and lattice changes Soluble salts hygroscopicity
Moving water vapor and/or liquid water.	Transport of reactive components SO_2, NO_x and CO_2 from the atmosphere.
Presence of liquid water.	Dissolution of soluble salts Transport of soluble salts and their eventual crystallization upon water evaporation. Development of microorganisms that may release acid and chelating agents.
Presence of adsorbed water	Biofilm formation and biocolonization enhancing water retention.

Table 2: Calculated time to reach 90% of the maximum theoretical height of water in straight cylindrical pores for various pore diameters and the time required to reach 1 cm height.
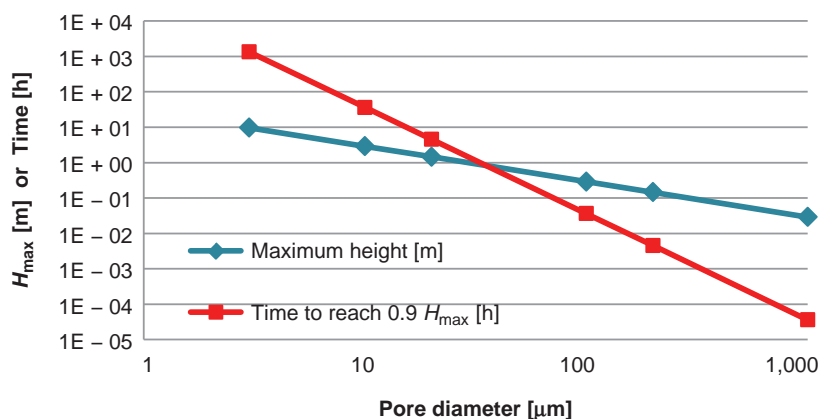
Pore diameter	0.1 μm	1 μm	100 μm	1000 μm
Maximum theoretical height	290 m	29 m	0.29 m	2.90 cm
Time to ascend 1 cm	33 s	5.5 s	55 μs	5.5 μs
Time to reach 90% of max. height	4000 years	4 years	2.2 min	0.13 s

treatment of this topic) and Table 2 summarizes some values calculated for straight cylindrical pores – neglecting their tortuosity and its effects – while Figure 1 plots the maximum theoretical height that can be reached in them and the time it takes to nearly reach this value. From this data it is clear that the overall contribution to high values of capillary rise is relatively small for pores with diameter below 1 μm as compared to larger pores.

From the above it follows that the pore range contributing to capillary rise and transport could theoretically be considered to range between 1 mm and 1 μm diameter [1, 5] as derived from theoretical calculations based on long, straight and uniform pores that do not exist in nature. Hence, there are differing opinions regarding the lower value that is set at 0.5 μm by Klopfer [6] and 0.1 μm by others [7–9]. While the contribution of pores smaller than 1 μm diameter is insignificant at initial absorption times – in comparison to that of larger pores – it can be critically important for materials with uniformly fine pores having an average diameter of 1 μm, as exemplified by the behavior of the micrite de Lourdines. This micrite has an overall porosity around 27% (total immersion under vacuum) which absorbs about 84% of this amount by capillarity (defined as the end value of the initial straight absorption line corresponding to the capillary absorption coefficient). For comparison, the Fontainebleau sandstone (12% total porosity) only absorbs 43% of that amount by capillarity [10]. But porosity is rarely uniform in stones and the pore network geometry is very difficult to categorize [9, 11, 12].

For most inorganic building materials the porosity, considered by volume, can be classified by pore

Figure 1: Maximum theoretical height reached by capillarity in straight cylindrical pores and the time it takes to nearly reach this value.

types: macropores, with diameters >1 mm; micropores (∅ between 1 mm and 0.1 μm); and nanopores (∅ < 0.1 μm). Capillary water transport will be the main mechanism in micropores, and water vapor transport takes precedence for nanopores.

In the case of a building, the maximum height that could be reached is limited by the interconnectivity of the capillary pore system allowing water to rise and move in all directions, as well as the evaporation that will occur ahead of the moving liquid front (or when reaching an exterior surface). Furthermore, difference in nature as well as porosity and pore size distribution between the building's foundations and the soils in which they are based, can also affect water transfer between them. Consequently, rising damp will never reach the heights calculated theoretically, and in practice, the maximum height reached by rising damp will oscillate between 15 cm [13] and 0.5–1 m [14]. However, when dealing with historic buildings, damp areas may appear at higher areas and these can usually be attributed to the presence of hygroscopic salts that take up significant amounts of water vapor as discussed in a subsequent section.

Total saturation of the porous network seldom occurs in inorganic porous building materials. Capillarity will completely fill smaller pores while only partially filling larger ones, where air is trapped. Filled macropores can only be found close to the water entry point [15].

3 Water vapor

Air, and any water vapor it may contain, will enter and circulate through a porous material and the latter will most likely be adsorbed onto the pore surface. The adsorption process results when the attraction between the substrate and the water molecule is higher than the attraction of the water molecules for each other in the liquid form [16]. Once a layer of water molecules forms on the mineral pore surface, subsequent layers will build up on it provided enough moisture is available (Figure 2). These form an ordered water structure – via hydrogen bonding – over a range of several nanometers since the chemical potential, μ, of water on solid mineral surfaces (~20 kJ/mol), is in the same order of magnitude as that required for the formation of hydrogen bonds [17]. The ordered water layers have an "attachment" (electrical potential) gradient that decreases with increasing distance from the mineral surface [18]. This ordered water structure will occupy a larger volume than a disordered one, as is the case for ice compared to water. So in the case of pores with a diameter >0.1 μm, the water
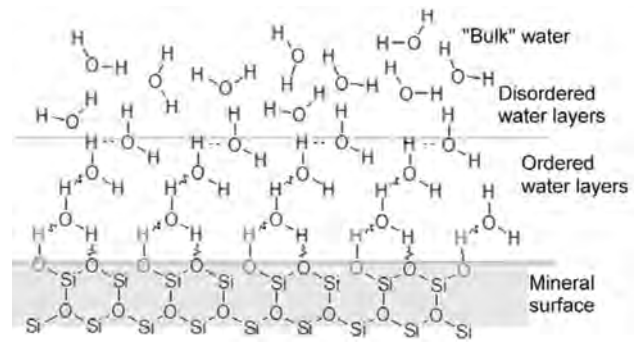

Figure 2: The first water layer adsorbed is in an ordered structure determined by the nature of the pore wall. Further adsorbed water layers gradually lose the ordered structure until they reach the disordered condition of liquid water. In the drawing, a silicate surface with silanol groups is shown in grey. In the adsorbed water layer, the squiggles represent cooperative hydrogen bonding that is fundamental for the formation of the ordered layer. In the bulk water layer, hydrogen bonding is not "organized" and therefore water molecules can pack closer and take up less space than the ordered structures.

attached to the pore surface will occupy more space than the water towards the center of the pore that can be considered liquid water, generally referred to as "bulk" water.

The amount of adsorbed moisture by an inorganic porous building material at a given relative humidity will depend on temperature, substrate type, pore size distribution and geometry as well as the presence of soluble salts in the material as discussed subsequently.

At constant temperature, the adsorbed moisture increases with increasing relative humidity (RH) of the surrounding air, as shown in the isotherms of Figure 3 – of type III consistent with weak gas–solid interactions following the Brunauer et al. classification [17]. These isotherms correspond to two German stones; the fine-pore clay-bound sandstone from Sand am Main, northern Bavaria (Schilf sandstone, open porosity ~15%) and the coarse-pore calcareous tufa from Polling, southern Bavaria (Kalktuff, open porosity ~18%). The latter practically does not adsorb water vapor except at high RH, however, because of the high number of large pores (≥1 mm diameter) it has a very high absorption rate for liquid water (see Table 2 and Figure 1).

As RH increases, water is adsorbed by the surface by gradual formation of several water layers, generally in the order of 3–5 (depending on the nature of the stone) at around 75–85% RH [19, 20]. When the RH increases above this point, the water adsorbed is no longer ordered and corresponds to capillary condensation following the Kelvin Thomson equation. Further increases in RH will
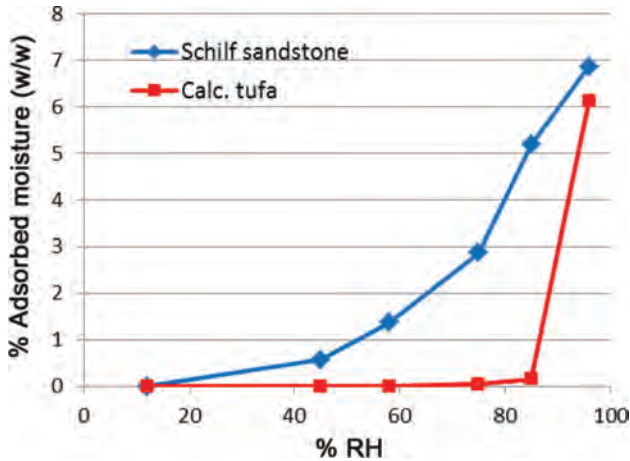
Figure 3: Adsorption isotherm (20°C) for two German stones, Schilf sandstone, a fine-pore clay-bound sandstone and a coarse-pore calcareous tufa. Note that the amount of moisture adsorbed may differ significantly in the range between 40% and 85% RH depending on the nature and porosity of the stone.

point is reached [19, 22] and liquid water forms on the surface of these pores. The calcareous tufa shown in Figure 4 practically does not absorb any moisture below the 80% RH turning point because of its large pores. Therefore, it is a relatively stable material as water can enter and leave it freely.

In some building materials, particularly clay containing ones, water vapor adsorption (starting at about 40% RH, see Schilf sandstone in Figure 3) can also induce hygric swelling as a result of the polar nature of the adsorbed water combined with a large inner surface of these materials. The hygric expansion curves as a function of RH for two German stones are shown in Figure 4. These are the clay-bound sandstone from Abtswind, northern Bavaria (Abtswind Schilf sandstone – open porosity ~17%) and a dense claystone from Wetzlar, Hesse (Schalstein – open porosity ~10%).

Although hygric swelling does not appear as dramatic as that resulting from total immersion in liquid water, it may well be the more relevant deterioration factor considering that porous building materials are seldom saturated with water while RH changes occur constantly since they are temperature dependent. So even if the total amount of moisture in the air is constant over a day, the RH will increase with decreasing temperature and vice versa. In unfavorable climatic
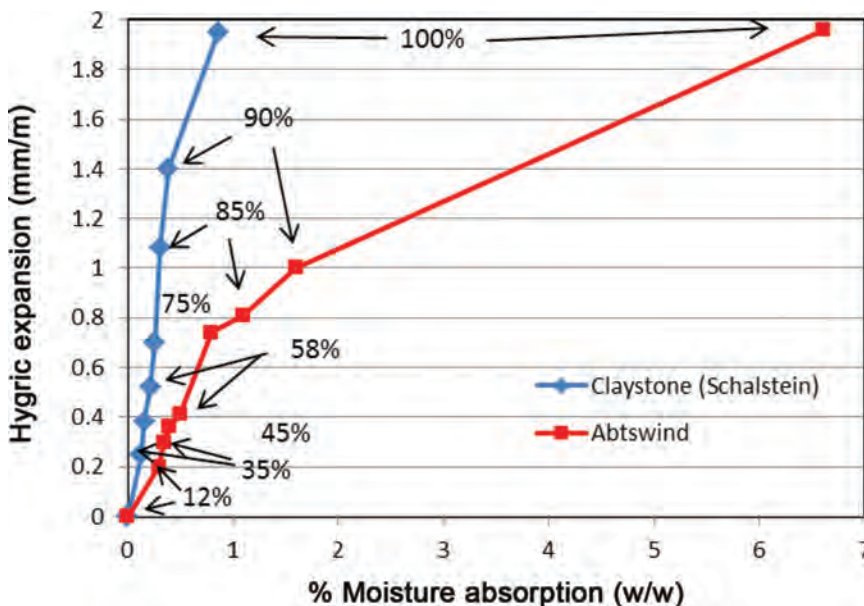
lead to condensation in larger pores. However, pores with diameter around or over 100 nm cannot be filled completely by adsorption as the maximum amount of ordered layers is estimated to be around 4 nm thick – corresponding to around 13 ordered layers [19, 21]. Therefore, in larger pores condensation can only occur when the dew

Figure 4: Hygric swelling for two German stones at 20°C as a function of moisture sorption. The stones are the clay-bound Abtswind sandstone and a very dense claystone (Schalstein). Numbers by the curves indicate the RH values at which moisture equilibrium was reached – around 2 weeks for each RH using 2–3 cm maximum dimension samples – except for the 100% value that corresponds to saturation in liquid water. Note that the hygric expansion of the claystone is higher at RH values over 75% RH although the amount of moisture taken up is far less than for the sandstone.

situations, shear forces between dry and wet zones may exceed the tensile strength of the material and lead to damage [23–25].

Linear elongation for German sandstones is below 0.6 mm/m for RH values of 75% and below [22], while for water saturated samples it can range from 0.05 to 8 mm/m. However, the elongation per amount of water present in the sample is found to be significantly higher for hygric adsorption than for hydric absorption as shown in Figure 5 where the elongation per degree of saturation (defined as the per cent moisture content relative to that at full liquid water saturation) is shown for two different sandstones equilibrated at different relative humidities as well as stationed in liquid water. The Sander sandstone contains swellable clays (open porosity ~15%), while the Uder sandstone is a quartz arenite with traces of muscovite–illite (open porosity ~23%) [22]. It is evident from the graph that liquid water is not as "efficient" as adsorbed water in inducing the swelling of the material confirming the fact that hygric moisture adsorption may well be more relevant deterioration factor. This is particularly noticeable for the case of the Uder sandstone.

The presence of expansive clays is readily noted in the higher elongation per saturation degree for total immersion saturation as shown by the Sander sandstone. Nonetheless, the ordered water structures that form on the mineral surfaces by water adsorption contribute significantly to the swelling of materials, i.e. hygric swelling, as illustrated by both sandstones confirming the hypothesis postulated by Stockhausen [21].
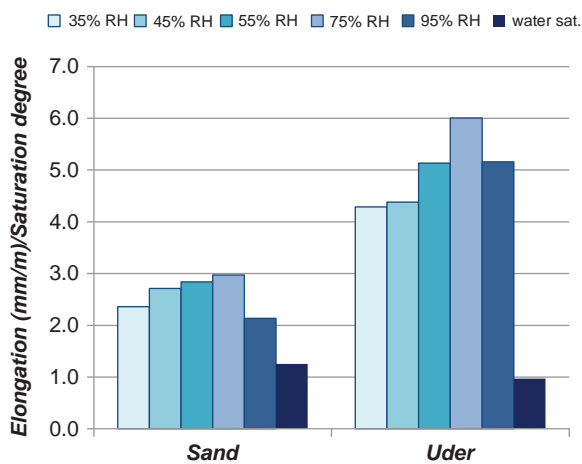

Figure 5: Elongation per degree of saturation for German sandstone samples stabilized at relative humidities between 35% and 95% RH and for samples saturated 24 h in liquid water. Note that elongation per degree saturation is higher for hygric adsorption than for hydric absorption (data courtesy of J. Ruedrich [22]).

The swelling effects induced by the lower energy ordered structures of the adsorbed moisture may be important if small pore sizes are predominant in the material and if the latter does not have the sufficient mechanical resistance to counterbalance them. In other words, the energy "saved" during the adsorption mechanism may be used for mechanical work, i.e. relative movements of material components against each other; or, may be stored as potential energy, i.e. pressure against the porous material structure.

Finally, it should be remembered that the presence of soluble salts changes significantly the swelling behavior of materials that contain them resulting in an increased deterioration process for both wet–dry or humid–dry cycling [4, 22].

4 Presence of soluble salts

Materials tend to reach equilibrium with their environment (temperature, humidity): wood is notoriously susceptible to dimensional changes induced by high relative humidity environment. But also inorganic porous building materials suffer similar changes, as for example the bowing of marble panels induced by a conjunction of temperature and humidity changes [25]. And among inorganic materials, salts are included.

Soluble salts, which can dissolve in water and thus enter the porous system of building materials, are probably the single most damaging factor for porous building materials [4, 26, 27]. But they are also able to adsorb sufficient water vapor from the air to the point of dissolving and forming a saturated solution, i.e. they are deliquescent. Each specific salt has a particular relative humidity above which it is deliquescent, the deliquescence relative humidity (DRH). For the particular case of sodium chloride, halite, probably the most ubiquitous salt, the DRH is around 75% at 20°C. In turn, a saturated salt solution has a given water vapor pressure that will take up moisture (via an osmotic process) when it is below the ambient air RH until the water vapor pressure of the solution and that in the air are at equilibrium.

When a mixture of salts is present, more complex situations develop where rather than a specific DRH, there is a range of DRH [4]. For example, for the case of a mixture of gypsum (calcium sulfate dihydrate) and halite (DRH 75% at 20°C), the low solubility of gypsum is increased and this decreases its DRH from 99% at 20°C to a lower value, so that the moisture uptake at 75% is increased as shown in Figure 6 (slightly more than the sum of the absorption of the individual salts), while for a
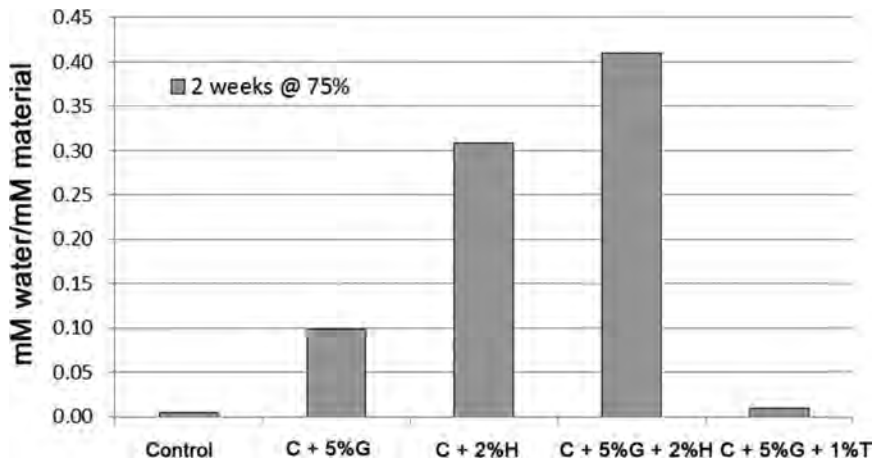
Figure 6: The control, a 1:1 mixture (by weight) of fine powdered calcite and silica, to mimic a lime mortar, was additioned with gypsum (G), halite (H) or thenardite (T) or a mixture of both G and H. Moisture absorption is given in millimoles of water per millimole of salt in the mixture.

mixture of gypsum and thenardite (sodium sulfate) (DHR 93% at 20°C) the solubility of thenardite is decreased because of the common ion effect so that the overall moisture is less than that for gypsum alone [28].

The fact that salts undergo deliquescence and can take up enough moisture from the environment to solubilize them will also contribute to their mobility in the porous material. Therefore, in a historic structure where rising damp is present, the fringe of the rising damp will be higher because of the deliquescent salts present, rather than from pure capillary rise [29].

5 Drying mechanisms

Understanding the mechanisms that control the drying of wet porous materials is just as important as those for its wetting. The drying process can be divided into three stages depending on the mechanisms that control it [10, 30]. The length of each of these stages depends on the material in question and in some cases may practically not be apparent.

The drying rate, i.e. change of moisture content with time as a function of time, $\Delta\Psi/\Delta t$ [g/cm^3 h] for two types of limestone, one from Indiana (Salem, IN, US), and the other from Egypt (Moqattam Hill formation near Cairo) are shown in Figure 7. The former is a dense oolitic limestone (open porosity ~9% v/v), while the latter is a fine grained, partially nummulitic, clay containing and inherent salt (NaCl) contaminated limestone (open porosity ~21% v/v).

Initially, when the porous body is saturated, or nearly saturated with water, evaporation takes place from the exposed surface, and as long as liquid water is supplied to the surface, i.e. when there is capillary transport moving the water to the surface, the drying rate will be constant. The rate will depend on the external conditions, such as temperature and relative humidity, or whether there is wind to allow a faster removal of the water molecules from the surface. In the first case, the removal of the water vapor molecules will be by diffusion, in the latter case, a convection mechanism will control it. Although the Egyptian limestone has an overall higher porosity, the clays and salt present in the stone will reduce its drying rate as compared to the Indiana limestone. The effective evaporating surface depends on the pore geometry and surface roughness, as these will define the water film at the surface of the sample [10, 31]. The drying rate will be constant until the moisture content within the porous material can no longer sustain capillary transport. This is referred to as the critical moisture content, Ψ_c (kg/m^3) [23].

The second stage starts when capillary transport in the porous material is slower than the evaporation rate at its surface. The evaporation front moves into the interior of the porous material and the drying rate decreases. Because materials are rarely homogeneous, areas having mainly smaller pores may still be able to sustain capillary transport while those having a higher number of larger pores are no longer saturated with water and drying will depend on the water evaporation of the remaining liquid water front and subsequent vapor diffusion. Thus the drying rate will be the result of the combination of these various mechanisms within the pore system and as it progresses, one or the other mechanism may be the rate controlling one. Therefore the drying rate changes as the drying progresses.

The third stage begins when practically no liquid water is left and the drying rate will be controlled only
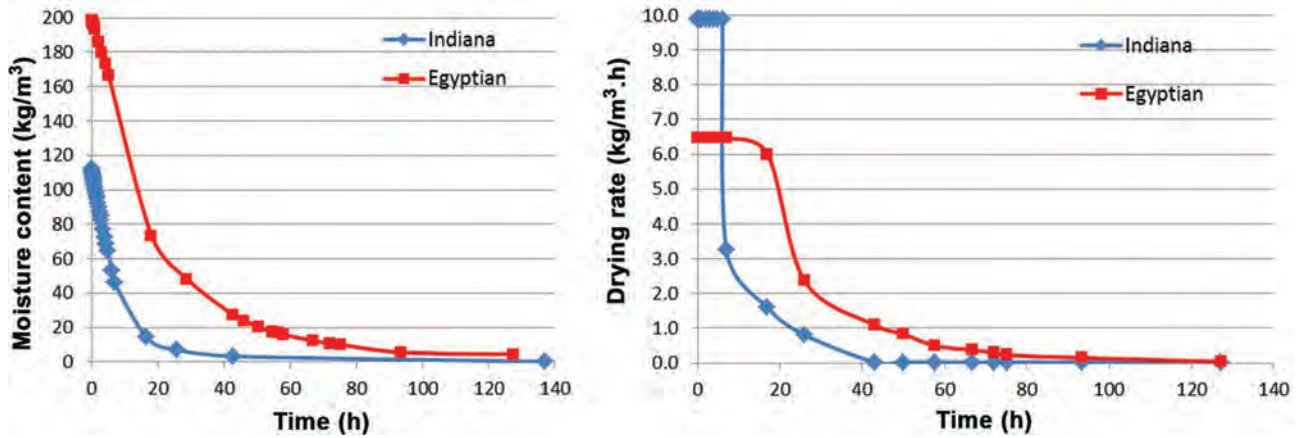
Figure 7: Drying curves (left) and drying rate curves (right) obtained at ambient laboratory conditions (22°C and 50% RH) for 5 cm cubic samples of Egyptian and Indiana limestone saturated by capillarity. Note that the drying rate is slower for the more porous Egyptian limestone because of the presence of clays and salt.

by the diffusion of water vapor to the surface and its diffusion or convection from the surface. At this stage the size and shape of the samples are critically important. For the same volume, the sample that has a significantly lower dimension in one direction will dry faster [32]. Because of the small amount of water left in the material, the drying rate will be very slow, nearly constant, while the moisture content of the materials tends towards the hygroscopic moisture content, Ψ_h, of the porous material at the particular RH of the drying conditions. The Egyptian limestone has higher moisture content for this stage because of the presence of moisture retaining clays and salt.

It is important to highlight that while capillary absorption is a relatively fast mechanism (for the examples given it took about 3–4 h to nearly saturate both samples), drying is comparatively slow as a consequence of the attraction of water molecules for the mineral surfaces. As can be seen in Figure 8 it takes approximately 50 h for the Indiana limestone to nearly dry and twice as long for the clay containing Egyptian limestone to reach that same stage, while it takes both stones some 3 hours to nearly "saturate" by capillary absorption. Therefore, a porous material in a building wetted during a rain event will take far longer to dry – about a hundred-fold order – than it took getting wet [33]. For example, specimens (20 × 20 × 20 cm) of a local soapstone (overall porosity of 1% v/v and with a large number of small pores ranging between 0.01 and 0.2 µm [34]) were exposed outdoors in the area of Congonhas, Brazil, during the 2-month rainy season. Five months later it was found that the samples still held water to a depth of 8 cm [35]. The reason for this is the large number of very small pores where water is tightly bound to the substrate (see Figure 8 in the following section).
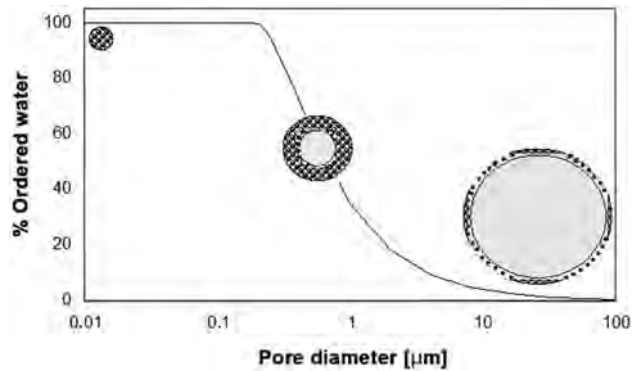

Figure 8: The relative amount of ordered (structured) water tightly bound to the surface (dark) decreases with increasing pore diameter and the center is filled with disordered "liquid" water.

6 Transport mechanisms

Between water vapor adsorption and capillary absorption of liquid water a mechanism based on the surface diffusion of the adsorbed water molecules has been postulated [17, 21]. The driving force for diffusion is the water vapor gradient and, with higher moisture content in the air, the water vapor adsorption process increases.

As pore size increases, the so-called capillary range of pore size is reached. The smallest pores of this range, i.e. having a diameter < 1 µm, are able to transport relatively small amounts of water that will move very slowly since most of the water will be found in low energy ordered state. For larger pores (>1 µm), only the

molecular layers close to the pore walls will form ordered structures while the major portion of the water in the center is in the high energy disordered structure of liquid water (Figure 8). Therefore, the driving force for capillary movement is given by the shift of water molecules from the high energy disordered center region in the water filled pores to the low energy structured arrangement they acquire when attaching to the "dry" (i.e. water-free) surface beyond.

During capillary transport, the major liquid water portion in the center of the pores is conveyed through cohesive forces by the adsorbed water structure on the walls of the pores. Thus, transport is facilitated and a relative small number of surface bound water molecules can help move far larger amounts of liquid water in larger pores than in smaller pores. And, as the diameter increases, larger quantities can be transported in a given time thus increasing the transport rate. However, the limit is found for the case of macropores, i.e. with diameter greater than 1 mm, where fluid flow characteristics take over.

From the above it is clear that the classic model of capillary water transport cannot be applied to pores beyond the 1–0.1 µm diameter range since most of the water is in an ordered state due to the electrostatic influence of the surrounding pore walls. The cluster-bound molecules filling these small pores are in a stable state and have no driving force to move forward to adsorb on to "dry" surfaces, i.e. surfaces that are not yet covered by adsorbed molecules. For the same reasons, drying is remarkably reduced in these small pores: evaporation is energetically diminished as compared to that of bulk liquid water. And it is precisely for this reason that drying of porous building materials is a slow process in comparison with its wetting as shown in the next section.

7 Discussion and conclusions

The classic model that only considers two phases for water transport, i.e. liquid and vapor, fails to consider the presence of ordered water structures that bind to the mineral surface. These ordered structures facilitate capillary movement while also inducing destructive expansion processes, when only considering water vapor. Table 3 gives an overview of the various transport mechanisms as a function of the pore size. The table follows the approach used in the published literature but it should be noted that mechanisms do not

change abruptly between pore sizes, rather, there is a phasing out of one mechanism while the next one takes over.

Table 3: Main water transport mechanisms depending on pore diameter. Note that the water molecule is around 0.3 nm in diameter.

Macropores	Micropores			Nanopores	
∅ > 1 mm	1mm–10µm	10µm–1µm	1µm–0.1µm	100nm–10nm	< 10 nm
Liquid water flow	Capillary absorption			Water vapor adsorption and surface diffusion	
Water vapor diffusion				Capillary condensation	

Since porous building materials will have a complex pore structure and size distribution it is evident that there is no clean break between transport mechanisms. Pores of even diameter are never found in nature over a long range, as assumed in the ideal cylinder pore model from which most of the described mechanisms are derived from. Instead, larger cavities are interconnected via smaller "throats" of different diameters and different lengths so that between wetting and drying periods on exposed building materials, many of the narrower pore segments are more or less filled with water while the major portion of the wider pores is empty. Continuous capillary transfer could only be the main transport mechanism in the unlikely case that all the larger pores are filled with water. Usually, larger pores are not completely filled. The water in them evaporates faster than what can be provided by capillary transport from the small pores connected to them.

Pores with diameters between 1 mm and 1 µm can be considered the main contributors to capillary transfer. However, water adsorption and surface diffusion seem to be more important for pores with diameters in the range of 1–0.1 µm, but the extent of these processes will depend on the mineral composition and pore geometry of the porous material.

What is clear is that when all the macropores are filled with water, fluid transport will be the main mechanism for water movement in the porous body. Furthermore, if hydrostatic pressure is present, as when some centimeter high water puddle collects over a surface so that its weight will increase the pressure on the pore system of the stone, then the capillary transfer changes into fluid flow processes, i.e. Darcy flow, particularly for pores with diameters around and above 1 mm [6, 19].

Finally, when dealing with historic structures, the presence of salts will significantly change the behavior of water in the material, both with regards to water vapor adsorption and the migration of fluid water in it. As aptly described by Puehringer "it is the salt that carries the water" [36].

Appendix

Theoretical calculation of maximum height reached in a cylindrical pore and the time it takes to reach it.

It is possible to calculate the theoretical maximum height that can be reached in a cylindrical pore and the time it takes to reach it [1, 6, 19]. For this purpose, the capillary force, F_c, and the corresponding capillary tension p_c, i.e. pressure, in a cylindrical pore can be expressed by

$$\text{capillary force} \quad F_c = 2r\pi\sigma \cos \Theta \quad [\text{N}] \tag{1a}$$

$$\text{capillary tension} \quad p_c = 2\sigma \cos \Theta / r \quad [\text{Pa}] \tag{1b}$$

where r = capillary radius [m]; σ = surface tension of the water [N/m] and Θ = contact angle between water and pore surface.

As can be seen from the above equations, adsorptive and cohesive forces are equal when $\Theta = 90°$, corresponding to p_c = zero, and capillary water absorption cannot take place. For materials with $\Theta < 90°$, adsorptive forces exceed cohesive forces resulting in capillary absorption as described above. Surfaces having a high polarity, such as silicate minerals, show Θ-values close to 0°, corresponding to total wetting.

For materials with $\Theta > 90°$, such as hydrophobized surfaces or an organic material, there will be a capillary depression and water will not enter the pore system unless an external pressure is applied. Since only water molecules close to the mineral surface (pore wall) can contribute to absorption, smaller pores show a larger capillary tension, according to eq. (1b).

To describe the maximum capillary rise as well as the dynamic transport, i.e. absorption rate, the influence of gravity and viscous resistance has to be considered since they are in opposition to the capillary force. The maximum height that can be reached by vertical transport is given by:

$$H_{max} = 2\sigma \cos \Theta / r\rho g \tag{2}$$

where σ = surface tension of the water [N/m]; r = capillary radius [m]; Θ = contact angle between water and pore surface; ρ = specific weight of water [kg/m³]; g = gravity force [m/s²].

Thus, smaller capillaries will give rise to higher capillary rise. Combining eqs (1b) and (2), the maximum height at 1 atm (0.1 MPa) can be calculated to be below 10 m for a straight, vertical pore of 1.5 μm radius, considering the density of water as 1,000 g/m³ and gravity as 10 m/s:

$$H_{max} = p_c / \rho g \leq 10\text{m} \tag{3}$$

Therefore, the lower limit for capillarity can be considered to be found in pores with a 3 μm diameter. The upper limit can be considered that of a 1 mm pore since water will only rise up to less than 3 cm.

The general equation that describes the transport mechanism can be derived from the Poiseuille and Laplace equations:

$$\partial h / \partial t = [r^2 / 8\eta h](2\sigma \cos \Theta / r + \rho g h_0 + \rho g h \cos \varphi) \tag{4}$$

where $\partial h / \partial t$ = capillary absorption rate [m/s]; h = distance reached by water in the capillary [m]; η = viscosity of the water [N s/m²]; σ = surface tension of the water [N/m]; r = capillary radius [m]; Θ = contact angle between water and pore surface; ρ = specific weight of water [kg/m³]; g = gravity force [m/s²]; h_0 = height of water above entrance pore [m]; φ = angle with vertical direction.

The last term of this equation turns negative for φ angles larger than 90°, i.e. for capillaries that are not vertical and the previous term turns constant for horizontal transport.

The above differential equation can be solved for time at specific heights, and from this, the rate of capillary rise can be calculated at different heights, since water will start at a maximum rate and reach zero at the maximum height. For the case of vertical transport, for building materials where cos Θ is practically equal to 1, the solution is

$$t = [(8\eta H_{max}) / (r^2 \rho g)]\{-(h/H) - \ln[1 - (h/H_{max})]\} \tag{5}$$

where h = is the height reached at the time in question.

It has been found through calculations that the above equation for vertical rise is valid down to one tenth of the maximum height that can be attained by any given pore diameter a fact that has not been previously published. Below this value, the results obtained coincide with those for capillary suction in the horizontal direction, as the influence of gravity becomes negligible. As mentioned previously, this equation has limitations given the non-uniformity of pore sizes, but the limitations

In the case of horizontal transport, the equation simplifies to

$$\partial x / \partial t = r\sigma / x 4\eta \qquad (6)$$

where x is the distance reached by the water.

The time it takes to reach a distance x in the pore is given by the equation:

$$t = 2\eta x^2 / \sigma r \qquad (7)$$

For a given time, the distance water penetrates into a horizontal pore is calculated by:

$$x = [\sigma r t / 2\eta]^{0.5} \qquad (8)$$

and this distance is a function of the square root of time. From the above, the instant rates at specific times can be calculated.

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