

WATER VAPOR ADSORPTION AND TRANSFER IN MICROPOROUS BUILDING MATERIALS. A NETWORK SIMULATION

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ABSTRACT

In this paper, we develop a discrete approach to describe the transport of condensable vapors through a microporous substance. We consider only isothermal water migration under uniform atmospheric air pressure, at temperature lower than 100°C with negligible gravity. The pore-structure which is supposed to be representative of the material is built on a 2D random network of tubes. The basic phenomena (adsorption/desorption, diffusion, condensation) that occur during the water vapor transport in a single cylindrical pore at the steady state are taken into account. We underline that capillary condensation can be expected to cause vapor flow amplification of some few orders of magnitude. This phenomenon provides us with a possible explanation of some experimental results.

1. INTRODUCTION.

Diffusion of water vapor acting with a condensed phase plays an important part in wide fields of research such as drying, catalysis and moisture transport in porous media. Especially in building materials there is more or less a continuous moisture transfer in the form of water vapor and condensed water. This means at least, slow desintegration of the materials due to relevant physical, chemical, and biological processes (shrinkage, freezing/thaw, swelling, mouldiness...). These processes really modify the thermal and mechanical properties of the materials too. High moisture content leads to sudden and disastrous damage, very low moisture content brings about more pernicious problems. Hence, building materials durability does depend on their behaviour towards humidity.

Several phenomenological and macroscopic theories describing heat and moisture transfers in porous media have been developed since the fifties: LUIKOV, PHILIP-deVRIES, WHITAKER. These theories are based on a continuous porous model where local values are identified to mean value on a Representative Elementary Volume (REV). The method which is generally used consists in measuring diffusion coefficients and resolving the coupled equations.

At this time, we have noticed through the analysis of the numerous studies carried out on soils and building materials that liquid water transport is generally well described (DAIAN 1986-1).

Unfortunately, liquid water flow occurs mainly for high moisture content and the building materials water content is generally far from the water content value where the liquid flow is predominant.

Furthermore, for low moisture content the mechanisms of moisture flow are not yet strictly analyzed and some discrepancies have been found between experimental and theoretical results (CRAUSSE & al. 1983-2).

A microlevel analysis of moisture flow through microporous building materials is presented. We apply the models proposed by RADJY (RADJY 1974-3) and LEE & al. (LEE & al. 1986-4) to describe the steady flow of condensible water vapor through a cylindrical pore.

Only the basic phenomena (adsorption/desorption, diffusion, condensation) that occurs during the water vapor transport in a single cylindrical pore at the steady state are taken into account. Moreover, we introduce the network method, widely used in petroleum engineering and geology, in order to build a numerical porous media which is supposed to be representative of a real microstructure.

2. ADSORPTION AND CAPILLARY CONDENSATION.

At the microscopic level (pore size), we describe moisture adsorption and moisture transport through a single pore. We consider only the basic mechanisms that contribute to sorption and flow: physical adsorption on the surface of the pore wall, capillary condensation, gas phase flow, surface flow and liquid flow. (figure 1).

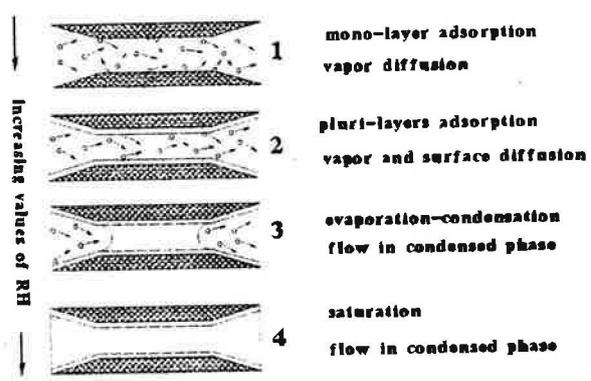


Figure 1: Basic phenomena that occur in a single cylindrical pore when the relative humidity is increasing.

2.1 physical adsorption

Generally speaking, the adsorption results of interactions between a gas and a solid surface. This process occurs until the thermodynamic equilibrium between the gaseous phase and the adsorbed layer is reached.

Since water is a molecule with a permanent dipole moment, we used the BRADLEY's equation to account for the statistical thickness e_a of the adsorbed water film.

$$e_a(RH) = K_1 + K_2 * (\ln(-\ln(RH))) \quad (1)$$

In the case of cement raw material BADMANN & al. (BADMANN & al. 1981- 5) found $K_1 = 3.85$ and $K_2 = -1.89$.

2.2 capillary condensation and hysteresis

For the capillary condensation, we write the equality of the chemical potential of the liquid and its vapor at equilibrium. By using the LAPLACE's equation, it directly leads to KELVIN's equation which relates the relative pressure to the radius of the largest pore in which condensation can occur. ($P_{vs} \& P_v \ll P_l$)

$$-\frac{2 \cdot \sigma \cdot \cos \beta}{R_{pK}} = \Gamma_1 * \left(\frac{R \cdot T}{M}\right) * \ln(RH) \quad (2)$$

The condition for condensation is that the effective pore radius R_p has to be lower than R_{pK} , value of the radius given by the KELVIN-LAPLACE's equation. (equation 2).

$$R_p(RH) = R_0 - e_a(RH) \quad (3)$$

with R_0 the initial radius of the pore.

The saturation rate of the single pore is defined as follows:

$$s_i = 1 \quad \text{if } R_p < R_{pK}$$

$$s_i = 1 - \left(\frac{R_p - e_a(RH)}{R_p}\right)^2 \quad \text{if } R_p > R_{pK}$$

These equations imply the following assumptions: all the single pores have the same volume, i. e. there are more small pores than large pores.

Hysteresis is represented as follows. In sorption, water vapor condenses in all the pores of which radius satisfies the previous condition. Desorption is supposed to be a process of displacement by a non-wetting phase (PARLAR & al. 1988-6), namely the air. Consequently, during desorption, a pore cannot desorb unless the following two conditions are met:

- the pore is allowed to desorb, i.e. $R_p > R_{pK}$

- the pore has access to a continuous path of air connected to the entry side of the network.

This phenomenon is generally called the 'ink-bottle' effect.

3. MOISTURE FLOW.

3.1: gas phase flow

The water vapor flow in a pore is governed by different mechanisms that depend on the vapor pressure P_v and the pore radius R_p . Each has its own expression depending on the KNUDSEN number which is the ratio of the mean free path l_m of the water vapor to the average diameter of the pore:

$$N_k = \frac{l_m}{2 \cdot R_p} \quad (4)$$

In this study, the total pressure ($P_t = P_v + P_a$) is assumed to be constant and equal to the atmospheric pressure.

The flux of water vapor through the pore may be described by a FICK-like law using the vapor pressure as potential.

$$q = -K_v * \text{grad}(P_v) \quad (5)$$

For vapor flow without capillary condensation, the water vapor permeability K_v is given by:

$$K_v = \left(\frac{D_{va}}{1 + l_m/2 \cdot R_p}\right) * \left(\frac{M}{R \cdot T}\right) \quad (6)$$

The formula 6 is valid for both diffusion cases; molecular diffusion ($2 \cdot R_p \gg l_m$ or low KNUDSEN's number) and KNUDSEN diffusion ($2 \cdot R_p \ll l_m$ or high KNUDSEN's number), where l_m is the mean free path of the water molecule.

The molecular diffusion coefficient D_{va} is, of course, independent of the size of the pore. The value of this diffusion coefficient of water vapor in air can be obtained from the following formula:

$$D_{va} = D_0 * \left(\frac{P_0}{P}\right) * \left(\frac{T}{T_0}\right)^{1.88} \quad (7)$$

with: $P_0 = 11325$ Pa, $T_0 = 273.16$ K and $D_0 = 21.6 * 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$.

3.2: surface flow

The surface flow is certainly the mechanism which is most difficult to analyze. Several interpretations have been proposed but a fully satisfactory explanation has not been yet provided. Two distinct approaches are commonly used: the site hopping model and the hydrodynamic model (LEE & al. 1986). The site hopping model is based on the assumption that the adsorbed water vapor molecules randomly hop and migrate from site to site on the surface. This model can be used only for the low range of adsorption (below the monolayer region) and it is not well developed quantitatively. The hydrodynamic model considers the adsorbed gas molecules on the solid surface as laminar flowing film of viscous liquid.

In this paper, as suggested by KAMP (KAMP 1988-7), we do not consider the surface diffusion because there are some indications that allow us to consider this mechanism only as of secondary importance in inorganic building materials. Actually, the thickness of the adsorbed film is very low (about 10 Angstrom) (BADMANN & al. 1981) and consequently the attraction forces (van der waals ...) are very high.

3.3: liquid phase flow

Assuming POISEUILLE flow with no slip at the boundary, the liquid flow obeys the HAGEN-POISEUILLE equation:

$$q_1 = - \left(\frac{\Gamma_1}{\mu_1} \right) * \left(\frac{R_p^2}{8} \right) * \text{grad}(P_1) \quad (8)$$

As we assume that the local equilibrium exists at the vapor-liquid interface, the KELVIN-LAPALCE's law allows us to convert the P_1 gradient into a P_v gradient. The mass conservation implies condensation or evaporation at each interface. Then, with the relative humidity playing the role of the potential, the equivalent water vapor permeability for a condensed pore is given by:

$$K_v = - \left(\frac{\Gamma_1}{\mu_1} \right)^2 * \frac{R \cdot T}{M} * \left(\frac{R_p^2}{8} \right) * \frac{1}{P_v} \quad (9)$$

In figure 2, we plotted K_v (equations 6 and 9) versus R_p and HR. The curve obtained suggests us an analogy between the vapor transfer in a cylindrical pore and a Zener diode.

4. THE NETWORK MODEL

The very complex microstructure of building materials is described by using a 2D network computer model in which the bonds are supposed to be a bundle of cylindrical pores of the same diameter. The length of each pore is equal to 1. Three kinds of networks have been built in order to study the effect of the connectivity: square, triangular and honeycomb. (figure 3)

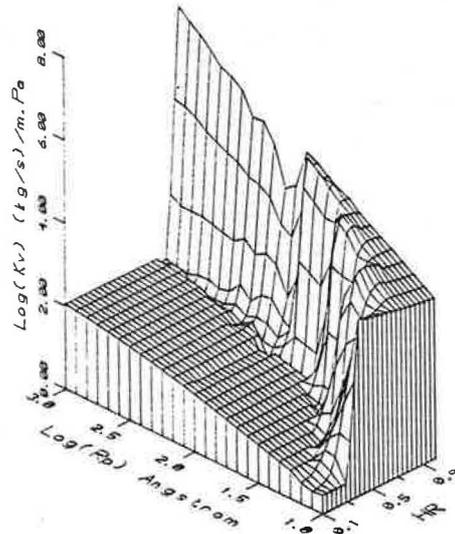


Figure 2: Water vapor permeability of a cylindrical pore versus the radius of the pore and the relative humidity.

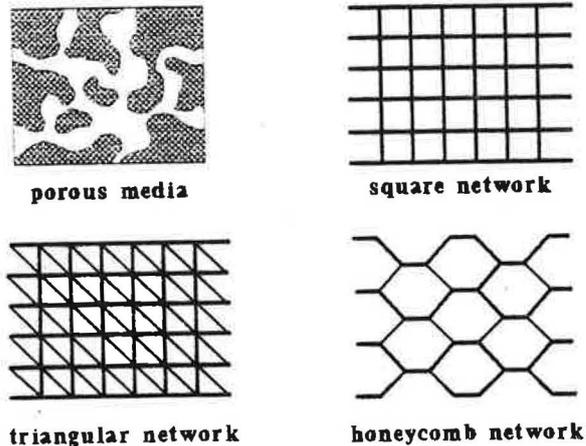


Figure 3: Network models: square, triangular and honeycomb.

A normalized Rayleigh distribution is used for simulating pore-size-distribution.

$$f(R) = \begin{cases} 0 & R < R_0 \\ \frac{1}{R_a - R_0} * \exp\left(-\frac{1}{2} * \left(\frac{R - R_0}{R_a - R_0}\right)^2\right) & R > R_0 \end{cases}$$

The results presented in paragraph 5 have been calculated with the following values: $R_0 = 10$ A and $R_a = 100$ A. We also assume that the maximum pore radius is smaller than $0.1 \mu\text{m}$ and therefore only KNUDSEN diffusion occurs.

The location in the grid is specified by using a random number generator.

The network theory, based on the analogy of DARCY's law for liquid flow to current in OHM's law, is a classical method for modeling transport phenomena in porous media. We applied the same analogy with the FICK's law and vapor transfer. Thus, each bond of the network has a conductance given by $K_v(R_p, HR)$.

The problem is now to estimate the equivalent conductance of the 2D network. The classical method is to calculate the potential at each node of the network when a potential is imposed between two faces of the 2D network, and to determine the mass flow across the model. This yields to a system of linear equations which is usually solved by using direct or iterative methods (GAUSS, relaxation method ...).

We do not choose these methods but we introduce the highly efficient algorithm proposed by FRANK & al (FRANK & al. 1988-8). This algorithm uses the series, parallel, 'star-triangle' and 'triangle-star' transformations to reduce a lattice of conductors to a single conductors.

5. SOME RESULTS AND COMMENTS.

5.1: sorption isotherms

In figure 4, we plotted the sorption isotherms calculated with the pore-size-distribution presented in paragraph 4. On the one hand we point out that the adsorption isotherms do not depend on the connectivity of the network, on the other hand we underline the hysteresis phenomenon for the desorption isotherms. This phenomenon appears naturally thanks to the 'inks-bottle' effect and the width of the hysteresis loop is all the more important than the network is ill-connected.

In figure 5, we visualize the hysteresis phenomenon. It is very interesting to notice that for the same potential, i.e same temperature and same relative humidity, the spatial water distributions are completely different. For adsorption we have an homogeneous distribution while for desorption we see some fingerings of dry pores appear.

The effect of the temperature is presented on figure 6 for the square network. We notice that as temperature increases the condensation zone is shifted to higher relative humidities.

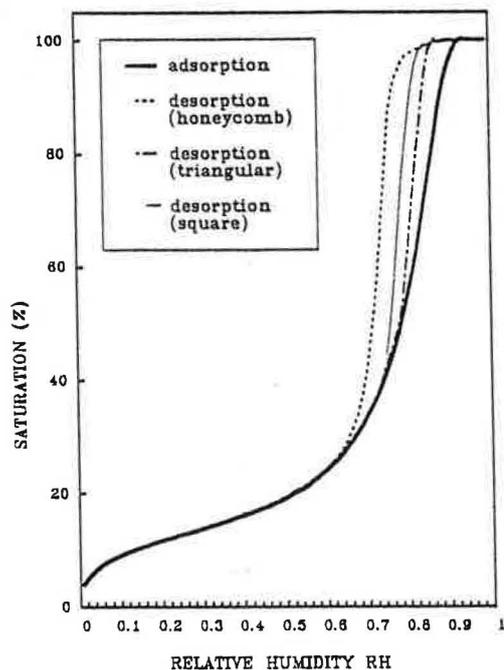


Figure 4: Sorption isotherms: effect of the connectivity on the desorption curves.

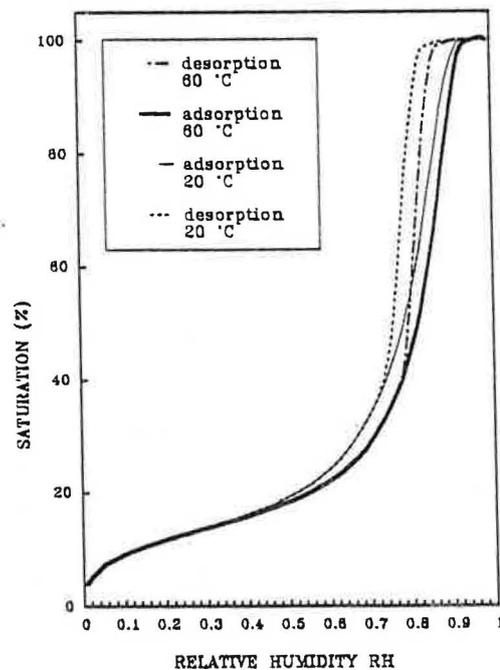
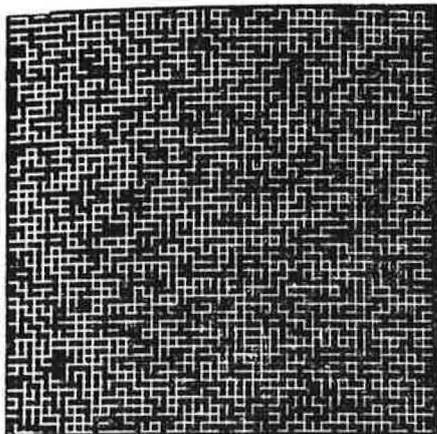
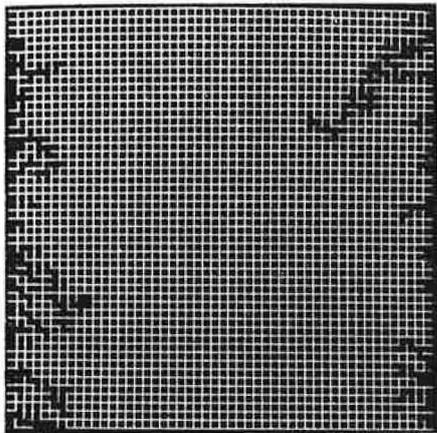


Figure 6: Effect of the temperature on the sorption isotherm curves.



adsorption



desorption

Figure 5: Visualisation of the hysteresis phenomenon, ($T=20\text{ }^{\circ}\text{C}$ and $\text{RH} = 82\%$)

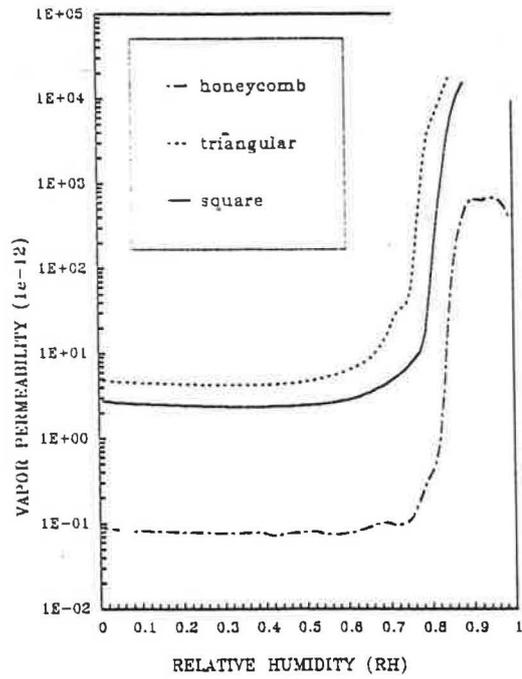


Figure 7: Effect of the relative humidity on the "water vapor permeability".

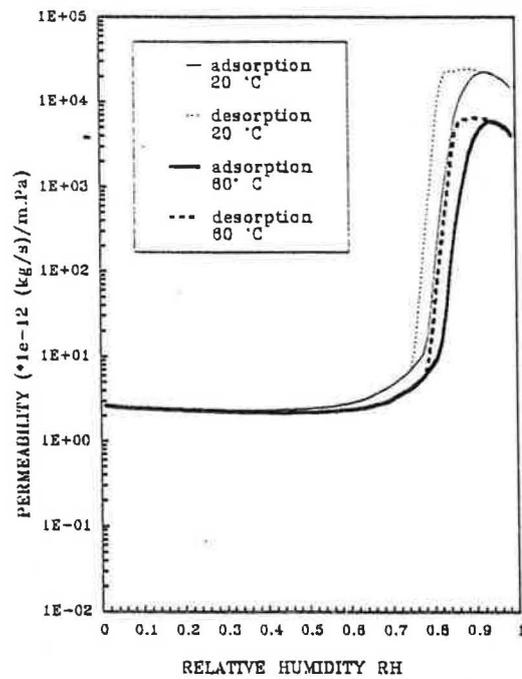


Figure 8: Effect of the temperature on the "water vapor permeability".

5.2: "water vapor permeability"

The water vapor permeability is estimated thanks to the electrical analogy. We emphasize an important amplification of the equivalent permeability when the relative humidity reaches a threshold value (figure 7). This phenomenon provides us with a possible explanation of numerous experimental results (Mc LEAN & al. 1990-9).

The effect of the temperature is presented in figure 8 for the square network. At high relative humidity, the 'water vapor permeability' decreases when the temperature increases. This effect is mainly due to the variation of the water properties versus the temperature.

6. CONCLUSION.

The main purpose of this paper has been to lay the foundation for a proper interpretation of water vapor flow in microporous media by using the network approach. In principle, this analysis establishes a self-consistent framework for relating structure to moisture storage and moisture transport by numerical techniques. We think that these techniques can really help us to improve our knowledge on fluid transport (gas, liquid ...) in microporous materials.

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D_{va} :	diffusion coefficient of water vapor in air	$m^2.s^{-1}$
K_v :	water vapor permeability	$(kg.s^{-1}).m^{-1}.Pa^{-1}$
e_a :	thickness of the adsorbed water film	μm
P_v :	relative vapor pressure	Pa
q :	mass flux density	$kg.m^{-2}.s^{-1}$
RH:	relative humidity	%
R_p :	pore radius	μm
R_{pK} :	pore radius given by the KELVIN's equation	μm
S:	saturation rate	%
T:	temperature	K

Greek symbols

β :	contact angle	rad
σ :	surface tension	$N.m^{-2}$
Γ :	density	$kg.m^{-3}$
μ :	dynamic viscosity	Pa.s