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MOISTURE TRANSPORT AND FIXATION IN POROUS MATERIALS AT HIGH MOISTURE LEVELS

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MOISTURE TRANSPORT AND FIXATION IN POROUS MATERIALS AT HIGH MOISTURE LEVELS

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PREFACE

This work has been carried out at the Division of Building Materials at the Lund Institute of Technology as part of the Moisture Research Group. The project was initiated by my supervisor, Professor Göran Fagerlund, whom I wish to thank for his support.

I also wish to express my gratitude to Professor Johan Claesson, Department of Building Physics, who came up with the original concept for measuring moisture diffusivities presented in this thesis. I would also like to thank all the staff at the Division of Building Material for their help and support.

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SUMMARY

The work presented in this thesis has focused on developing methods of measuring moisture properties at high moisture levels. Paper I deals with a new method of measuring moisture diffusivity at high moisture levels. The method is applied to several different porous building materials. Papers II to IV present methods of measuring moisture storage capacity as well as results from such measurements. In Paper V a technique for using thermal imaging to measure transient moisture profiles is evaluated. Paper VI shows how measured moisture properties can be used in calculations. In this example, moisture movement in Gotland sandstone, which was used in the construction of many historical buildings, is calculated and the degradation processes that this moisture transport might cause are discussed.

The prefatory chapter '*Moisture transport and fixation in porous materials*' gives a brief survey of the theory of moisture transport and moisture fixation as well as introducing some existing methods of measuring accompanying moisture properties.

The six papers included in this thesis are as follows:

Paper I: 'Moisture diffusivities evaluated at high moisture levels from a series of water absorption tests'

This paper presents measured moisture diffusivities for sedimentary calcareous sandstone, lime silica bricks, bricks, and autoclaved, aerated concrete. The moisture diffusivities were calculated from the relation between the water sorption coefficients and the initial water content in the specimen before testing. The method used is based on Boltzmann transformation. The relation between the water sorption coefficients and the initial water content is measured by letting specimens, preconditioned to different initial water contents, suck de-ionized water while the water uptake is measured. This process ensures that the moisture diffusivities are valid for the wetting phase. According to some investigations (e.g. Krus, 1995), moisture diffusivities are far lower during desorption.

Paper II: 'Technique for measuring moisture storage capacity at high moisture levels'

Knowledge of moisture storage capacity above the hygroscopic range is essential when calculating moisture, especially when different materials are to be connected. Generally storage capacity is represented by water retention curves, in which suction is plotted against moisture content. In a number of laboratories in Europe and North America, the pressure plate and pressure membrane technique is used to measure water retention curves. There are, however, various ways of carrying out the actual measurements. This paper compares two different methods of presaturating specimens before testing, namely capillary and vacuum saturation.

It also examines the effect of different beddings between the specimen and the ceramic plate. It is shown, as expected, that capillary and vacuum saturated specimens give different results. Absorption tests clearly show that, for some materials, capillary saturation is a vague concept. For this reason, vacuum saturation is generally to be preferred. In the test with different beddings, no significant differences were found.

Paper III: 'A test of four different experimental methods to determine sorption isotherms'

Sorption properties (i.e. information about how much water a porous material holds in different environments) are of interest in many applications. In the research reported in this paper, the sorption properties of sandstone were measured using four different methods. The first method was to equilibrate samples over saturated salt solutions. The second method used a sorption balance in which small samples were weighed as they were exposed to different relative humidity (RH). Both these methods give the sorption isotherm in the hygroscopic range (i.e. up to approximately 98% RH). The third method used the pressure membrane and pressure plate technique. Totally wet samples were equilibrated at various overpressures corresponding to specific relative humidities. This method gives sorption properties from 93% RH and upwards. In the fourth method, a newly developed micro-calorimetric technique was used. This method, too, gives the sorption isotherm in the hygroscopic range.

Despite the differences in the methods, satisfactory agreement was found between the three methods in the hygroscopic range. There was also agreement in the area of overlap (93–98% RH) between the methods measuring sorption properties in the hygroscopic range and the pressure membrane and pressure plate technique.

This paper was written in collaboration with Björn Johannesson, who performed the measurements with the sorption balance and most of the evaluations.

Paper IV: 'Measurement of moisture storage capacity using sorption balance and pressure extractors'

This paper presents measurements of the moisture storage capacity of several different porous building materials. The storage capacity was measured by a sorption balance in the hygroscopic range and with pressure plate and pressure membrane extractors in the superhygroscopic range. The results are presented in both retention curves and sorption isotherms. The results indicate, among other things, that some materials have a large hysteresis between absorption and desorption in the superhygroscopic range. This is contrary to what has often been thought.

This paper, too, was written in collaboration with Björn Johannesson, who performed the measurements with the sorption balance.

Paper V: 'Evaluation of thermal imaging as a method of measuring moisture profiles over an interface between cement-lime mortar and brick'

Moisture profiles reveal much about the moisture behavior of a material or combination of materials. Measured transient moisture profiles can also be used to verify and determine moisture diffusivities. One possible method of measuring these profiles is thermal imaging. This paper evaluates this technique on bricks with and without cement-lime mortar attached. The measured temperature profiles are transformed to moisture profiles through calibration curves obtained by measuring the temperature decrease on well-conditioned specimens. The use of calibration curves avoids problems arising from possible differences in emittance between wet and dry surfaces.

Most of the thermal imaging was performed by the co-author, Peter Johansson.

Paper VI: 'Moisture transport in a sedimentary calcareous sandstone and its effect on different degradation processes'

Degradation of historical buildings and monuments is an increasing problem in most countries around the world. The cost of preserving these buildings is substantial. In order to take the correct measures to preserve the buildings, the process causing the degradation must be identified. One technique for excluding or identifying probable causes of damage to porous materials is demonstrated in this paper. The technique is based on moisture transport calculations and is exemplified using sedimentary calcareous sandstone from the island of Gotland, Sweden. The calculations are made at very high moisture levels, both under and over capillary saturation. A traditional Fickian approach is used for calculations up to capillary saturation. Above capillary saturation, a mathematical method based on the solubility of air is used. The calculations are then supplemented by a discussion of which degradation processes, such as frost action and leaching, are affected by the calculated moisture movements and moisture levels.

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LIST OF PAPERS

Paper I

Janz, M., 'Moisture diffusivities evaluated at high moisture levels from a series of water absorption tests' (submitted for publication).

Paper II

Janz, M., 'Technique for measuring moisture storage capacity at high moisture levels', *Journal of Materials in Civil Engineering* (in press).

Paper III

Johannesson, B. and Janz, M., 'A test of four different experimental methods to determine sorption isotherms' (submitted for publication).

Paper IV

Janz, M. and Johannesson, B., 'Measurement of moisture storage capacity using sorption balance and pressure extractors' (submitted for publication).

Paper V

Janz, M. and Johansson, P., 'Evaluation of thermal imaging as a method of measuring moisture profiles over an interface between cement-lime mortar and brick' (submitted for publication).

Paper VI

Janz, M., 'Moisture transport in a sedimentary calcareous sandstone and its effect on different degradation processes' (submitted for publication).

MOISTURE TRANSPORT AND FIXATION IN POROUS MATERIALS

Introduction

Porous building materials will always contain a certain amount of water. The presence of free water or very high relative humidity is strongly associated with almost all durability problems in structures, including freeze damage in materials, flaking of grout and paint caused by frost, mold and rot on organic materials, and corrosion of steel reinforcement. Most durability problems occur at very high moisture contents in the material. Such moisture contents can only be obtained by capillary suction, or occur at very high relative humidity. Consequently, accurate prediction of the service life of structures requires good models of moisture and liquid transport, including knowledge of related properties such as moisture diffusivity and moisture storage capacity.

It is, of course, desirable to have the simplest possible mathematical description of moisture transport. The corresponding transport properties should also be easy to measure. Fick's law is often used to describe moisture transport in the hygroscopic range. (A practical definition of the hygroscopic range is used in this thesis; it is defined as the moisture range within which the equilibrium moisture content can be described and experimentally determined as a function of the relative humidity. Thus, the hygroscopic range corresponds to a moisture range from 0% RH up to approximately 98% RH.) Several well-documented methods of measuring the corresponding transport properties are available (see Hedenblad, 1993). Generally the mathematical description (Fick's law), together with applicable transport properties, gives satisfactory results within the hygroscopic range. Transport properties have been measured on several different materials (e.g. Hedenblad, 1996).

Diffusion theory based on Fick's law is also often used at high moisture levels; even though moisture transport principally occurs in the liquid phase. It is convenient not to have to change the mathematical description of the transport when the moisture level reaches a certain level. In Paper I, for example, it is shown that good agreement can be obtained on some materials with this approach. However, for most materials the agreement of moisture calculations is lower at high moisture levels, partly because of the lack of reliable transport properties. It is considerably more difficult and requires major technical effort to measure moisture properties at high moisture levels. Therefore new methods of measuring moisture diffusivity and moisture fixation at high moisture levels have been studied in this thesis.

This introductory chapter presents some basic theory of moisture transport and moisture fixation and briefly describes various methods of measuring transport properties.

Moisture transport in porous materials

General

Moisture transport phenomena in porous media can be divided into *diffusion*, *saturated viscous flow*, and *capillary (liquid) transport*.

Diffusion at isothermal conditions is driven by a difference in vapor pressure, i.e. the water molecules are moving toward a lower vapor pressure. The most common way to describe the diffusion process is Fick's law:

$$g = -\delta_p \nabla p_v \quad (1)$$

which in one dimension becomes:

$$g = -\delta_p \frac{\partial p_v}{\partial x} \quad (2)$$

where

- g is the density of moisture flow rate [$\text{kg}/(\text{m}^2 \cdot \text{s})$]
- δ_p is the moisture permeability [$\text{kg}/(\text{m} \cdot \text{s} \cdot \text{Pa})$];
- p_v is the vapor pressure [Pa].

The moisture permeability is a function of the vapor pressure, i.e. $\delta_p = f(p_v)$.

Viscous saturated flow is driven by a difference in water pressure. The flow depends both on the pore geometry of the porous material and on properties of the fluid itself. Saturated flow g [$\text{kg}/(\text{m}^2 \cdot \text{s})$] is often described by Darcy's law, which expressed in the three-dimensional pressure field becomes:

$$g = -\frac{k_p}{\eta} \nabla P \quad (3)$$

For a one-dimensional case, Darcy's law becomes:

$$g = -\frac{k_p}{\eta} \frac{dP}{dx} \quad (4)$$

where P is the water pressure [Pa], k_p is the permeability [kg/m^2] and η is dynamic viscosity [$\text{Pa} \cdot \text{s}$].

Fick's law and Darcy's law are widely used for calculating diffusion and saturated flow in porous material. However, there is no such generally accepted formula for calculating *capillary transport* through a porous material.

Capillary transport

The simplest model of calculating *capillary transport* is to approximate the wetted region as a fully saturated rectangular wet front, a sharp wet front or a moving boundary. For many applications, this model is accurate enough. The penetration depth of a sharp wet front can be calculated by:

$$x = B\sqrt{t} \quad (5)$$

where B [$\text{m/s}^{1/2}$] is the penetration coefficient, which has to be determined experimentally, and t is the time. The magnitude of B is dependent on the geometry of the liquid–vapor menisci, the surface tension, the contact angle, and the viscosity of the liquid. Since the geometry of the liquid–vapor menisci is in turn dependent on the degree of saturation, the penetration coefficient B will also be a function of the state of saturation in the material.

If it is assumed that the moisture penetration is a sharp wet front, the total amount of absorbed liquid W [kg/m^2] can be denoted by:

$$W = A\sqrt{t} \quad (6)$$

where the sorption coefficient A [$\text{kg}/(\text{m}^2 \cdot \text{s}^{1/2})$] is:

$$A = \rho P_a B \quad (7)$$

and where

ρ is the liquid density [kg/m^3];

P_a is the active porosity available for capillary transport [m^3/m^3].

The flow rate $g_{x=0}$ [$\text{kg}/(\text{m}^2 \cdot \text{s})$] through the material boundary exposed to the liquid is the time derivative of W . Since a sharp wet front is approximated, the flow in the entire saturated region is equal to the boundary flow, i.e.

$$g = g_{x=0} = \frac{dW}{dt} = \frac{A}{2\sqrt{t}} \quad (8)$$

Capillary flow is driven by the pressure difference across a meniscus. The magnitude of this pressure gradient is a function of, among other things, the structural properties of the pore system, i.e. the geometry of the liquid–vapor menisci present in the porous medium. Thus the driving potential is the pressure gradient caused by the meniscus. It is assumed that the same pressure gradient applies in all pores irrespective of their size and shape. Thus the parameter $(1/r_1 + 1/r_2)$, where r_1 and r_2 are the principal radii of the meniscus in two orthogonal directions, is assumed to be the same for all menisci in all pores.

A basic weakness of the simple capillary suction theory is the assumption that moisture transport involves a moving boundary. Another weakness is that it fails to recognize that in real materials there will always be a combination of liquid and vapor transport and a moisture front that is not completely sharp. Consequently, other theories have been developed.

In soil science, one-dimensional capillary flow is often described by an equation similar to Darcy's law. The driving potential used is the soil water potential Ψ , which is proportional to the pressure (Hall, 1994):

$$g = -K(u) \frac{\partial \Psi}{\partial x} \quad (9)$$

where $K(u)$ is the unsaturated permeability. Ψ is the energy required to transfer a unit weight of liquid from the porous material to a reservoir of the same liquid at the same temperature and elevation. The units of Ψ can be [J/kg] (Nielsen et al., 1986) or [m] (Hall, 1994). In the latter case, Ψ expresses the height to which a unit weight of the liquid will rise at equilibrium.

The soil water potential Ψ can be divided into the following parts (Nielsen et al., 1986):

$$\Psi = \sum \Psi_i = \Psi_p + \Psi_s + \Psi_e + \Psi_z \quad (10)$$

where

- Ψ_p is the pressure potential;
- Ψ_s is the solute potential;
- Ψ_e is the electrochemical potential;
- Ψ_z is the gravitational potential.

The pressure potential Ψ_p applies to both the saturated and the unsaturated zone. In the unsaturated zone, Ψ_p represents the capillary potential; in the saturated zone it represents the applied pressure. The solute potential depends on the solute concentration. The electrochemical potential depends on the interaction of the soil particles and the solute. The solute potential and the electrochemical potential can often be ignored (Jonasson, 1991).

Another approach to capillarity is to use Darcy's law with the pore water pressure P_t [Pa] as the driving potential:

$$g = -D_t \frac{\partial P_t}{\partial x} \quad (11)$$

where the transport coefficient D_t [kg/(m·s·Pa)] is a function of the pore water pressure P_t . The pore water pressure P_t [Pa] is here defined as:

$$P_t = P_{atm} - s \quad (12)$$

where P_{atm} is the atmospheric pressure [Pa] and s is what is known as suction [Pa]. The suction is the pressure difference over a meniscus between water and air, which is given by the Laplace equation:

$$s = \sigma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (13)$$

where σ is the surface tension between liquid and gas [N/m] (sometimes also expressed as the surface free energy of a surface liquid gas [J/m²]) and r_1 and r_2 are the radii of the curvature of the meniscus in two orthogonal directions. In equation 12 the atmospheric pressure P_{atm} is normally negligible. It is therefore normally omitted:

$$P_t = -s \quad (14)$$

If the atmospheric pressure is omitted, equation 11 can be rewritten:

$$g = \lambda_m \frac{\partial s}{\partial x} \quad (15)$$

where λ_m is the moisture conductivity [kg/(m·s·Pa)] that is a function of the suction. In three dimensions the equation becomes:

$$g = \lambda_m \nabla s \quad (16)$$

Total moisture transport: Isothermal conditions

When calculating moisture distribution, it is advantageous to have only one equation with a single transport coefficient that describes the total moisture transport in both vapor and liquid phases. One reason for this is that it is difficult to distinguish between vapor and liquid transport when measuring moisture transport coefficients. For materials in which there is no temperature gradient, such a formulation of the transport equation is possible, as shown below.

If the assumptions in equations 2 and 15 are valid (i.e. the moisture flow is linearly proportional to the gradient of vapor pressure and suction), the total transport can be described (here, in one dimension) by:

$$g = -\delta_p \frac{\partial p_v}{\partial x} + \lambda_m \frac{\partial s}{\partial x} \quad (17)$$

At local equilibrium a relation exists between p_v and s , as well as among all of the following moisture state variables: vapor content v [kg/m³], vapor pressure p_v [Pa], relative humidity ϕ , pore suction s [Pa], moisture content mass by mass u [kg/kg], and moisture content mass by volume w [kg/m³]. The relation between u and w is:

$$w = u\rho \quad (18)$$

where ρ is the dry bulk density [kg/m³]. The state variables ϕ , v , and p_v are related to each other by:

$$\phi = \frac{v}{v_s} = \frac{p_v}{p_s} \quad (19)$$

where the index s refer to saturation. Both the vapor content and the vapor pressure at saturation are dependent on the temperature.

The general gas law relates the vapor content to the vapor pressure:

$$p_v = \frac{RT}{M_w} \cdot v \quad (20)$$

where R is the gas constant (8.314 J/(mol·K)), T is the temperature [K], and M_w is the molar weight of water (0.018 kg/mol).

The relation between the relative humidity and the principal radii of the curvature of the meniscus in two orthogonal directions, r_1 and r_2 [m], is given by Kelvin's equation:

$$\ln \phi = -\frac{\sigma M_w}{RT \rho_w} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (21)$$

where ρ_w is the density of water [kg/m³]. Combining Kelvin's equation with the Laplace equation (equation 13) gives the relationship between the relative humidity and the suction:

$$\ln \phi = -\frac{s M_w}{RT \rho_w} \quad (22)$$

The moisture contents u and w are related to the relative humidity ϕ by the sorption isotherm (moisture content versus RH) and to the suction s by a water retention curve (moisture content versus suction). These relations must be determined experimentally.

According to Claesson (1993), the moisture state in a porous material can be characterized by three independent state variables; the total air pressure, the tem-

perature, and any of v , p_v , ϕ , s , u , or w . If the total air pressure is assumed to be constant, there will be only two independent state variables. At isothermal conditions there will be only one independent state variable, i.e. any one of v , p_v , ϕ , s , u or w . Since there is a unique relation between p_v and s through equations 19 and 22, equation 17 can be rewritten for isothermal conditions:

$$\frac{\partial s}{\partial x} = \frac{\partial s}{\partial p_v} \frac{\partial p_v}{\partial x} = -\frac{RT \rho_w}{M_w} \frac{1}{p_v} \frac{\partial p_v}{\partial x} \quad (23)$$

This leads to:

$$g = -\delta_p \frac{\partial p_v}{\partial x} - \lambda_m \frac{RT \rho_w}{M_w} \frac{1}{p_v} \frac{\partial p_v}{\partial x} = -D_{tot} \frac{\partial p_v}{\partial x} \quad (24)$$

where the new merged moisture diffusivity D_{tot} is:

$$D_{tot} = \delta_p + \lambda_m \frac{RT \rho_w}{M_w} \frac{1}{p_v} \quad (25)$$

Generally equation 24 can be written:

$$g = -D_\phi \frac{\partial \phi}{\partial x} \quad (26)$$

where D_ϕ is the moisture diffusivity, which is dependent on the moisture content, and ϕ is any of the moisture state variables v , p_v , ϕ , s , u , or w . Moisture balance requires:

$$\frac{\partial w}{\partial t} = -\frac{\partial}{\partial x}(g) = \frac{\partial}{\partial x} \left(D_\phi \frac{\partial \phi}{\partial x} \right) \quad (27)$$

which in three dimensions becomes:

$$\frac{\partial w}{\partial t} = \nabla \cdot (D_\phi \nabla \phi) \quad (28)$$

Equations 26, 27, and 28 are valid at isothermal conditions and at local equilibrium since there are unique relations among all these state variables. It is not obvious, however, that there is a local equilibrium in the material in transient cases. The rate of the phase change in nonequilibrium thermodynamics is considered to be proportional to the difference between the thermodynamic potentials of each phase (Daian, 1989). In transient transport processes the liquid and vapor phases will consequently not be in local equilibrium as, for example, Kelvin's equation presupposes.

The advantage of equations 26, 27, and 28 is that the potential ϕ can be chosen to fit a special application or measurement. Relative humidity or moisture content are often practical choices since these potentials are directly measurable. But there are also disadvantages to using an arbitrary potential ϕ . For example, the equation is not pedagogically clear, so one might be led to erroneously believe that ϕ is the correct driving potential.

At isothermal conditions it is also possible to choose a flow potential for which the moisture diffusivity is always equal to 1. This potential is called *Kirchhoff's flow potential* and its use is advantageous when both the measuring techniques and the numerical calculations of moisture flow are taken into account (Arfvidsson, 1998). Kirchhoff's flow potential ψ [kg/(m·s)] is defined by:

$$\psi = \psi_{ref} + \int_{w_{ref}}^w D_{\phi} d\phi \quad (29)$$

i.e.:

$$\frac{d\psi}{d\phi} = D_{\phi} \quad (30)$$

The moisture flow is described by:

$$g = -\nabla \psi \quad (31)$$

ψ_{ref} is the reference value at a moisture content $w = w_{ref}$ which can be chosen arbitrarily. The moisture balance equation expressed by Kirchhoff's flow potential becomes:

$$\frac{\partial w}{\partial t} = \nabla \cdot (\nabla \psi) \quad (32)$$

or:

$$C_{\psi} \frac{\partial \psi}{\partial t} = \nabla \cdot (\nabla \psi) \quad (33)$$

with the moisture capacity, C_{ψ} [s/m²], described by (see equation 30):

$$C_{\psi} = \frac{dw}{d\psi} = \frac{1}{D_{\phi}} \quad (34)$$

Total moisture transport: Non-isothermal conditions

In solid wall structures, facades exposed to solar radiation, and other structures with large temperature gradients, the temperature gradient itself will impel moisture transport. In insulated multi-layer walls, most of the temperature gradient will occur across the insulation. The temperature gradients in other parts of the wall will be negligible.

If the temperature gradient is to be taken into account, there will be two independent state variables. In this case, the simplification done in the previous section is not possible (i.e. the vapor and liquid flows in equation 17 must stay separate):

$$g = -\delta_p \frac{\partial p_v}{\partial x} + \lambda_m \frac{\partial s}{\partial x} \quad (35)$$

All other state variables are known functions of p_v and s . Here the transport coefficients δ_p and λ_m are functions of the two state variables used (i.e. δ_p and λ_m are functions of both s and p_v). Although the state variables used in equation 35 are the physical determinants of diffusion and liquid flow, any other pair of independent state variables could be used. It is possible to change from one pair of state variables to another pair (Claesson, 1993).

Künzel (1995) has presented an overview of the different methods of calculation used. The most commonly used pairs of state variables in these equations are (w, p_v) , (p_v, s) and (w, T) . If, and how, the corresponding transport coefficients have been measured for some materials is not clear in Künzel's work. Künzel (1995) suggests the following balance equation:

$$\frac{\partial w}{\partial t} = \text{div} (D_\phi \nabla \phi + \delta_p \nabla p_v) \quad (36)$$

where D_ϕ depends on the temperature and the moisture content, and δ_p depends on the temperature but not on the moisture content. According to Künzel (1995), the gradient of ϕ determines the liquid flow and the gradient of p_v determines the vapor flow. D_ϕ can be calculated from moisture distributions measured at various times in a material specimen undergoing capillary absorption. δ_p is obtained from cup-method measurements in the hygroscopic range. Thus two of the prerequisites for equation 36 are that all moisture transport in the capillary absorption test occurs in the liquid phase, and all moisture transport in the cup-method measurement occurs in the vapor phase. This is, of course, to some extent an oversimplification. Nevertheless, calculations (using equation 36) of moisture profiles during and after capillary suction on sandstone exposed to a varying climate show an impressive agreement with measured values (Künzel, 1995).

Two-phase flow and interaction

In some applications it is desirable to distinguish between liquid flow and vapor flow. For example, dissolved chloride ions are transported by convection in the liquid phase but not in the vapor phase. In order to separate the flow of these two different phases, each phase needs its own equation to describe the transport. Moreover, an equation that describes the balance between the two phases is needed. The following reasoning is based on Johannesson (1996).

If the mathematical formulations describing vapor transport and liquid transport used in equation 2 and equation 15 are correct, the one-dimensional balance equations become:

$$\frac{\partial w_v}{\partial t} = \frac{\partial}{\partial x} \left(\delta_p \frac{\partial p_v}{\partial x} \right) \quad (37)$$

and

$$\frac{\partial w_\ell}{\partial t} = -\frac{\partial}{\partial x} \left(\lambda_m \frac{\partial s}{\partial x} \right) \quad (38)$$

Here, w_v is the vapor content mass per volume material [kg/m^3] and w_ℓ is the liquid content mass per volume material [kg/m^3]. The sum of the two phases consequently is the total moisture content w :

$$w = w_v + w_\ell \quad (39)$$

During a water transport process there will always be evaporation or condensation at the water menisci. Thus, there will be a phase transformation between the vapor and liquid phases. This is ignored in equations 37 and 38. The total equations that describe two-phase flow are:

$$\frac{\partial w_v}{\partial t} = \frac{\partial}{\partial x} \left(\delta_p \frac{\partial p_v}{\partial x} \right) + \hat{w}_v \quad (40a)$$

and

$$\frac{\partial w_\ell}{\partial t} = -\frac{\partial}{\partial x} \left(\lambda_m \frac{\partial s}{\partial x} \right) + \hat{w}_\ell \quad (40b)$$

where

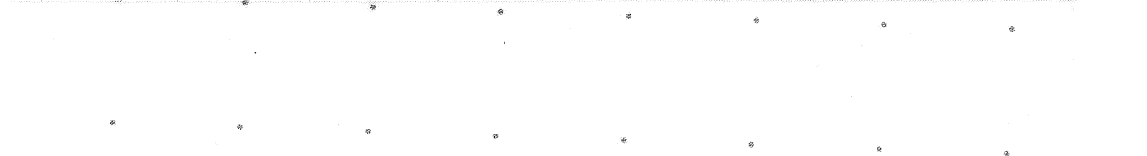
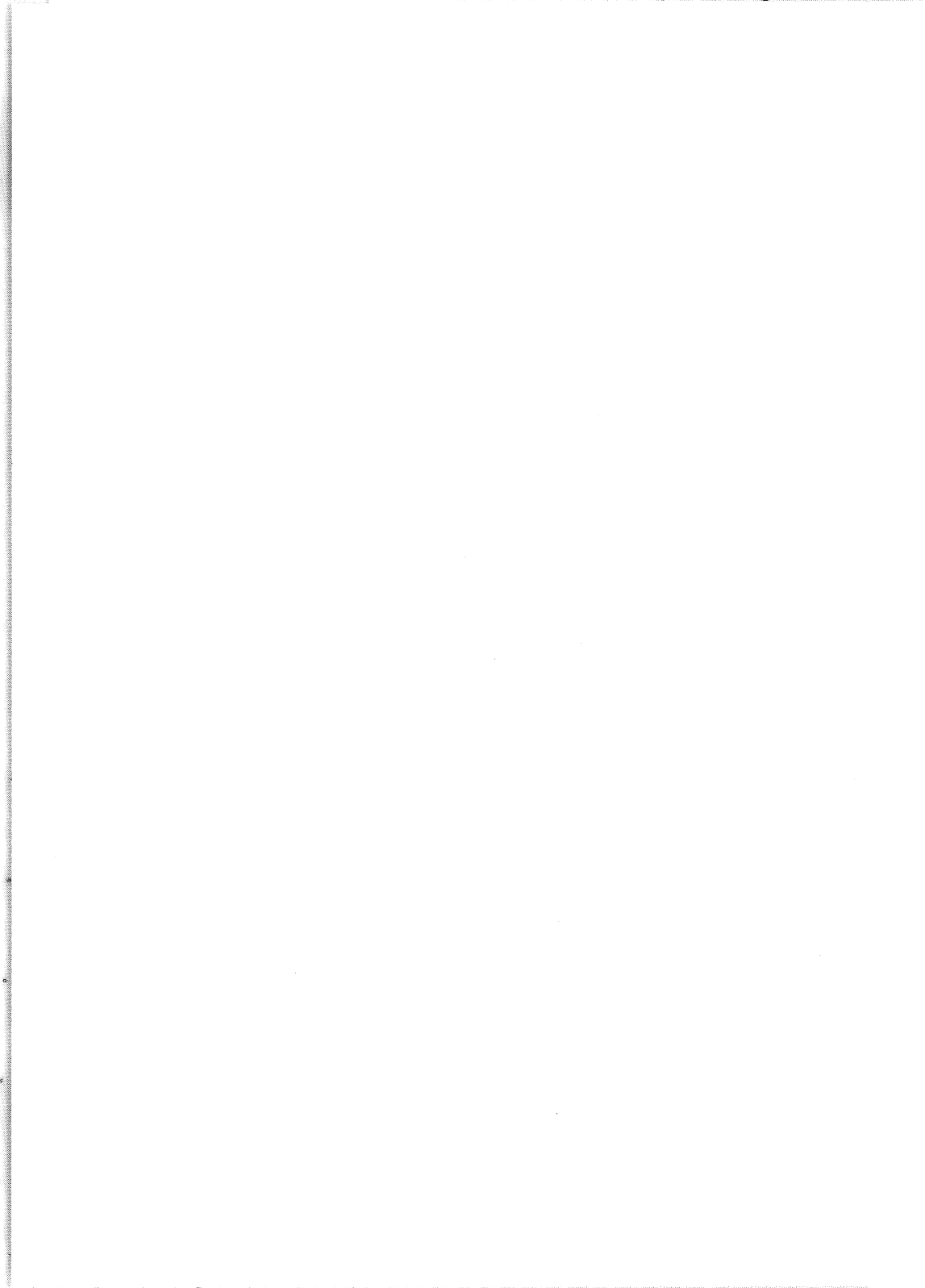
\hat{w}_v is a function describing the rate of water transformation from liquid to vapor [$\text{kg}/(\text{m}^3 \cdot \text{s})$];

\hat{w}_ℓ is a function describing the rate of water transformation from vapor to liquid [$\text{kg}/(\text{m}^3 \cdot \text{s})$].

0 1 2 3 4 5 6 7 8 9

0 1 2 3 4 5 6 7 8 9

0 1 2 3 4 5 6 7 8 9



The relation between \hat{w}_v and \hat{w}_ℓ is:

$$\hat{w}_v = -\hat{w}_\ell \quad (41)$$

Consequently, the equations needed to describe the two-phase flow are:

$$\frac{\partial w_v}{\partial t} = \frac{\partial}{\partial x} \left(\delta_p \frac{\partial p_v}{\partial x} \right) + \hat{w}_v \quad (42a)$$

$$\frac{\partial w_\ell}{\partial t} = -\frac{\partial}{\partial x} \left(\lambda_m \frac{\partial s}{\partial x} \right) - \hat{w}_v \quad (42b)$$

In the general three-dimensional case we have:

$$\frac{\partial w_v}{\partial t} = \nabla \cdot (\delta_p \nabla p_v) + \hat{w}_v \quad (43a)$$

$$\frac{\partial w_\ell}{\partial t} = \nabla \cdot (\lambda_m \nabla s) - \hat{w}_v \quad (43b)$$

Besides these two equations, a third equation describing the phase transformation between the liquid and vapor flow is needed.

$$\hat{w}_v = f(w_v, w_\ell, |\text{grad}(w_v)|, |\text{grad}(w_\ell)|, T, \text{pore geometry}, \dots) \quad (44)$$

Even though it is sometimes desirable to distinguish between liquid and vapor flow, it is impossible to measure the phase transformation (evaporation and condensation at the water menisci) with the measuring techniques available today. The same is true for the two ‘clean’ transport coefficients δ_p and λ_m . The transport coefficients obtained always describe the total moisture transport, since only the total moisture transport can be measured. Therefore, the coefficients in the separate processes must be estimated. So, the possibility of using equations 42, 43, and 44 is limited. These equations can, however, be of use when parameter studies are done.

Pore space models

It would be desirable to have a universal pore structure model from which the capillary transport or the transport coefficient could be determined. Such a model would be independent of the material, and be based on measurable geometric properties such as the porosity, the specific area, and the pore shape. This is probably not possible, since the pore system is always extremely complex and difficult to quantify geometrically.

Many different pore space models have been proposed. These models are of varying usefulness when it comes to modeling capillary transport in different types of materials. They can be divided into one-, two- and three-dimensional models. The one-dimensional models require one-directional flow only; in the two-dimensional models the flow takes place in a plane; and in the three-dimensional models the transport can occur in all directions in space. Since capillary transport always takes place in three-dimensional networks, the three-dimensional models are, of course, the most suitable in this context.

The pore system in porous materials is very complex and irregular, and the inevitable approximations made in pore space models decrease these models' usability and reliability. Van Brakel (1975) enumerated and classified almost all the proposed pore space models. He wrote: 'In order to remove too optimistic ideas about the use of pore space models, all models are checked against the phenomena of capillary rise (e.g. water in sand). The predictions of the models regarding statics and dynamics of capillary rise are compared with the experimental facts and it appears that none of the models can give even a qualitative description of the observed phenomena.' Since 1975, the rapid development of computers has created opportunities for more advanced modeling of the microstructure (see Garboczi and Bentz, 1998). Modern computer models probably give a better description of moisture transport than the models van Brakel checked in 1975.

Moisture transport above capillary saturation

Gradual water absorption above capillary saturation is very important since several durability problems occur at moisture levels above capillary saturation. There is clearly a lack of knowledge about this moisture transport, for very few attempts have been made to describe the process physically and mathematically. One attempt was made by Fagerlund (1993), who examined long-term water absorption above capillary saturation theoretically and experimentally. Fagerlund's work was drawn on in Paper VI, in which the moisture transport in sedimentary calcareous sandstone was calculated both below and above capillary saturation.

When actual capillary absorption comes to an end, there is always a certain amount of air trapped in the pore system. Thus the material is not completely saturated. This air will gradually dissolve in the water and diffuse to larger pores or out of the pore system to the surface of the material, which will lead to slow water absorption above capillary saturation. The rate at which this process will

take place is proportional to the solubility of air in water, which is in turn proportional to the internal overpressure ΔP [Pa] in the enclosed air. Thus the rate of gradual water absorption will be proportional to the dissolution rate of air in water and the diffusivity of air in the pore water. An air bubble with the radius r [m] that becomes enclosed in a coarse pore during the capillary absorption process is exposed to an internal overpressure that is inversely proportional to its radius. The overpressure is given by the Laplace equation:

$$\Delta P = \frac{2\sigma}{r} \quad (45)$$

In order to lower the overpressure, the air will endeavor to form the largest bubbles possible. If free water surrounds the material, equilibrium within the material will be reached when the radius of the air bubble is equal to the radius at the boundary of the material, i.e. infinite. Hence, at equilibrium the material will be fully saturated.

Methods of determining moisture diffusivity

Introduction

As shown above, several different models can be used to describe moisture transport in porous materials. It is important to keep the mathematical model in mind when working with measured data. For example, transport coefficients measured under isothermal conditions cannot automatically be used in non-isothermal models. If the moisture content w and the temperature T are used as state variables in the non-isothermal model, the transport coefficients will be $D_w(w, T)$ and $D_T(T, w)$, respectively. In this case, measurements must be performed at varying moisture contents and moisture gradients, at different temperature levels and temperature gradients.

It should also be noted that the choice of state variables influences the numerical value of the transport coefficients, e.g. δ_p in equation 35 is not equal to δ_p in equation 36. If the state variables (p_v, s) (used in equation 35) are changed to a new pair of state variables (ϕ, p_v) , the 'new' $\delta_p(\phi, p_v)$ becomes (Claesson, 1993):

$$\delta_p(\phi, p_v) = \delta_p(p_v, s) - \lambda_m(p_v, s) \frac{\partial s}{\partial p_v} - D_\phi \frac{\partial \phi}{\partial p_v} \quad (46)$$

Thus, there is a close link between the transport coefficients measured, the theoretical physical model to which they are to be applied, and the potential used.

At isothermal conditions and in the hygroscopic range (up to approximately 98% relative humidity) several well-documented measurement methods are available (see Nilsson, 1980 and Hedenblad, 1993). The most frequently used is probably the cup method. For materials with little or no superhygroscopic range

(i.e. with pore radii smaller than approximately 50 nm), the cup method alone is sufficient to measure the moisture diffusivity. This is due to the fact that these materials are already water saturated at equilibrium with approximately 98% relative humidity. An example of such a material is concrete with a low water to cement ratio. Hedenblad (1996) reports the moisture permeability δ , [m²/s] with v used as potential and the Kirchhoff's flow potential ψ [kg/(m·s)] for a large number of different building materials. Values were measured by the cup method in the hygroscopic range under isothermal conditions but at different temperatures for some materials. The cup method is described in detail in that paper.

For materials with a coarse pore system (e.g. some natural sandstones, brick, lime silica brick, and aerated autoclaved concrete) cup method measurements must be supplemented by some other method at high moisture levels.

In general, moisture diffusivity at high moisture levels is presented with the moisture content as driving potential (D_w). The moisture content is, of course, not the correct driving potential, but is nevertheless generally used since it is directly measurable. According to some investigations, the moisture diffusivity D_w is higher during absorption than during desorption (see Krus, 1995). This might be a consequence of hysteresis in the sorption isotherm as described below. D_w is recalculated to the moisture diffusivity D_ϕ with the theoretically more logical relative humidity as driving potential by:

$$D_\phi = D_w \frac{\partial w}{\partial \phi} \quad (47)$$

where $\partial w / \partial \phi$ is the slope of the sorption isotherm. A higher slope on the sorption isotherm results in a higher moisture diffusivity D_ϕ . For most materials the gradient during absorption is higher than during desorption at high moisture contents (see Figure 1).

The relative humidity also differs between absorption and desorption at a certain moisture content w_1 , i.e., during absorption the relative humidity corresponding to a given moisture content is higher than during desorption. This in turn entails that the moisture diffusivity D_ϕ is higher during the wetting phase than during the drying phase at the same moisture content w_1 since the coefficient D_ϕ increases with increasing relative humidity (see Figure 1).

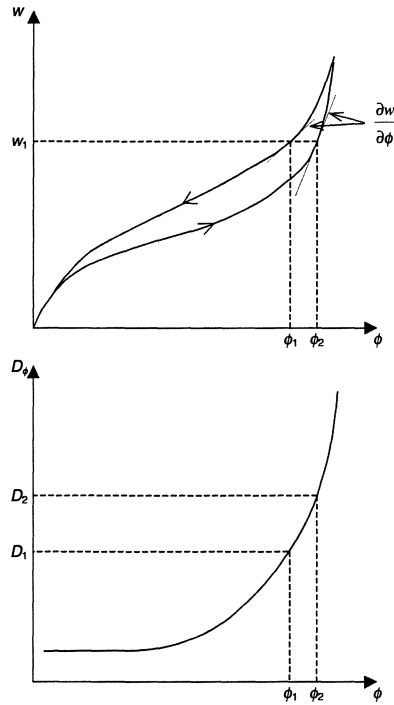


Figure 1 The moisture diffusivity corresponding to a certain moisture content w_1 differs dependent on whether the material is undergoing absorption or desorption.

Determining moisture diffusivity from the sorption coefficient

At high moisture levels, moisture diffusivity can be calculated from the relation between the water sorption coefficients and the initial water content in the specimen before testing. This method is presented in detail in Paper I and in Janz (1997).

The method is based on Boltzmann transformation. In order to determine the relation between the sorption coefficients and the initial water content, a series of absorption tests are performed. These tests require little more than a balance by way of equipment. Paper I presents the use of this method to determine the moisture diffusivities of sedimentary calcareous sandstone (Gotland sandstone), lime silica bricks, bricks, and cement-lime mortar.

Determining moisture diffusivity from steady state moisture profiles

The moisture diffusivity at high moisture levels can also be determined from moisture profiles at steady state. One method of this type will be described.

The method is based on measurements of the relation between the moisture content and Kirchhoff's flow potential up to capillary saturation. It is described in Arfvidsson (1994) and Hedenblad (1993). Moisture profiles are measured only after the flux has reached a steady state. The moisture flow through the specimen at steady state, $g_{t=\infty}$ must also be known. The profile can be measured in terms of degree of saturation or in terms of moisture content (mass per mass, or mass per volume). Relative humidity is not suitable at the high moisture levels occurring during capillary suction since the resolution of relative humidity is poor in this region. In what follows, the moisture content mass per volume w [kg/m³] will be used. Using Kirchhoff's flow potential (see equation 29), Fick's law is

$$g = -\frac{\partial \psi}{\partial x} \quad (48)$$

Here Kirchhoff's flow potential ψ is a function of the moisture content

$$\psi = \psi(w) \quad (49)$$

If we assume steady state through a specimen $0 \leq x \leq \ell$, at $x = 0$ there is capillary saturation and at $x = \ell$ there is a constant value $w(\ell)$. The steady state moisture profile is $w = w(x)$ and the flux $g_{t=\infty}$. Then we have:

$$g_{t=\infty} = -\frac{d}{dx}[\psi(w(x))] \quad (50)$$

Integration from 0 to x gives

$$g_{t=\infty} \cdot x = -\psi(w(x)) + \psi(w_{cap}) \quad (51)$$

or

$$\psi(w) = \psi(w_{cap}) + (-g_{t=\infty}) \cdot x \quad (52)$$

Equation 52 can now be used to calculate the stepwise relation $\psi(w)$.

Example (notations according to Figure 2): At steady state the difference in Kirchhoff's flow potential between two points, $\Delta\psi$, within a distance of Δx in a homogenous material is described by equation 51:

$$\Delta\psi = -g_{t=\infty} \cdot \Delta x \quad (53)$$

The difference in the Kirchhoff flow potential through the whole specimen ($\Delta x_1 = x_1 = \ell$) is calculated by

$$\Delta \psi_1 = \psi(w_1) - \psi(w_{cap}) = -g_{t=\infty} \cdot x_1 \quad (54)$$

With $\psi_{ref} = \psi(w_1) = 0$, $\psi(w_{cap})$ is calculated (ψ_{ref} can be chosen arbitrary):

$$\psi(w_{cap}) = g_{t=\infty} \cdot x_1 \quad (55)$$

The difference in the Kirchhoff flow potential, from the exposed surface to the level $x = x_2$ ($\Delta x_2 = x_2$), is calculated by (see Figure 2):

$$\Delta \psi_2 = \psi(w_2) - \psi(w_{cap}) = -g_{t=\infty} \cdot x_2 \quad (56)$$

According to equation 55 $\psi(w_{cap}) = g_{t=\infty} \cdot x_1$. That is:

$$\psi(w_2) = g_{t=\infty} \cdot (x_1 - x_2) \quad (57)$$

A stepwise linear relation $\psi(w)$ can accordingly be calculated by

$$\psi(w_1) = \psi_{ref} = 0 \quad (58a)$$

$$\psi(w_2) = g_{t=\infty} \cdot (x_1 - x_2) \quad (58b)$$

$$\psi(w_3) = g_{t=\infty} \cdot (x_1 - x_3) \quad (58c)$$

$$\vdots$$

$$\psi(w_{cap}) = g_{t=\infty} \cdot x_1 \quad (58N)$$

A disadvantage of this method is that it takes a considerable time for the specimen to reach steady state. It is also difficult to use the method on materials with very steep moisture profiles.

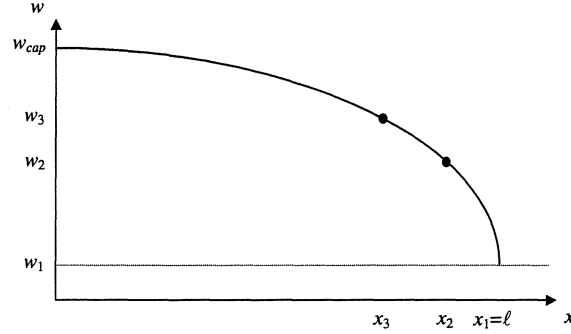


Figure 2 The moisture profile at steady state through a specimen with a length ℓ and with one boundary exposed to water (capillary saturation on the surface) and the other boundary exposed to a constant climate corresponding to w_1 .

Determining moisture diffusivity from transient moisture profiles

The moisture diffusivity at high moisture levels can also be calculated from the moisture profile measured at various times after the start of water uptake or the start of moisture redistribution. The profiles are measured on specimens that are absorbing liquid water from the boundary, or on specimens subjected to the redistribution process occurring when the absorption process is interrupted. Two possible methods of calculating moisture diffusivity from transient moisture profiles are the Boltzmann transformation method and the profile method (see Freitas et al., 1995).

The Boltzmann transformation method necessitates a step change of the boundary moisture level ($w(x, 0) = w_m$; $w(0, t) = \text{constant}$) and is valid only for a semi-infinite volume. In other words, with the Boltzmann transformation method the moisture diffusivity can only be calculated from absorption profiles. The material must also have a linear correlation between mass flux and the square root of time. The moisture diffusivity D_w is calculated by (see Figure 3):

$$D_w(w_2) = -\frac{1}{2 \cdot \frac{\partial w}{\partial U}} \cdot \int_{w_m}^{w_2} U dw \quad (59)$$

where w is the moisture content [kg/m^3] and U is the Boltzmann's variable [$\text{m/s}^{1/2}$] defined by

$$U = \frac{x}{\sqrt{t}} \quad (60)$$

The profile method can be used on profiles measured during both the absorption and the redistribution process. The moisture diffusivity is expressed as a function of an average moisture profile curve between two measured profiles (see Figure 3):

$$D_w = -\frac{1}{dt} \cdot \frac{\int_{x=x_0}^{x=\ell} (w_{t+dt}(x) - w_t(x)) dx}{\frac{\partial w_0}{\partial x_0}} \quad (61)$$

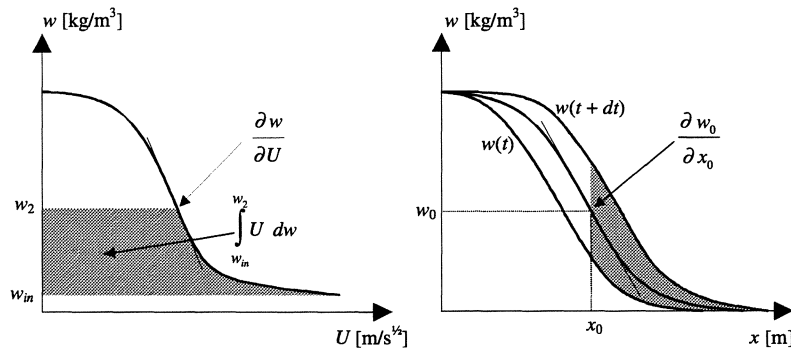


Figure 3 Principle of the Boltzmann method (left) and the profile method (right)

Some possible methods of experimental determination of the moisture profile in unidirectional water absorption or desorption are described below.

Methods of measuring unidimensional transient moisture profiles

Introduction

Measured transient moisture profiles reveal much about the moisture behavior of a material or combination of materials. They can be used to calibrate models of moisture transport or, as shown above, the moisture diffusivity can be determined from the measured profiles. Several different methods of determining moisture profiles exist. An overview of these methods is shown below.

Slice-dry-weigh method

In order to measure the moisture profile the specimen that has been exposed to unidirectional water uptake or drying is rapidly sliced into discs that are weighed, dried, and weighed again. The water in the disc evaporates during the drying and the water content in mass by mass can be calculated from the weight loss. The drying procedure can be executed in several different ways, depending on the material tested and its ability to resist heat. The quickest and most common way is to use an oven at 105°C. Materials that cannot resist heat can be dried in some other way, for example, in an exsiccator with a drying agent like silica gel or sulfuric acid. This procedure is rather time-consuming.

This method has several disadvantages. One major problem is that it is destructive, for one specimen is destroyed each time the moisture profile is measured. Consequently many specimens are required. It may even be impossible to get sufficient specimens if they have to be taken from an existing building. The slicing itself presents further problems. It cannot be done by sawing as this would generate heat, or would involve adding water to the specimen. Splitting is thus the only option. However, it is difficult to get a specimen to split perfectly parallel to the surface exposed to water or the drying climate. A parallel split is essential to avoid an error in the x-coordinate of the disc. It can also be difficult to split a specimen into discs thin enough for use when evaluating a very steep moisture front. Finally, this method is only suitable when water and non-volatile fluids are used for the absorption experiment. It cannot be used with volatile fluids, as these would evaporate from the disc during the splitting process.

Provided that the slicing can be done accurately, this method is the most accurate because the actual amount of water in the specimen is measured. It can therefore be used to calibrate and verify all the other methods described below.

Electrical methods

Two non-destructive electrical methods are available for determining moisture profiles. One is based on measuring the variation in electrical conductivity of a material, and the other is based on measuring the variation in electrical capacitance. For most materials the electrical conductivity increases with increasing moisture content. For all materials the capacitance increases with the moisture content due to the high dielectric constant of water (Adamson et al., 1970). Both methods, especially the resistance method, are inexpensive.

The conductivity (actually the electrical resistance) is measured between two electrodes in direct contact with the material. The water content is determined from the resistance measured using a calibration curve valid for the particular material. The calibration curve is obtained from extensive, rather time-consuming, calibration tests. However water content is not the only factor that can affect conductivity. So can other factors such as salts, temperature, density, etc. According to Wormald and Britch (1969), the resistivity of concretes with the same water

content may vary by as much as 40% with changes in the salt concentration of the pore water. The use of this method is therefore limited when these factors may vary. Conductivity measurements are mostly used with wood but have also been used with other materials. For example, Sandin (1978) used conductivity to measure the moisture content of aerated autoclaved concrete with an accuracy of $\pm 10\%$. One way of avoiding the effect of salts is to measure the conductivity in a special sensor (e.g. a piece of wood) that is embedded in the material to be studied. The sensor can be protected from salts in the material. In time, it will have the same moisture state as the material. However, a calibration curve for the sensor is required, and this type of sensor can only be used when measuring slow changes in the moisture state because of the time it takes for the sensor to achieve the same moisture state as the material.

The capacitance method uses the tested material as a dielectric. According to Krus (1995), the dielectric constant of water is 10 to 40 times larger than that of a dry building material when the frequency is 1 GHz. Therefore, changes in the capacitance are a measure of changes in the water content of the material. The capacitance method is less influenced by salts in the pore water and by density differences in the material than the conductivity method. It does, however, require a more complicated laboratory set up. According to Wormald and Britch (1969), the accuracy of the capacitance method applied to concrete is $\pm 0.25\%$ of moisture content mass, per mass in the range 0 to 6.5%.

Gamma-ray attenuation

Gamma-ray attenuation is a non-destructive method of measuring water content. If two different gamma-ray sources are used, both the water content and the material density can be measured. The gamma rays (photons) interact with the orbital electrons in the material and are absorbed or scattered. The intensity of a narrow beam of gamma rays passing through a material can be expressed by the following formula (Nielsen, 1972; Descamps, 1990):

$$I = I_0 e^{-\mu \rho x} \quad (62)$$

where

- I is the gamma-ray intensity after passing through the material [counts/s];
- I_0 is the intensity without absorbing material [counts/s];
- μ is the mass absorption coefficient of the material [m^2/kg];
- ρ is the density of the material [kg/m^3];
- x is the thickness of the material sample [m].

In order to measure the moisture profile, a gamma-ray source and a detector are needed. The source can be buried in the material with the detector on the surface, or, more commonly, the specimen can be placed between the source and the

Microwave beam

Non-destructive measurement of a moisture profile can also be carried out with a microwave beam. Microwave attenuation is strongly influenced by the dielectric constant of the material (Adamson et al., 1970). The dielectric constant of water is 10 to 40 times higher than that of dry material.

During the measurement the specimen is placed between a transmitter and a receiver and the attenuation of the beam caused by the oscillation of the water molecules is measured. The magnitude of the attenuation corresponds to the water content of the tested material. The equipment used must be calibrated against the specific material in question. One possible problem is that if the power of the beam is set too high, the temperature of the water in the material will increase markedly during the test, which may lead to moisture migration caused by the temperature gradient. This measuring technique and some results are described in detail in Volkwein (1993), Wittig and Lingott (1992), and Volkwein (1991).

Thermal conductivity

The thermal conductivity of a material increases with increasing moisture content. If the relation between the moisture content and the thermal conductivity of a particular material is known, the moisture content can be measured.

The principle of the method is to generate a known amount of heat locally in the material and then measure the temperature vs. time curve at a set distance from the heat source. This temperature curve is a measure of the thermal conductivity. The moisture content can then be calculated from the known relation between the moisture content and the thermal conductivity. One possible source of error with this method is that the heat source will generate a temperature gradient, which will influence the moisture flux. However, according to Vos (1965) is it possible to measure the moisture content with a precision of ± 1 vol.%.

Thermal imaging

Thermal imaging is a simple method of determining moisture distribution or the distribution of volatile fluids. It is based on the principle that the temperature decreases when liquids evaporate. The method is destructive and one specimen is used every time the moisture profile is measured. The method involves splitting a specimen into two halves, perpendicular to the exposed surface, and immediately measuring the temperature of the split surface with an infrared camera. The moisture profile can be determined from the temperature distribution. According to Sosoro and Reinhardt (1995), the moisture profile in a specimen with a constant cross-section over the depth can be calculated by:

$$\varepsilon(x) = \frac{(T_0 - T_s(x))^2}{\frac{S}{V_{fl}} \cdot \int_0^\ell (T_0 - T_s(x))^2 dx} \quad (64)$$

where

- ε is the water content volume, per volume [m^3/m^3];
- T_0 is the temperature of the surrounding air [K];
- T_s is the surface temperature [K];
- x is the co-ordinate in the direction of water transport [m];
- S is the surface area exposed to fluid [m^2];
- V_{fl} is the total absorbed test fluid [m^3];
- ℓ is the specimen length [m].

Another method is to calibrate the measured temperature of the split surface against the temperature of split surfaces of well-conditioned specimens. The calibration is performed using specimens of the specific material with different, known moisture contents. Both the measuring and conditioning procedures must take place in a climate room with constant relative humidity and temperature, and the measurements must be taken at the same time after splitting the specimen. This method is used and described in detail in Paper V, in which moisture distributions across an interface between cement-lime mortar and brick are measured. Measured profiles and laboratory arrangements are also described in Sosoro and Reinhardt (1995), Sosoro (1995), and Johansson (1999).

Moisture fixation

Introduction

Water can be bound in porous materials in several different ways, both physical and chemical. In contact with moist air, water molecules are physically bound to the surfaces of the pore system until equilibrium with the humidity of the ambient air is reached. Chemically bound water only exists in some materials, such as cement-based materials, in which some of the mixing water is bound in the cement gel. Such water is not lost until the gel is dried above 105°C.

Water in porous materials is often classified as evaporable or non-evaporable. Normally, evaporable water is water lost by drying at 105 degrees C. It is often assumed that physically bound water is evaporable while chemically bound water is not. Ahlgren (1972) regards this classification as somewhat ambiguous because different methods of evaporating water give different results. The classification into evaporable and non-evaporable water is, however, practical and probably accurate enough for most applications.

Water can be physically bound in the pores through *adsorption* of water molecules on the surface of the pore or through surface tension effects causing *capil-*

lary condensation of surrounding water vapor or *capillary uptake* of water. Adsorption takes place at low moisture levels and the adsorbed water molecules are bound to the pore surface by van der Waal forces. At equilibrium the amount of adsorbed water per square meter of pore surface is a function of the temperature and the relative humidity of the ambient air. There is never a static condition. As some water molecules leave the pore surface, other water molecules become attached. At equilibrium, the number of molecules leaving is the same as the number becoming bound to the surface. The total number of water molecules on the pore surface, i.e. the thickness of the adsorbed water layer, increases with increasing relative humidity in the pores.

Capillary condensed water molecules are condensed on curved water menisci that are formed in small pores and other narrow spaces. Kelvin's equation (equation 21) gives the relation between the relative humidity ϕ when condensation take place and the principal radii of the curvature of the meniscus in two orthogonal directions, r_1 and r_2 . Theoretically there is no upper moisture level for capillary condensation, but normally this phenomenon is assumed to be restricted to the hygroscopic range while capillary water uptake occurs in the superhygroscopic range.

Salts dissolved in pore water lower the relative humidity at which capillary condensation takes place. This effect is similar to that occurring for a curved water surface (i.e., the material will absorb more water from the ambient air if salt is present in the pore water).

In the hygroscopic range, the relation between the moisture content of the ambient air and the moisture content of the material represents the moisture storage capacity. This relation is given by sorption isotherms. In the superhygroscopic range, the relation between the suction s [Pa] and the moisture content of the material represents the moisture storage capacity. This relation is shown in what are called water retention curves. For many materials there is hysteresis between absorption and desorption (i.e., the relations are different, depending on whether equilibrium is reached by absorption or desorption). Paper IV presents measurements of moisture storage capacity for several different porous building materials. The moisture storage capacity is measured both in the hygroscopic and superhygroscopic range.

In equation 22 the relationship between the relative humidity and the suction is reached by combining Kelvin's equation (equation 21) with the Laplace equation (equation 13). Thus, it is possible to represent the moisture fixation in both the hygroscopic and the superhygroscopic range with one single relationship with either relative humidity or suction as the moisture storage potential. Using relative humidity as the moisture storage potential will result in a very steep curve in the superhygroscopic range (i.e., the resolution in this region will be poor). At high moisture levels, it is therefore better to choose the suction as the moisture storage potential (i.e., water-retention curves).

If a cylindrical pore model is used to model the pore system (i.e. if the pore system is considered as consisting of cylindrical tubes with varying radii r), the pore size distribution can be calculated from the moisture storage capacity. In a cylindrical pore the curvature of the meniscus is equal in all directions, that is $r_1 = r_2 = r$. The relation between the radius of the meniscus and the tube is therefore:

$$r_1 = r_2 = \frac{r}{\cos \theta} \quad (65)$$

where θ is the contact angle and r is the pore radius. (In the hygroscopic range r is often assumed to be equal to the radius of the pore reduced by the thickness of the adsorbed water layer. In the superhygroscopic range the thickness of the adsorbed water layer is of minor importance.) The contact angle is usually set to zero, although this is probably not true for many materials. For example, according to Letey et al. (1962) the contact angle between a certain type of sand and water is 50° . But since the cylindrical pore model is far removed from the actual pore geometry in porous building materials, the magnitude of the contact angle is fairly unimportant. The calculated radius r will never correspond to the 'true' pore radius. It is, however, important to use the same contact angle when pore size distributions are compared. Thus, it should always be clear which contact angle has been used when pore size distributions are presented.

With Kelvin's equation (equation 21) and equation 65, it is possible to calculate the pore radius from the relative humidity, and consequently it is also possible to obtain the pore size distribution from the sorption isotherm:

$$r = - \frac{2\sigma \cos \theta M_w}{\ln \phi RT \rho_w} \quad (66)$$

Thus, the pore radius r corresponds to a specific relative humidity. The cylindrical pore model can also be used to calculate the pore size distribution from the water retention curve using the Laplace equation (equation 13) and equation 65:

$$r = \frac{2\sigma \cos \theta}{s} \quad (67)$$

Pore radius is an additional possible measure of moisture storage potential. It has the same resolution and advantages as the suction, in that the pore size distribution gives good resolution in the superhygroscopic range.

Methods of measuring moisture storage capacity

There are several different methods of measuring moisture storage capacity in the hygroscopic and superhygroscopic range.

The classical, and probably most common, method of measuring fixation in the hygroscopic range uses different saturated salt solutions. Specific levels of relative humidity exist above saturated salt solutions in closed climate boxes. By placing samples of a material in boxes with different salt solutions, each one corresponding to different relative humidity, the sorption isotherm can be measured. The method is robust and relative simple, but also quite time-consuming. Depending on the material and the size of the specimen, the experimental time may vary from a month to a year.

Faster methods of measuring sorption isotherms exist. One possibility involves using a twin double microcalorimeter. A detailed account of this method is given by Wadsö and Wadsö (1996, 1997). Yet another approach to measuring moisture storage capacity in the hygroscopic range involves using a sorption balance. In Paper III three complementary methods of measuring moisture storage capacity in the hygroscopic range are described, discussed, and compared. A review of other methods of measuring moisture storage capacity in the hygroscopic range can be found in Wadsö (1997).

There is no established method of determining moisture storage capacity in the superhygroscopic range, for saturated salt solutions cover only the hygroscopic range. However, a technique using pressure plate and pressure membrane extractors is gaining acceptance. A standard method for using this technique has existed since 1997 and is set out in Nordtest Standard NT BUILD 481. The technique is described in detail in Paper II, in which different methods of presaturating the specimens and handling the equipment are tested and discussed. The lowest moisture levels measurable with the pressure plate and pressure membrane technique overlap the highest moisture levels measurable in the hygroscopic range. This overlapping is studied in Paper III.

Paper IV presents measurements of the moisture storage capacity of several different porous building materials. In the hygroscopic range a sorption balance was used, and above this range the pressure plate and pressure membrane technique was used.

Proposals for future study

Existing transport properties and models of moisture transport at high moisture levels should be verified by comparing calculated results with well-controlled laboratory tests. The necessary material properties should, of course, be determined in independent experiments. It is unfortunate that the transport properties are usually determined from the same experiments used for verification.

It is my belief that laboratory tests will show that the agreement between the calculated and experimental results is low for some models and materials. The results will indicate where further study is called for.

More knowledge is needed about moisture transport and moisture equilibrium above capillary saturation. Paper VI presents an attempt to calculate slow moisture absorption, based on the theory presented in Fagerlund (1993). But in order to understand the physics of moisture transport and moisture equilibrium above capillary saturation – and ultimately also to be able to develop better models – more fundamental research is needed.

Finally, the study of moisture transport over interfaces that was started in Paper V should continue since a large number of practical problems are a consequence of high moisture levels at interfaces. This study should be both theoretical and experimental.

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