

Water and its Interaction with Porous Inorganic Building Materials

E. Wendler¹ and A.E. Charola²

¹Munich Conservation Laboratories, Munich, Germany

²Scientific Consultant in Architectural Conservation, Lisbon, Portugal

Abstract

Water has long been identified as one of the key factors in the deterioration of porous inorganic building materials. Therefore its behaviour with regards to these materials is fundamental. Although this area has been studied exhaustively by scientists in various disciplines, there has been a lack in trying to bring together, and to present a comprehensive and comprehensible image of the reason for the interaction water has with these materials.

It has been the aim of the paper to put forward a broader picture of the water-porous inorganic material interaction, rather than focusing on the mathematical expressions that have been developed to describe them. Starting with the abundance of oxygen in both the lithosphere and the atmosphere, to its particular electronic configuration that allows the formation of hydrogen bridges that are the reason for the anomalous behaviour of water, i.e., the expansion it suffers upon freezing.

The balance of the cohesive forces between water molecules and the adsorption that water has for mineral surfaces are at the origin of all the observed occurrences in the water-porous inorganic material interaction. The adsorption of water on the pore surfaces leads to the formation of ordered water structures. These structures play an active role in the transport of liquid water through capillaries and lead, in smaller pores, to the condensation phenomena. In summary, water can be in a totally disordered state as in water vapour, in a labile order as in liquid water, as a short range ordered structure when adsorbed on a mineral surface and as a totally ordered structure as ice.

Keywords: water, inorganic materials, ordered structures, capillary action, adsorption, absorption, drying

1 Introduction

Already in the 6th century BC, Thales of Miletus considered water to be the origin of all things. While the scope of this concept has been narrowed over more than two millennia, the fact remains that water is what makes life possible, and it certainly is a fundamental factor in the deterioration of porous building materials. Much has been written about water and its interaction with these materials, yet there is much that still is not well understood. It is important, therefore, to summarize the available knowledge so as to be able to identify those areas where knowledge is as yet incomplete.

Many books have addressed this topic [1-6], some of which can be considered classics. The number of papers published is staggering since there are so many interactions and mechanisms to consider, such as liquid water absorption, water vapour sorption, the influence of porosity and mineralogy of the substrate, to name a few. A recent review paper [7] has provided a critical evaluation of the most important publications, but is rather unsatisfactory in summarizing the current knowledge. It is the aim of this paper to present a more didactic outline of the various interactions of water with porous inorganic building materials.

2 Geological perspective

Among all the elements, oxygen is by far the most abundant one in the outer crust of the earth comprising the lithosphere and the atmosphere, exceeding even the sum of all the other elements (Fig. 1). Together with Si, Al, Fe, some elements of the groups I and II and hydrogen, it forms the major portion of the natural mineral substrates which are mostly thermodynamically stable. Furthermore, some 6% of the oxygen is bound in water, present in oceans, rivers and in the atmosphere, as well as an intrinsic component of many rocks, depending on their formation history.

In contrast to widespread minerals like quartz, feldspars or clays which are solid (except in case of volcanic activities), the abundant compound water is capable of changing phases, from solid through liquid to gas, within the normal range of temperature in the outer lithosphere and atmosphere. Consequently, water is highly mobile and may impact those materials with which it comes in contact. Another important aspect is the large volume changes associated with the water phase transitions that might affect neighbouring structures.

In all cases when natural minerals and water come in contact with each other (which happens very frequently due to the large abundance of both), a complex weathering process can take place (Table 1). Except for the simple physical erosion and the release of water from thermodynamically unstable minerals, such as found in volcanic tuffs, all other processes of weathering require a direct interaction of the mineral surface and the water molecules.

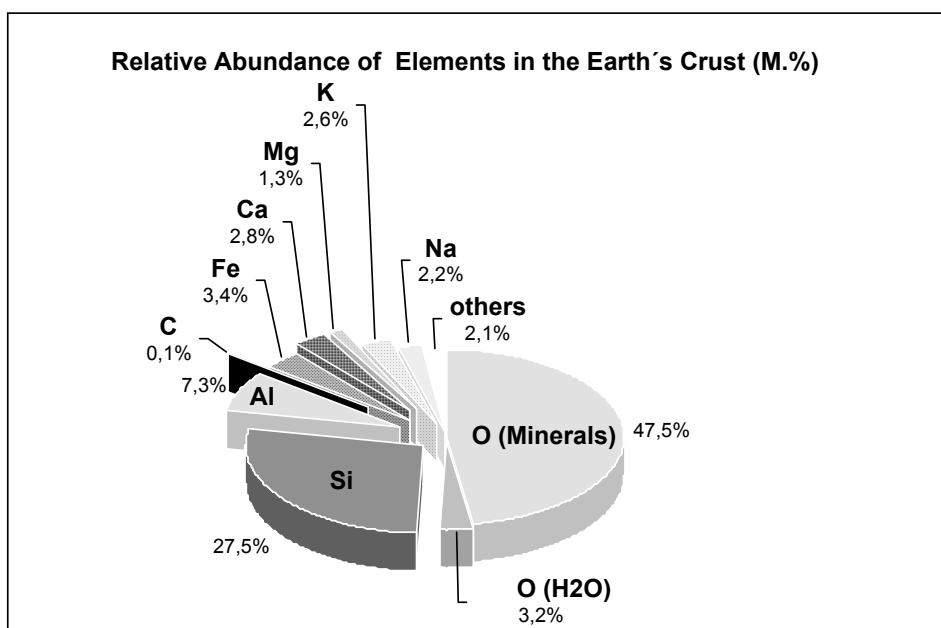


Figure 1: Relative abundance of elements, expressed as mass percentages, in the lithosphere and atmosphere of the earth. Note that the amount of oxygen in liquid water is roughly equivalent to the amount of iron and that carbon as the essential element of life is only present as 0.1%! Hydrogen makes up about 1.0 %.

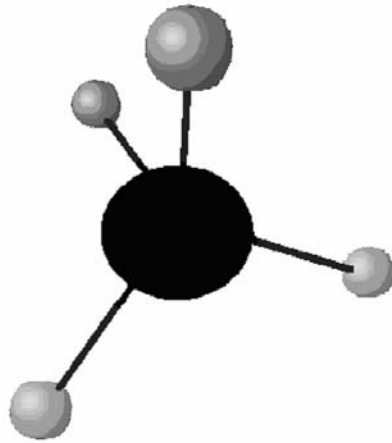
3 Interactions: cohesion and adhesion

Both water and minerals show a high polarity in their structures due to differences in the electronegativity between oxygen and the other elements participating in the chemical bonds. Furthermore, because of its dipolar nature, water is able to make cohesive intermolecular bonds, i.e., hydrogen bonds, also called hydrogen bridges, between the oxygen and the hydrogen atoms of neighbouring water molecules. This is possible due to the two free electron pairs of each O-atom (Fig. 2) and the relatively small size of this atom, since in the homologous compound hydrogen sulfide (H₂S), sulfur does not form hydrogen bonds although it also has two free electron pairs.

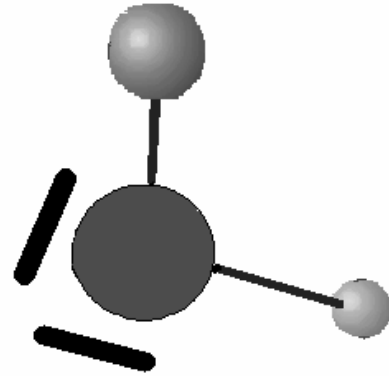
As can be seen in Figure 2, methane (CH₄) is a compound of similar molecular mass but is unable to interact this way because the C-atom does not have free electron pairs. Consequently, the boiling point of methane (-162°C) is much lower than the one of water (100°C), as is the one for hydrogen sulfide (-62°C).

Table 1: Role of water in the weathering process of mineral substrates.

Factor	Mechanism
Flowing water (liquid or solid, ice) over minerals	Physical/mechanical erosion.
Water release from unstable mineral compositions, i.e., vitreous tuff, opal or similar amorphous silicate structures, "Bergfeuchte" in sedimentary rocks.	Mineral lattice shrinkage.
Freezing of liquid water.	Ice crystal formation may induce mechanical pressure in the pore space of mineral materials.
Adsorption/desorption of water (liquid or vapour).	Dilatation (swelling/shrinking) of minerals.
Liquid water in contact with mineral materials	Solubilization, i.e., feldspars (show alkaline reaction in contact to water), gypsum.
Water vapour and/or liquid water.	Transport of reactive components SO ₂ , NO _x and CO ₂ from the atmosphere.
Presence of liquid water.	Transport of soluble salts. Eventual crystallization of these salts upon evaporation.
	Hydration of salts present in the substrate: Na-carbonate, Na-sulfate, Mg-sulfate.
Presence of absorbed water	Biofilm formation, biocolonization and micro-organisms that are capable of water retention and releasing acid and chelating agents that will affect mineral materials; higher plants induce mechanical stresses that will affect structural stability of buildings.



Methane CH₄
Boiling Point: -162 °C
Heat of Evaporation: 8 kJ/mole



Water H₂O
Boiling Point: 100 °C (H₂S: - 62°C)
Heat of Evaporation: 41 kJ/mole

Figure 2: Molecular structure of (non-polar) methane and (polar) water in comparison. Hydrogen bridges can only develop between water molecules. Note that the evaporation enthalpy of water is 5-fold higher than that for methane.

The dissociation energy of hydrogen bonds is much smaller than the bond energy of the covalent O-H-bond of the water molecule (some 400 kJ/mole). Furthermore, the dissociation energy of these bonds depends on the surroundings and may range between 20 to 40 kJ/mole. For isolated situations, i.e., two water molecules interacting, it will be smaller, and for cooperative H-bond-systems, where the O-H-vectors are coupled, it will be larger. This is the case when water molecules undergo an intensive interaction with each other (as in ice, see Figure 3) or with a polar surface (adsorption). Ordered structures may develop over a range of several nanometers (see Figure 4) and it should be remembered that these structures require more space as compared to disordered ones. This is reflected by the increase in volume when water turns to ice. It is to be pointed out that this expansion is not the reason for the freeze-thaw damage as generally believed, since contracting liquids are capable of inducing the same type of damage upon freezing.

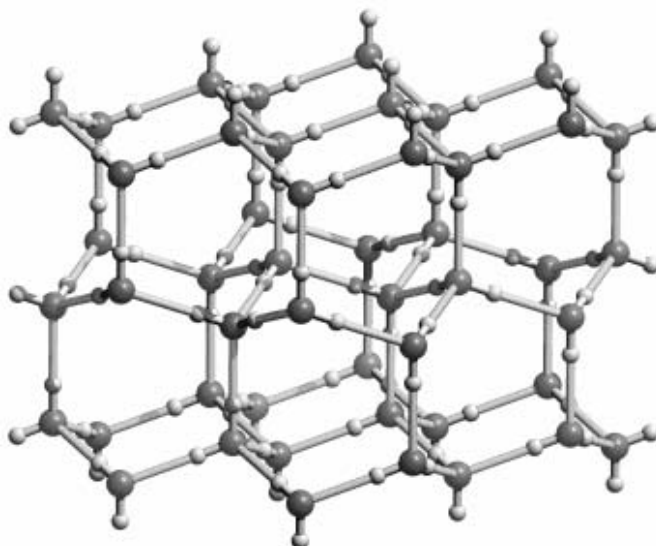


Figure 3: Ordered structure of ice, the hydrogen bonds [8] are the longer, pale grey lines. Note the hexagonal structure which is reflected in the symmetry of ice crystals seen as six pointed stars. At ordinary temperatures, the hydrogen bonds can be cleaved and rearranged in different positions. This is part of the reason for the creep of ice in glaciers.

The high cohesive forces in water will result in the formation of spherical drops, as is the case when humid air is cooled to below its dew point, if there is no interaction of water with the surrounding matter. It is important to remember that detaching one water molecule from a drop requires energy. This can be obtained by simple heating but it also can be provided by an exothermic chemical reaction, such as could result from the interaction of the water molecules with neighbouring minerals.

If a water drop comes in contact with a non-polar surface, e.g., a wax layer on a plant leaf, since no possible molecular interaction can occur, the drop will run off. On the other hand, when water comes in contact with a mineral surface, as these in general are hydroxylated, i.e., hydroxyl-groups are present on their surface, interactions will take place (Fig. 4). These can occur with water both in vapour and/or liquid phase resulting in the formation of a stable adsorptive structure with hydrogen bonds yielding adsorption enthalpies that may be sufficient to separate water molecules from their arrangement in the drop. Thus, there is a competition between the cohesion of water molecules themselves and the adhesion of water molecules layers to the mineral surface.

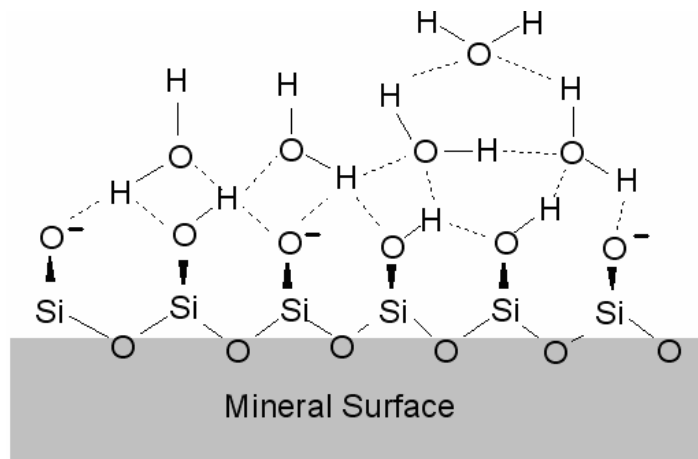


Figure 4: Molecular interaction between a polar mineral surface and adsorbed water molecules by hydrogen bridges (marked as dashed lines). Note that quasi-ordered structures require more space than liquid water.

Under these conditions, competition between adsorption forces to a polar mineral surface with the cohesive forces between water molecules, capillary rise may occur even against gravity, if the pores are small enough.

4 Interaction of liquid water with porous inorganic materials

When a porous building material is in contact with liquid water, water will enter the pore system of the material. The initial amount of water absorbed by the material is proportional to the square root of time bespeaking of a diffusion type mechanism. The initial slope of the plotted amount of water per unit surface as a function of the square root of time is called the *capillary water absorption coefficient* [$\text{kg}/\text{m}^2\text{h}^{1/2}$] and will be dependent on whether the absorption takes place on only one surface of the sample or whether the sample is totally immersed in water. The proportionality will be longer for horizontal absorption than for vertical absorption, because gravity acts against for the latter. It is important to remember that a porous material, even when totally immersed in water, may require years to fill all its pores completely since air gets trapped within the larger pores. A laboratory sample, such as a testing cube, can take about two years [9].

What makes water enter the capillaries and even rise against gravity is the balance between the cohesive forces within the liquid water, which can be defined by its surface tension σ [N/m], and adsorption forces to a polar mineral. The surface energy of the solid will define the contact angle Θ that water will form on that solid. This “attractivity” between water and solid

may result in the tendency of water to enter the pore system of the solid by the so-called capillary action (or capillary rise), sometimes referred to as capillary suction. Surfaces having a high polarity, such as silicate minerals, show Θ -values close to 0° , corresponding to total wetting, while non-polar surfaces, such as waxes, polyfluorocarbons or silicone resins, show Θ -values $> 90^\circ$.

The capillary force, F_c , and the corresponding capillary tension p_c , i.e., pressure, in a cylindrical pore can be expressed by:

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

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

where: r = capillary radius [m]; σ = surface tension of the water [N/m].

As can be seen from the above equations, adsorptive and cohesive forces are equal when $\Theta = 90^\circ$, corresponding to $p_c =$ zero, and capillary water absorption cannot take place. For materials with $\Theta < 90^\circ$, adsorptive forces exceed cohesive forces resulting in capillary absorption as described above. For materials with $\Theta > 90^\circ$, such as a hydrophobized surface, 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 equation (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:

$$H_{\max} = 2 \sigma \cos \Theta / r \rho g \quad (2)$$

While the general equation that describes the transport mechanism can be derived from the Poiseuille and La Place equations:

$$\Delta h / \Delta t = [r^2 / 8 \eta h] (2 \sigma \cos \Theta / r + \rho g h_o + \rho g h \cos \varphi) \quad (3)$$

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

Thus, smaller capillaries will give rise to higher capillary rise, but larger capillaries will provide faster water absorption rate due to their larger cross-section. This is shown graphically in Figure 5. To be considered is that these are just theoretical calculations, because there is no straight, uniform sized pore of any length in nature. The pore network geometry is very difficult to categorize, and porosity is in general not uniform in the small range.

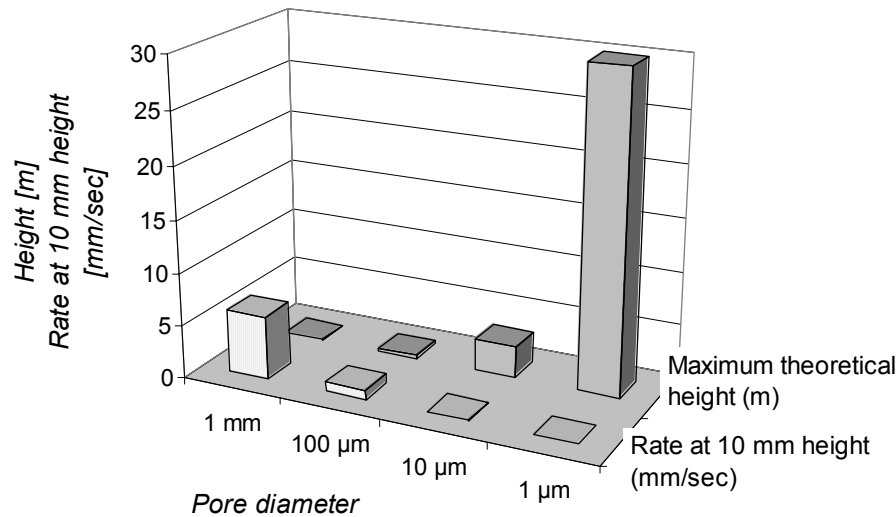


Figure 5: Maximum theoretical height reached by water in a vertical pore as a function of pore diameter and the capillary suction rate, as calculated at a height of 10 mm, expressed in mm/sec. It has to be mentioned that the calculation is valid for the idealized assumption of cylindrical pores over the whole range which is not the case under real conditions in the pore space.

What can be deduced from Fig. 5 is that capillary rise and the rate of capillary rise, as expressed by equations (2) and (3) are valid only for pores ranging in diameter from 1 mm to 10 μm , as already pointed out by Klopfer [10]. This is the range where water will move by capillary transport. In larger pores, water will not rise and in smaller pores, i.e., below 1 μm diameter, the rate is extremely slow. ~~For example, according to eq. (3), the time it would take for water to reach a height of 10 μm in a 10 μm diameter pore is 5 hours!~~ It is clear therefore, that other phenomena become relevant, such as adsorption, as illustrated in Fig. 4. As pores get smaller, the ratio of amount of water to material surface decreases and therefore these interactions take over. Furthermore, the role of water vapour becomes important as capillary condensation starts to occur. In the example of the 10 μm diameter pore, condensation will occur at RH around 99.95%, a likely value to be valid if liquid water is present at the entrance of the pore.

Erratum:

For example, according to eq. (3) the time it would take for water to nearly reach the maximum height, e.g., 0.9 H_{max} , is about 4000 years for a 0.1 μm diameter pore, 6 months for a 1 μm pore and only 3.62 hours for a 10 μm pore.

In most inorganic building materials the porosity, considered by volume, falls in the capillary pore size range, i.e., pores with radii ranging from 1 mm down to some nanometers. While for the former, capillary water transport, as defined by eq. 2 and 3, will be valid, for the nanopores (pores with radii smaller than 0.1 μm) the interaction with water vapour takes precedence as discussed in the following section.

Once the porous body is filled, completely or not, with water, it is important to understand how the water will get out of it. The drying process can be divided into three stages depending on the mechanisms controlling this rate. Figure 6 plots the drying rate, i.e., change of moisture content with time as a function of time, $\Delta\Psi/\Delta t$.

Initially, when the porous body is saturated with water, evaporation takes place from the exposed surface, and as long as liquid water is supplied to the surface, i.e., there is capillary transport moving the water to the surface, the drying rate will be constant. The rate will depend only 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 vapour molecules will be by diffusion, in the latter case, a convection mechanism will control it. The drying rate will be constant until the moisture content within the porous material can no longer sustain capillary transport. This moisture content is called the critical moisture content, Ψ_c [kg/m^3].

At this point, the second stage starts, where the drying rate decreases and can be controlled by different mechanisms. The reason for this is that porous building materials are generally heterogeneous and therefore moisture distribution will be uneven. Areas having mainly smaller pores may still be able to sustain capillary transport, however, other areas, having a higher number of large pores are no longer saturated with water and drying will depend on the water evaporation from the remaining liquid water front and subsequent vapour 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. In summary, during this step the evaporation front will move into the porous material.

The third stage begins when no liquid water is left and the drying rate will be controlled only by the diffusion of water vapour to the surface and its diffusion or convection from the surface. The rate will therefore 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.

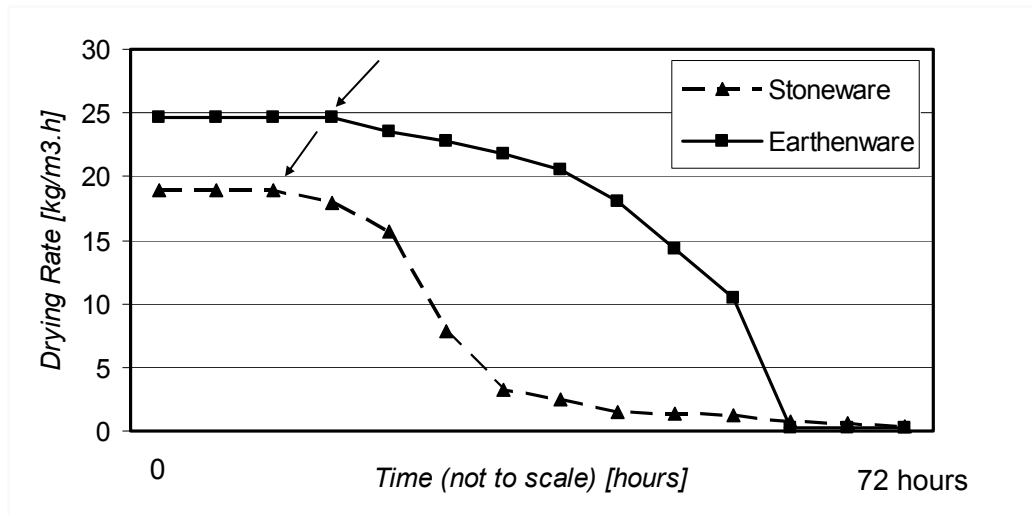


Figure 6: Drying rate curve for ceramic bodies. The three different stages during the drying of the porous material are defined by the transfer mechanism of moisture. Arrows point to the change of drying mechanism from surface evaporation to combined mechanisms that result as the drying front moves into the interior of the material. At this point, the material has reached its critical moisture content. Note the influence of the clays in the earthenware ceramic on the drying rate. Curves obtained from data presented in [11].

It is important to highlight that while capillary absorption is a relatively fast mechanism, drying is comparatively slow as a consequence of the attraction of water molecules for the mineral surfaces. Consequently, a porous material in a building wetted during a rain event will take far longer in drying, sometimes up to 100 times longer, than it did in getting wet [12]. This situation will be aggravated if there are fissures in the material or leaks that will continue feeding water into it.

5 Interaction of water vapour with porous materials

When a porous building material is exposed to humid air, water molecules are adsorbed by the surface due to the polar interactions described above. The amount of adsorbed moisture at a certain partial pressure will depend on temperature, the type of substrate, its pore size distribution and geometry. At constant temperature, the adsorbed moisture increases with increasing relative humidity of the surrounding air, as shown in the isotherm plotted in Figure 7. The shape of the plot is best described by the BET-type, i.e., adsorption is not restricted to a monolayer, and its velocity decreases with increasing degree of adsorption. As Badmann et al. [13]

could demonstrate, the chemical potential μ of water on solid mineral surfaces is in the order of 20 kJ/mole, which corresponds to the formation energy of the intermolecular hydrogen bonds (i.e., smaller than the energy of a covalent bond, but much larger than the energy of a van der Waals interaction).

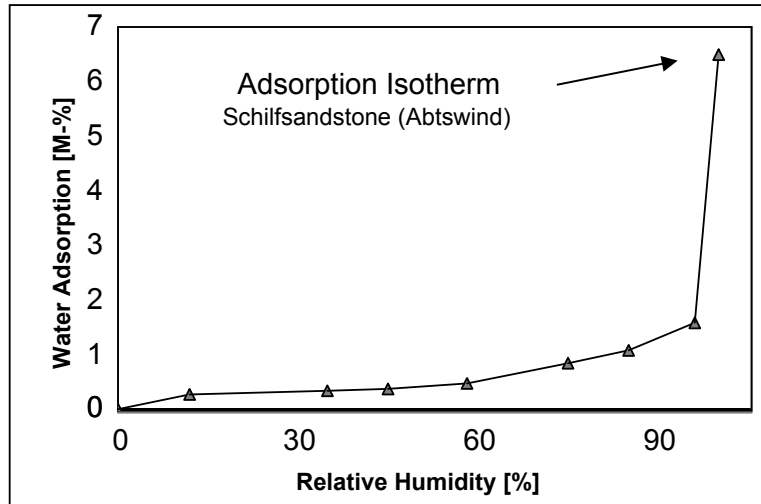


Figure 7: Adsorption isotherm (20°C) for Abtswind sandstone, a clay bound sandstone from Franconia (Northern Bavaria, Germany). The arrow indicates the water saturation point.

In the left section of the plot shown in Figure 7, a constant slope is reached when the adsorption of a monolayer of water molecules has been achieved, i.e., at about 30% RH. The increase of the curve in the right section (>60 % RH) indicates the beginning of multilayer structure formation. Above 75% RH, capillary condensation starts to take place in small pores (1 to 10 nm diameter). This occurs when the pore walls are so close to each other that the polarization of the adsorbed multilayers of water molecules on these pore surface leads to ordered water structures (ice-like structures with intermolecular hydrogen bonds) over a range of several nanometers. As the formation of these ordered structures is exothermic, more water can be retained at a given RH by a porous substrate than would be adsorbed on a flat mineral surface.

Once water is adsorbed it is capable of migrating in a moisture gradient. Therefore, wet building materials show a larger drying rate as compared to only damp materials having few adsorption layers (see Fig. 6). As shown in the last drying stage, the simple diffusion of water (vapour) molecules through the pore space of a building material is of minor importance in the drying process.

Adsorbed water layers are also capable of dissolving soluble salts which then will migrate with the water whenever a concentration gradient is present. Thus, the transport of salts is not necessarily combined with a salt solution filling the pore space to a large extent. Salt diffusion may occur even at rather dry conditions, even below the equilibrium RH for the particular salt as has been shown experimentally [14]. The same effect can be observed in the laboratory, known as “salt creep” when salts migrate up a glass vessel partly filled with a salt solution [15].

The adsorption process of water vapour can also induce hygric dilatation in some building materials. This may be another important damage factor apart from the hydric dilatation which occurs upon the uptake of liquid water. Figure 8 shows the moisture dilatation function of the same Abtswind sandstone from Figure 7.

Dilatation can be explained in part by a formation of space-consuming hydration structures, e.g., as for certain clay minerals. However, as postulated by Stockhausen [16] who found dilatation effects also in clay-free materials, water forms ordered adsorption structures on the surface of minerals which require more space than liquid water. Thus, the polar nature of the adsorbed water, combined with a large inner surface of some mineral structures, may lead to large dilatation values. In unfavourable climatic situations, shear forces between dry and wet zones may exceed the tensile strength of the material and lead to damage [17]. Since rapid changes in humidity are more frequent than intensive wetting by rain showers, the former may play an even more important role in material deterioration than the latter.

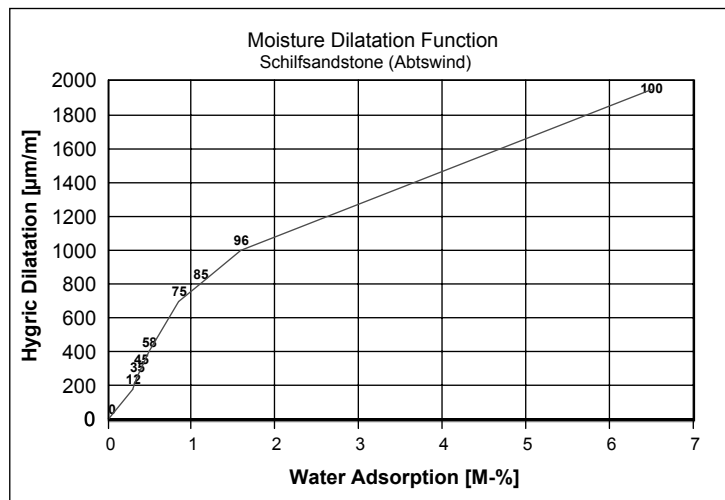


Figure 8: Moisture dilatation function for Abtswind sandstone at 20°C. Numbers by the curve indicate the RH values at which the moisture equilibrium was reached except for the 100% value that corresponds to saturation in liquid water.

6 Discussion

Due to the unique position of oxygen in the periodic system of elements, H₂O-molecules are able to form multi-directed H-bridges not only between each other, but also to X-O-H groups on the surface of minerals (X = Si, Al, Fe, Ca, Mg etc.). Since oxygen makes up to 92% by volume of the entire lithosphere, these bonds have a large significance with respect to cohesion forces between minerals as well as adsorptive forces to water. It is to be remembered that water can increase the intergranular forces between mineral grains, as evidenced by one of the oldest building materials man used, i.e., adobe, with its generic meaning as material, not just mud-brick. Other examples can be observed when children build sand castles with the help of water on the beach (the presence of salts and clays will contribute in retaining moisture and holding the castle together longer).

Adsorbed water at polar mineral surfaces, especially inside the pore space of building materials, shows a higher degree of order than liquid water but a lower one than ice. The cooperative H-bonds in these relatively ordered structures lead to a gain of energy. The directed electrostatic interactions at the surface, –these depend on the nature of the specific mineral–, are transferred through numerous mono-layers of water, and in small pores having diameters of 10 nanometers or less, the influence of opposite pore walls may reach through the whole pore. Thus, capillary condensation in nanopores can be explained by the spontaneous formation of adsorbed, ordered water structures which are energetically favoured. Due to the larger space required, this may lead to dilatation effects if these pore sizes are predominant and if the porous material does not have the sufficient mechanical resistance to counter balance them. In other words, the energy gained from capillary condensation 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.

As the pore size increases, the so-called capillary range of pore size is reached. The smaller pores of this range, i.e., those larger than 0.1 μm , are able to transport smaller amounts of water but these can reach greater heights defying gravity. However, this transport is extremely slow as discussed in the previous section.

When larger pores ($> 1 \mu\text{m}$) are filled with water, only the molecular layers close to the pore walls form ordered structures. These, can range in thickness from 100 to 1000 mono-layers (approx. 30 to 300 nm) and this will depend on the specific charge distribution of the mineral surface. Therefore, the major portion of the water close to the center of those pores has no short range order and can be regarded as liquid water with randomly directed H-bonds (Fig. 9). The driving force for the capillary movement is given by a shift of water molecules from the center region towards charged surface positions which are still “dry”. 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, because of gravity, they will not reach such heights. Table 2 presents a summary of the water transport mechanisms depending on pore size.

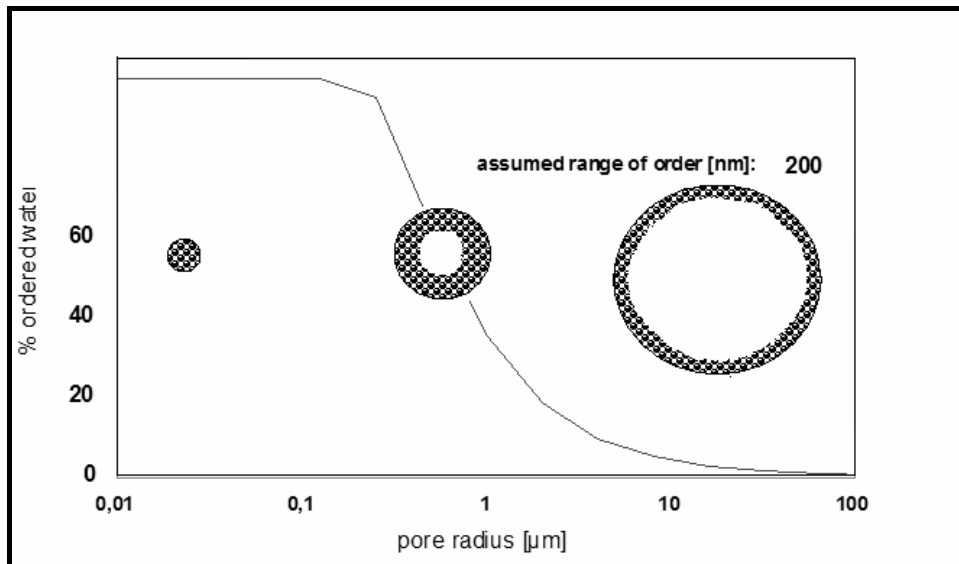


Figure 9: With increasing pore diameter, the relative amount of ordered (structural) water tightly bound to the surface (dark) decreases.

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 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 the 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 “free”, i.e., liquid water.

Table 2: Water transport mechanisms depending on pore size; expressed as pore diameter.

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

Adsorbed water on the pore network of a building material is able to transport dissolved salts through this network thus distributing the salts according to the porosity of the material. And this can happen at moisture contents far below those required for capillary transport. Although this mechanism may take much longer than capillary transport, it is highly effective, because building materials are relatively seldom sufficiently wet throughout to allow capillary transport.

Soluble salts play an active role in their transport by their hygroscopic nature and, if in solution, by the so-called osmotic process, the tendency for the solution to dilute itself. The latter explains the slower drying rate of salt laden building materials. It is known that crystallized soluble salts will concentrate in the larger pores so that when water reaches these pores through a capillary the salts will tend to “pull it out” enhancing its transport into the large pores, a process that otherwise would take far more time. And that is where creep phenomena come into play. As pointed out by Pühringer, “it is the salt that carries the water” [18].

7 Conclusions

To understand deterioration mechanisms on building materials the complex interactions of water with the specific polar mineral surfaces are basic. The above discussion has shown that, apart from water vapour and liquid water, the presence of an ordered water structure bound to the mineral surface has to be taken into account. It is at this point, where the classic models fail. These models, apart from the solid mineral phase, only consider two phases for water while there is a third one present: the bound ordered water structure. Therefore, it can be said that in the

interaction of water with porous materials, water can interact as a liquid, as a vapour and as a bound ordered phase. The latter is the driving force for capillary movement as well as for destructive expansion processes. And this is the area where further research is required.

Finally, and in the context of water repellent treatments, the question then arises as to whether water repellent molecules can compete with adsorbed water molecules on the surface of small pores, such as those under 0.1 μm where liquid water no longer exists.

Acknowledgements

The authors would like to thank Prof. F. H. Wittmann for valuable discussions regarding the terminology used in the field of capillarity.

References

- [1] E. Tammes, B.H. Vos. Vocht in bouwconstructies. Bouwcentrum, Rotterdam, 1966.
- [2] H. Klopfer. Wassertransport durch Diffusion in Feststoffen, Bauverlag Wiesbaden, Berlin, 1974.
- [3] G. Massari, I. Massari. Risanamento igienico dei locali umidi. Ulrico Hoepli Editore, Milan, 1985.
- [4] F.A.L. Dullien. Porous Media: Fluid Transport and Pore Structures. 2nd Ed., Academic Press, San Diego, 1992.
- [5] F.M.A. Henriques. Humidade em paredes. Laboratório Nacional de Engenharia Civil, Lisbon, 1994.
- [6] C. Hall, W.D. Hoff. Water Transport in Brick, Stone and Concrete. Spon Press, London, 2002.
- [7] R.J. Pender. The Behaviour of Water in Porous Building Materials and Structures. Reviews in Conservation 5 (2004) 49-62.
- [8] http://www.cup.uni-muenchen.de/ac/kluefers/homepage/L_ac1.html
- [9] D.J. Honsinger. Strukturmerkmale polymerimprägnierter Sandsteine. Ein Betrag zur makroskopischen Beurteilung. Doctoral Thesis, Rheinisch Westfallische Technische Hochschule Aachen (1990).
- [10] H. Klopfer. Das Kapillarverhalten poröser Baustoffe. Lehrgang Nr. 4406/79.88, Technische Akademie Esslingen (1980).

- [11] A.E. Charola, S. Nunberg, J. Freedland, Salts in Ceramic Bodies. I: Introducing Salts into Ceramics. *International Journal for Restoration of Buildings and Monuments* 7 [2] (2001) 117-130.
- [12] C. Bläuer Böhm. Auswirkungen von hydrophoben Fassadenmaterialien auf die Erhaltung und Pflegefähigkeit von Baudenkmälern. Beobachtungen aus der Praxis- Klimastabilisierung und bauphysikalisch Konzepte. ICOMOS Hefte des Deutschen Nationalkomitees XLII, M.Exner and D.Jakobs. Eds. (2004) 117-128.
- [13] R. Badmann, N. Stockhausen, M.J. Setzer. The Statistical Thickness and the Chemical Potential of Adsorbed Water Films. *J. Colloid Interface Science* 82 (1981) 534-542.
- [14] S. Nunberg, A.E. Charola. Salts in Ceramic Bodies. II: Deterioration due to Minimal Changes in Relative Humidity. *International Journal for Restoration of Buildings and Monuments* 7 [2] (2001) 131-145.
- [15] J. Pühringer. Salt Disintegration. Salt migration and degradation by salt–A Hypothesis. D15:1983. Swedish Council for Building Research. Stockholm, 1983
- [16] N. Stockhausen. Die Dilatation hochporöser Festkörper bei Wasseraufnahme und Eisbildung. Doctoral Thesis, TU München (1981).
- [17] E. Wendler. Contour Scaling Damage on Natural Stone: Mechanisms of Development – Possibilities and Limits of Consolidation. Int. Seminar “Theory and practice in conservation. A tribute to Cesare Brandi”, J. Delgado Rodrigues and J.M.Mimoso, Eds., Laboratório Nacional de Engenharia Civil, Lisbon 2006, 463-471.
- [18] J. Pühringer. Salzwanderungen und Verwitterung durch Salze. In: *Materials Science and Restoration*, F. Wittmann, Ed., Edition Lack + Chemie, Filderstad, (1983) 361-366