Pergamon

Cement and Concrete Research 32 (2002) 955–962

CEMENT AND CONCRETE RESEARCH

Prestudy on diffusion and transient condensation of water vapor in cement mortar

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Received 29 November 2000; accepted 7 January 2002

Abstract

The kinetics of sorption of water vapor in mature cement mortar are examined experimentally by the use of a sorption balance (DVS-1000). The relative humidity in the sample chamber is obtained by mixing dry and saturated air using flow regulators with very high accuracy. A predefined change of relative humidity in the sample chamber can be obtained in about 30 s. The time needed for equilibration in terms of the mass of a finely grained mortar sample is shown to be in the order of 2500 min for a 0–96% step in relative humidity at 25 °C. This fact calls for a refinement of modeling of diffusion of water vapor in materials such as mortar to take into account the kinetics of sorption. The established model involves a transient mass exchange term that explicitly describes the rate of condensation at internal material surfaces. This function becomes zero when located at the equilibrium sorption isotherm. The 'global' mass diffusion velocity of water vapor in the air-filled porosity is assumed to be significantly affected by the mass concentration of liquid water in the pore space. A satisfying match between the proposed model and measurements presented by J.F. Daïan [Transp. Porous Media 4 (1989) 1.] was obtained by using nonlinear diffusion and sorption characteristics. In order to get a satisfying match, the sorption kinetics was, however, forced to be much slower than the recorded values obtained by the sorption balance. Some speculations as to the reason of this marked difference are performed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Diffusion; Transient condensation; Water vapor; Mortar

1. Introduction

Cement-based materials are affected by moisture and moisture variation in a number of ways. A knowledge of the behavior of cement-based material subjected to humid air is therefore of importance. A change in the moisture condition can cause cracking of the material that can reduce the serviceability. Further, freeze–thaw damage in cement-based materials is occurring at high moisture contents. Other problems associated with moisture are related to having combinations of cement-based materials and other materials such as plastic carpets glued onto concrete floors.

Transport of vapor in a porous cement-based material is mainly influenced by three different phenomena:

1. Diffusion, i.e., gradient-dependent mass flow of vapor molecules in the air-filled parts of the porous network.
2. Condensation and vaporization, i.e., the transient mass exchange between water at material surfaces and water molecules in the air in the pore structure.
3. Chemical reactions, e.g., consumption of water due to hydration or expelled water due to carbonization.

Measurements on the transient mass exchange between water at material surfaces and water molecules in the air in the pore structure of concrete are performed in order to show its relevance.

The general description of the transport mechanism becomes quite complicated, mainly for two reasons. The first is that the equilibrium condition for condensation and vaporization is dependent on whether drying or wetting is active, i.e., the hysteresis in the sorption. Furthermore, the kinetics of sorption must be described when the state variables are displaced from their equilibrium state. The second main mechanism that must be dealt with is that the diffusion of humid air depends strongly on the porosity and the geometrical arrangement of the pore space, and also its dependence on the liquid water content in the pores.

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PII: S0008-8846(02)00736-6

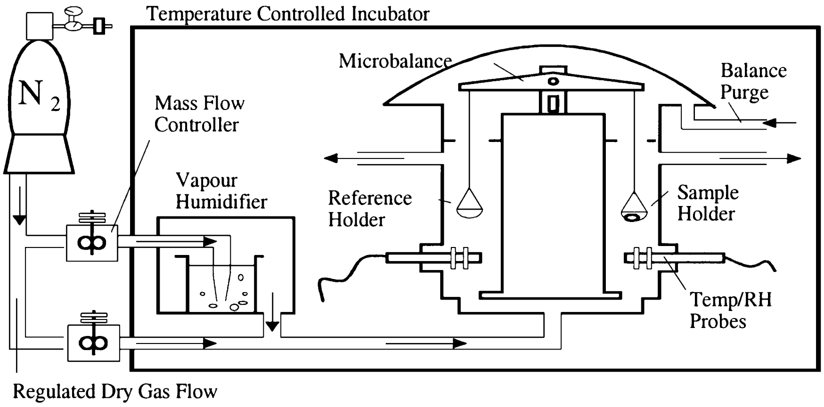

Fig. 1. Schematic sketch of the dynamic vapor sorption instrument (DVS-1000). Dry and saturated air is mixed in desired proportions using flow regulators. The sample is placed on a symmetric microbalance to eliminate effects caused by sorption on holders.

When nonisothermal conditions are considered, the equilibrium condition for condensation and vaporization is not only a function of water vapor concentration in pore space and liquid water concentration in material but also a function of the temperature. In this case, the rate constants describing the kinetics in the sorption also become dependent on temperature. The diffusion coefficient for water vapor in air is, however, weakly dependent on temperature.

It might, furthermore, be of interest to develop models including effects caused by temperature gradients. One possibility is that temperature gradients can affect the mass diffusion flow of vapor, the so-called Sorret effect.

2. Transient condensation and vaporization—experimental verification

The experiment performed is mainly used to confirm that transient vapor condensation, in cement mortar in contact with humid air, is a relevant phenomenon that can be incorporated into moisture diffusion models. In order to verify all parameters describing the equilibrium conditions and rate constants describing the kinetics of condensation, a whole series of experiments must be performed, i.e., the complete set of equilibrium sorption curves and the corresponding kinetics of reaching these equilibrium values must be measured. No such detailed experiments have been carried out in this investigation. The experimental procedure described in this section can, however, easily be extended and be used to evaluate the complete shape of the material parameters of interest.

The experiment is performed in an explicit manner with a minimum of assumptions. The equipment used is a DVS-1000 sorption balance. This balance measures the change in mass of a small sample that is lower than 1 part per 10 million. The relative humidity surrounding the sample holder is obtained by mixing dry and saturated nitrogen using flow regulators. The use of nitrogen prevents the cement mortar to be carbonated during test. The range of available temperatures in instrument is about 0–75 °C. Humidity probes are situated just below the sample holder to give independent verification of the performance of the system. The microbalance is constructed symmetrically. In other words, a reference holder and a sample holder are placed symmetrically on the microbalance. The mixed saturated and dry nitrogen passes through both the reference holder and the sample holder, which means that sorption on holders and suspension devices cancel each other out. The velocity of the air passing the sample holder is approximately 1 mm/s. The complete instrument is housed in a temperature-controlled incubator (see Fig. 1).

By adjusting the relative humidity in the sample chamber, using flow regulators, the climatic variations become well defined and reach the desired target value in a few seconds. This is desirable when measuring the kinetics of sorption, as certain humidity steps are used and the mass response of the sample is recorded in this situation. Controlling the relative humidity directly by flow regulators is superior to controlling it by using the humidity probes, since these respond relatively slowly to a change in humidity and also due to the probes being subjected to hysteresis. The performance of the flow regulators is checked regularly by calibrations using measurements on well-defined salt solutions. The accuracy of the relative humidity generated by the flow regulators can be estimated to ± 0.4% by this calibration method.

Table 1
Mix proportions of the tested OPC mortar

	Mass density (kg/m^3)	Actual weight (kg)
Cement (OPC)	545	0.774
Aggregate		
0–0.125 mm	422	0.600
0.125–0.250 mm	422	0.600
0.250–0.500 mm	422	0.600
Water	300	0.426

Water-to-binder ratio: 0.55. OPC = ordinary Portland cement (Degerhamm standard is a low-alkali, sulfur-resistant cement).

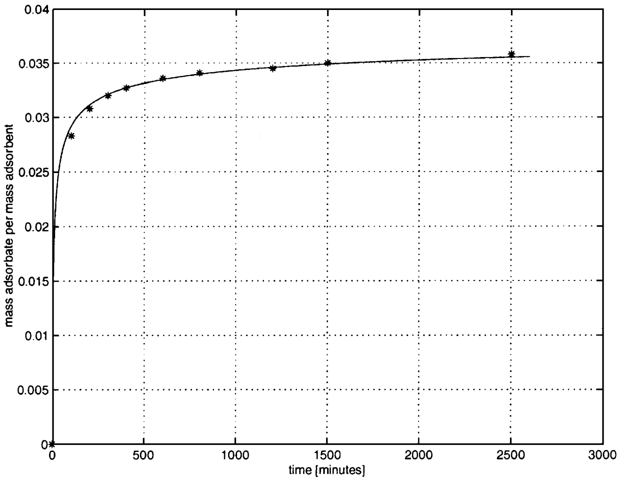

Fig. 2. Mass adsorbate per mass adsorbent as a function of time during a step in relative humidity from zero to 96% at 25 °C on cement mortar. The stars represent measured values and the solid line is the 'best'-fitted curve using Eq. (1).

The sample tested is a mature noncarbonated cement mortar (see Table 1). A small representative part of this material was crushed and about 125 mg of the material was placed in the microbalance. The size of the grains of the crushed material was typically in the range of 0.05–0.005 mm. The sample was dried at zero relative humidity at 25 °C for several days. When no significant mass change was registered the climate in the sample and the reference chamber were set to 96% relative humidity. The stars in Fig. 2 show the measured mass adsorbate per mass adsorbent at different times from initiation of the 0–96% relative humidity step. The solid line, in Fig. 2, is the best-fitted solution to the equation

$$\frac{\partial \rho_{\mathrm{w}}}{\partial t} = R^{*}(\rho_{\mathrm{w}}^{\mathrm{eq}} - \rho_{\mathrm{w}})^{n}, \tag{1}$$

where $R^{*} = 0.1 \times 10^{-7}$ s^{-1}, $n = 4$, and $\rho_{\mathrm{w}}^{\mathrm{eq}} = 70$ kg/m^3, which is the equilibrium mass density concentration of water in material at 96% relative humidity. The mass density concentration ρ_{w}, as a function of time, is recalculated to the mass adsorbate per mass adsorbent by using the dry mass density of the tested cement mortar.

The measured kinetics of sorption on cement mortar during the relative humidity step 0–96% is much faster than the corresponding property evaluated from the experiments presented in Ref. [1]. This subject will be analyzed further in the following sections.

3. Mass balance laws

In the so-called mixture theory, e.g., see Ref. [2], balance principles are postulated for mass, momentum, and energy for a whole mixture consisting of several different constituents. The same kind of balance laws is also postulated for the individual constituents. A summation of the balance principles for the individual constituent should constitute the whole mixture as described by its balance laws. The postulated mass, momentum, and energy equations must be complemented by so-called constitutive equations. The constitutive equations, or equally the material functions, describe the specific behavior for a certain material.

In the model to be presented, dealing with wetting of cement-based materials, only the mass balance principles for the individual constituents and for the mixture will be invoked. The mass balance consists of two parts, one for the individual constituent and one for the whole mixture. Here two constituents will be considered only, the water vapor phase and the liquid water phase.

The mass balance of different constituents present in a mixture may be formulated as, e.g., compare Ref. [2],

$$\rho \frac{\partial c_a}{\partial t} = -\mathrm{div}(\rho_a u_a) - \rho \dot{x} \mathrm{grad} c_a + \hat{c}_a; \quad a = 1, \ldots, \mathcal{R}, \tag{2}$$

where $c_a(x,t)$ is the mass concentration of an arbitrary constituent denoted as a. The total number of constituents is denoted $\mathcal{R}$. The mass concentration is defined as $c_a = \rho_a/\rho$, where $\rho_a(x,t)$ is the mass density of the constituent and where $\rho(x,t)$ is the mass density of the whole mixture, i.e., the sum of all ρ_a. The diffusion velocity u_a is defined as $u_a = \dot{x}_a - \dot{x}$, where $\dot{x}_a(x,t)$ is the velocity of the a-th constituent and $\dot{x}(x,t)$ denotes the velocity of the whole mixture, which is the mass weighted sum of the individual velocities of the constituents, i.e., $\dot{x} = 1/\rho \sum_{a=1}^{\mathcal{R}} \rho_a \dot{x}_a$. The mass exchange rate between the a-th constituent and all other constituents is denoted as $\hat{c}_a(x,t)$.

Due to the mass balance for the whole mixture one must assure that there is no net production of mass in a material point, i.e.,

$$\sum_{a=1}^{\mathcal{R}} \hat{c}_a(x,t) = 0. \tag{3}$$

This relation is obtained by summing all mass balance equations for the individual constituents.

An alternative version of Eq. (2) can, also, be formulated as

$$\frac{\partial \rho_a}{\partial t} = -\mathrm{div}(\rho_a \dot{x}_a) + \hat{c}_a; \qquad a = 1, \ldots, \mathcal{R}, \tag{4}$$

where the 'absolute' velocity $\dot{x}_a$ is used instead of the relative velocity u_a. A summation of all $\mathcal{R}$ mass balance equations for the constituents in Eq. (4) should result in the mass balance of the whole mixture being obtained. The mass balance for the whole mixture is the postulate

$$\frac{\partial \rho}{\partial t} = -\mathrm{div}(\rho \dot{x}). \tag{5}$$

That is, a summation of all $\mathcal{R}$ equations in Eq. (4) gives Eq. (5) as a result only if relation (3) is fulfilled.

It is, further, easily shown that Eq. (4) can be brought to the form illustrated in Eq. (2) by using the definitions $u_a = \dot{x}_a - \dot{x}$ and $c_a = \rho_a/\rho$.

4. Constitutive relations

The mass balance laws for the two considered constituents, i.e., liquid water and vapor, do not contain enough information to make a complete description of the system. The lacking information are the so-called constitutive relations, which must be confirmed by experimental observations. There are a number of different theories on which the reliability of introduced constitutive relations can be judged. The most commonly used principles are given from the second axiom of thermodynamics and from the frame-indifference principle. The second axiom of thermodynamics is usually used to check that a specific choice of constitutive relations is arranged in such a way that the entropy inequality is always fulfilled. It should be remembered, however, that every constitutive model is defined by the choice of constitutive independent and dependent properties. Therefore, the restrictions imposed by the second axiom of thermodynamics will be different for different models. The frame-indifference principle also places restrictions on the constitutive relations. The principle states that physical properties must transform between different frames in a specific manner. Loosely speaking, the frame-indifference principle states that the physical process should be independent of the coordinate reference frame in which one happens to describe the physical event.

The choice of constitutive independent properties in the model to be presented are the mass concentration of vapor ρ_v, the gradient of the mass concentration of vapor gradρ_v, and the mass concentration of liquid water ρ_w. The constitutive dependent properties are the macroscopic velocity of the water vapor molecules in air $\dot{x}_v$ and the mass exchange rates $\hat{c}_v$ and $\hat{c}_w$.

The constitutive dependent properties can only be a function of the constitutive independent properties and their gradients in a way such that the second axiom of thermodynamics and the principle of frame indifference are always satisfied. The following choice (Eq. (6)) can be proven to follow these two principles

$$(\dot{x}_v, \hat{c}_v, \hat{c}_w) = f(\rho_v, \mathrm{grad}\rho_v, \rho_w). \tag{6}$$

The specific constitutive relation for the velocity of the water vapor is a version of Fick's first law, i.e.,

$$\dot{x}_v = \frac{D_v(\rho_w, a)}{\rho_v} \mathrm{grad}\rho_v, \tag{7}$$

where D_v is the positive number determining the diffusion parameter that is assumed to be a function of the mass concentration of water in the material ρ_w and the porosity a. Another type of assumption that explicitly involves the air pressure in the relation for the velocity of the water vapor in pore system of permeable materials has been proposed in Refs. [3,4].

It will be explicitly assumed, due to simplicity, that the velocity of the liquid water is zero, i.e., capillary suction is not considered in this model. The consequence is that the mean velocity, $\dot{x}$, is related to the velocity of water vapor, $\dot{x}_v$, as: $\dot{x} = \frac{1}{\rho}\sum_{a=1}^{\mathscr{R}} \rho_a \dot{x}_a = \frac{\rho_v}{\rho}\dot{x}_v$. That is, when $\rho \gg \rho_v$, which is almost always the case in the studied application, the mean velocity $\dot{x}$ is very small compared to $\dot{x}_v$.

Owing to the experimental facts illustrated in Section 2, it will be assumed that the vapor in pore space and water adsorbed at solid material surfaces do not reach equilibrium instantaneously as assumed in most models used to evaluate measured moisture profiles. The constitutive dependent mass exchange rate $\hat{c}_v$ must, therefore, be explicitly described as a function of the constitutive independent properties defined in the model. The mass exchange rate $\hat{c}_v$, i.e., the rate of gain of mass to the vapor phase from the liquid water phase, is the constitutive assumption

$$-\hat{c}_v = \hat{c}_w = R(\rho_w, \rho_v)(\rho_w^{eq} - \rho_w)^n, \tag{8}$$

where the mass balance relation (3) is also used. A similar assumption has been proposed in Ref. [5]. The property R is a rate parameter that is assumed to be given by a function of the mass density concentration of liquid water ρ_w and the mass density concentration of water vapor ρ_v in the material. The property ρ_w^{eq} is a value describing an equilibrium condition, i.e., the case when $\hat{c}_v = -\hat{c}_w = 0$ and n is a material constant. The property ρ_w^{eq} is a function of the mass concentration of water vapor in the material. It is assumed that this function can be fitted using a third-order polynomial, as

$$\rho_w^{eq} = \alpha_1\rho_v + \alpha_2\rho_v^2 + \alpha_3\rho_v^3; \qquad \text{at equilibrium,} \tag{9}$$

where the material constants α_1, α_2, and α_3 should be chosen in such a way that a satisfying match between the measured sorption isotherm, at a given temperature, is obtained. It is noted that when ρ_w^{eq} equals the actual value of the mass concentration of water in the material ρ_w, the mass exchange rate $\hat{c}_v$ between the water vapor in pore space and the water liquid phase in material becomes zero (see Eq. (8)); naturally, this is the desired behavior.

5. Governing equations for transient vapor condensation and diffusion

The combination of the mass balance laws defined in Section 3 and the constitutive relations described in Section 4 together with appropriate description of boundary conditions, gives a model for diffusion and transient vaporization and condensation in a porous material. The reason for including the transient vaporization and condensation is based on the experimental fact shown in Section 2.

By combining the mass balance law (4) and the assumptions (7) and (8), the governing equation for the mass concentration of water vapor (Eq. (10)) is obtained as

$$\frac{\partial \rho_{\mathrm{v}}}{\partial_{\mathrm{v}}} = -\mathrm{div}(D_{\mathrm{v}}(\rho_{\mathrm{w}}, a)\mathrm{grad}\rho_{\mathrm{v}}) - R(\rho_{\mathrm{w}}, \rho_{\mathrm{v}})(\rho_{\mathrm{w}}^{\mathrm{eq}} - \rho_{\mathrm{w}})^n. \tag{10}$$

Because of the assumption that the velocity of the liquid water in this model is restricted to be zero, the mass balance laws (3) and (4) together with Eq. (8) combine to yield

$$\frac{\partial \rho_{\mathrm{w}}}{\partial t} = R(\rho_{\mathrm{w}}, \rho_{\mathrm{v}})(\rho_{\mathrm{w}}^{\mathrm{eq}} - \rho_{\mathrm{w}})^n, \tag{11}$$

which is the equation to calculate the mass concentration of liquid water in the material.

It is noted that the equations are coupled due to the mass exchange between the vapor phase and the liquid water phase but also due to the dependence of the diffusion parameter D_{v} on the mass concentration of liquid water ρ_{w} in the material.

Assuming the constant related to the kinetics of sorption R to be a constant property, as

$$R(\rho_{\mathrm{w}}, \rho_{\mathrm{v}}) = r_1. \tag{12}$$

The explicit expression for the time derivative of ρ_{w}, when setting $n=1$, can be brought to the form

$$\frac{\partial \rho_{\mathrm{w}}}{\partial t} = r_1\left(\left(\alpha_1 + \alpha_2\rho_{\mathrm{v}} + \alpha_3\rho_{\mathrm{v}}^2\right)\rho_{\mathrm{v}} - \rho_{\mathrm{w}}\right), \tag{13}$$

where Eqs. (9), (11), and (12) are used.

The explicit expression for the function $D_{\mathrm{v}}(\rho_{\mathrm{w}},a)$ in use is the assumption (Eq. (14))

$$D_{\mathrm{v}}(\rho_{\mathrm{w}}, a) = \frac{D_{\mathrm{v}}^0 k_a a}{(1 + k_{\mathrm{w}}\rho_{\mathrm{w}}^2)}, \tag{14}$$

where D_{v}^0 is the diffusion coefficient for water vapor in air, $D_{\mathrm{v}}^0 = 25 \times 10^{-6}$ m^2/s. k_a (−) and k_{w} [(m^3/kg)^2] are constants related to the effect on diffusion caused by the porosity a and the mass concentration of liquid water ρ_{w}, respectively.

Another way to describe the sorption kinetics will also be tested in which the material function $R(\rho_{\mathrm{w}},\rho_{\mathrm{v}})$ is assumed to be linearly related to the ‘distance’ from equilibrium, i.e., by the factor $(\rho_{\mathrm{w}}^{\mathrm{eq}} - \rho_{\mathrm{w}})$, by using the material constant r_2. By using Eq. (9), this assumption can be written as

$$\begin{aligned} R(\rho_{\mathrm{w}}, \rho_{\mathrm{v}}) &= r_2(\rho_{\mathrm{w}}^{\mathrm{eq}} - \rho_{\mathrm{w}}) \\ &= r_2\left(\left(\alpha_1 + \alpha_2\rho_{\mathrm{v}} + \alpha_3\rho_{\mathrm{v}}^2\right)\rho_{\mathrm{v}} - \rho_{\mathrm{w}}\right). \end{aligned} \tag{15}$$

Using, further, Eq. (11) with $n=1$, one obtains a different assumed expression describing the time derivative of ρ_{w}, i.e.,

$$\frac{\partial \rho_{\mathrm{w}}}{\partial t} = r_2\left(\left(\alpha_1 + \alpha_2\rho_{\mathrm{v}} + \alpha_3\rho_{\mathrm{v}}^2\right)\rho_{\mathrm{v}} - \rho_{\mathrm{w}}\right)^2. \tag{16}$$

In Section 7, the solution behavior of the governed equations will be compared to measured water content profiles at different exposure times. Both types of assumptions concerning the sorption kinetics, i.e., Eqs. (13) and (16), will be tested.

It is noted that the Eq. (1) used to fit the experimental results on the kinetics of sorption, shown in Fig. 2, is a generalized version of Eq. (16).

6. Numerical solution strategy

Due to nonlinearities and coupling of the governing differential equations, given in Section 5, a numerical method capable of solving the system will be discussed. A one-dimensional case will be studied using linear finite elements. The concept of the finite element method as used for solving transient systems can be studied in, for example, Refs. [6–9]. The main numerical issue is to find a stable nonoscillated method. This can be obtained by using one of the unconditionally stable time integration methods that is a family of implicit schemes. Further, the nonlinearities of $D_{\mathrm{v}}(\rho_{\mathrm{w}},a)$ and $R(\rho_{\mathrm{w}},\rho_{\mathrm{v}})$ must be considered. Here a simple Euler-forward method will be used. That is, the nonlinear parameters will be evaluated at each time level without making any equilibrium iterations within the time steps. A natural improvement is to search for a minimum of out-of-balance flows at each time step. This method is, however, associated with a special kind of problems when truly transient equation systems are considered. One problem is, for example, that simple Newton–Raphson methods may give inaccurate equilibrium solutions when using too many iterations with too strong criteria for equilibrium. This is usually not a problem for nonlinear equations that are homogeneous in time.

A finite time increment Δt will be considered, which is related to the time levels t_i and t_{i+1} as $t_{i+1} = t_i + \Delta t$, in order to obtain so-called recurrence relations. A time integration parameter Θ is introduced where $\Theta = 0$ is a truly explicit scheme, $\Theta = 1$ is a truly implicit scheme, $\Theta = 0.5$ is the Crank–Nicholson scheme, and $\Theta = 0.878$ is the Liniger scheme, in which Θ is chosen to minimize the whole domain error. Values of Θ greater than or equal to 0.5 are shown to be unconditionally stable for equation systems that are symmetric and positive definite. Indeed, the whole system of equations becomes unsymmetrical. Stable solutions were, however, obtained by using relatively small elements and time steps. The reliability of the solution was checked by successively decreasing the time step Δt

until the solution no longer was affected. The time integration parameter in use is $\Theta = 0.878$.

Only the equation system where the sorption kinetics are described as in Eq. (13) will be treated, for simplicity reasons. The inclusion of the sorption described by Eq. (16) into the numerical solution scheme is straightforward and will not be discussed.

The total equation system can be written in the form

$$\mathbf{C}^{\mathrm{tot}}\dot{\boldsymbol{a}}^{\mathrm{tot}} + \mathbf{K}^{\mathrm{tot}}\dot{\boldsymbol{a}}^{\mathrm{tot}} + \boldsymbol{f}^{\mathrm{tot}} = \mathbf{0}, \tag{17}$$

where $\mathbf{C}^{\mathrm{tot}}$ is the damping matrix for the whole equation system, $\mathbf{K}^{\mathrm{tot}}$ is the stiffness matrix for the whole system, and $\boldsymbol{f}^{\mathrm{tot}}$ is the boundary and load vector in the problem. The nodal vector $\boldsymbol{a}^{\mathrm{tot}}$ includes the discrete values of the mass concentration of water vapor ρ_{v} and liquid water ρ_{w}, using the shape function $\mathbf{N}(x)$ as $\rho_{\mathrm{v}} = \mathbf{N}(x)\boldsymbol{a}_{\mathrm{v}}$ and $\rho_{\mathrm{w}} = \mathbf{N}(x)\boldsymbol{a}_{\mathrm{w}}$. The property $\dot{\boldsymbol{a}}^{\mathrm{tot}}$ includes the corresponding spatial time derivatives of the discrete mass concentrations ρ_{v} and ρ_{w}.

When using a single time-step algorithm, the semidiscretization of Eq. (17) takes the form

$$\mathbf{0} = \frac{\mathbf{C}^{\mathrm{tot}}(\boldsymbol{a}_{i+1}^{\mathrm{tot}} - \boldsymbol{a}_{i}^{\mathrm{tot}})}{\Delta t} + \mathbf{K}^{\mathrm{tot}}(\boldsymbol{a}_{i}^{\mathrm{tot}} + \Theta(\boldsymbol{a}_{i+1}^{\mathrm{tot}} - \boldsymbol{a}_{i}^{\mathrm{tot}})) + \boldsymbol{f}_{i}^{\mathrm{tot}} + \Theta(\boldsymbol{f}_{i+1}^{\mathrm{tot}} - \boldsymbol{f}_{i}^{\mathrm{tot}}). \tag{18}$$

Eq. (18) is used to solve the unknown vector $\boldsymbol{a}_{i+1}^{\mathrm{tot}}$. The nodal vector $\boldsymbol{a}_{i}^{\mathrm{tot}}$ represents the known values at the current time levels t_i and $\boldsymbol{a}_{i+1}^{\mathrm{tot}}$ is the unknown vector searched for at time level $t_{i+1} = t_i + \Delta t$.

The total damping $\mathbf{C}^{\mathrm{tot}}$ is formed by assembling the damping matrixes for the individual diffusion equations as block matrixes. The matrix $\mathbf{C}^{\mathrm{tot}}$ can be formed as (Eq. (19))

$$\mathbf{C}^{\mathrm{tot}}\dot{\boldsymbol{a}}^{\mathrm{tot}} = \begin{bmatrix} [\mathbf{C}_{\mathrm{v}}] & \mathbf{0} \\ \mathbf{0} & [\mathbf{C}_{\mathrm{w}}] \end{bmatrix} \begin{bmatrix} [\dot{\boldsymbol{a}}_{\mathrm{v}}] \\ [\dot{\boldsymbol{a}}_{\mathrm{w}}] \end{bmatrix}, \tag{19}$$

where $[\mathbf{C}_{\mathrm{v}}]$ is expressed with the shape function $\mathbf{N}(x)$ as $\mathbf{C}_{\mathrm{v}} = \int_V \mathbf{N}^{\mathrm{T}}\mathbf{N}\,\mathrm{d}V$, and where $\dot{\boldsymbol{a}}^{\mathrm{tot}} = (\boldsymbol{a}_{i+1}^{\mathrm{tot}} - \boldsymbol{a}_{i}^{\mathrm{tot}})/\Delta t$.

The stiffness matrix for the concentration gradient dependent diffusion is formed as $\mathbf{K}_{\mathrm{v}} = \int_V \mathbf{B}^{\mathrm{T}}(D_{\mathrm{v}}^{0}k_a a/(1 + k_{\mathrm{w}}\rho_{\mathrm{w}}^{2}))\mathbf{B}\,\mathrm{d}V$ where $\mathbf{B}(\boldsymbol{x})$ is defined as the gradient of the shape function, i.e., $\mathbf{B}(\boldsymbol{x}) = \nabla\mathbf{N}(\boldsymbol{x})$. The terms related to the mass exchange rate between the vapor and liquid water are formulated as $\mathbf{R}_{v}(\boldsymbol{a}_{v}) = \int_{V} \mathbf{N}^{T} r_1(\alpha_1 + \alpha_2\rho_v + \alpha_3\rho_v^2)\mathbf{N}dV$ and $\mathbf{R}_{w} = \int_V \mathbf{N}^{T} r_1 \mathbf{N} dV$.

The total stiffness $\mathbf{K}^{\mathrm{tot}}$ can, for this problem, be written as (Eq. (20))

$$\mathbf{K}^{\mathrm{tot}}\boldsymbol{a}^{\mathrm{tot}} = \begin{bmatrix} [\mathbf{K}_{\mathrm{v}}(\boldsymbol{a}_{\mathrm{w}}) + \mathbf{R}_{\mathrm{v}}(\boldsymbol{a}_{\mathrm{v}})] & [\mathbf{R}_{\mathrm{w}}] \\ [-\mathbf{R}_{\mathrm{v}}(\boldsymbol{a}_{\mathrm{v}})] & [-\mathbf{R}_{\mathrm{w}}] \end{bmatrix} \begin{bmatrix} [\boldsymbol{a}_{\mathrm{v}}] \\ [\boldsymbol{a}_{w}] \end{bmatrix} \tag{20}$$

where $\boldsymbol{a}^{\mathrm{tot}} = (\boldsymbol{a}_{i}^{\mathrm{tot}} + \Theta(\boldsymbol{a}_{i+1}^{\mathrm{tot}} - \boldsymbol{a}_{i}^{\mathrm{tot}}))$.

The total load and boundary vector $\boldsymbol{f}^{\mathrm{tot}}$ is expressed as (Eq. (21))

$$\boldsymbol{f}^{\mathrm{tot}} = \begin{bmatrix} [\boldsymbol{f}_{\mathrm{v}}] \\ [\boldsymbol{f}_{\mathrm{w}}] \end{bmatrix}. \tag{21}$$

The load and boundary vector $\boldsymbol{f}_{\mathrm{v}}$, for the diffusion equation, is in general terms written as $\boldsymbol{f}_{\mathrm{v}} = -\int_{S_h} \mathbf{N}^{\mathrm{T}} h_{\mathrm{v}}\,\mathrm{d}S - \int_{S_{n=g}} \mathbf{N}^{\mathrm{T}} q_{\mathrm{v}}\,\mathrm{d}S$ where h_{v} is a prescribed value of the normal flow of water vapor through the boundary surface S_h and q_{v} is the value of the flow through the boundary surface $S_{n=g}$ on which the mass concentration ρ_{v} has been prescribed. The value of the flow q_{v} can be calculated whenever the mass concentration ρ_{v} is prescribed at the same spatial point.

7. A schematic example of the performance of the model

Here two schematic test examples will be illustrated. A simulation of diffusion and transient condensation will be compared with measurements, presented in Ref. [1], on moisture profiles in mature cement mortar, taken at different times from exposure to saturated water vapor. The finite element procedure outlined in Section 6 is used to solve the equations.

The measured values shown in Figs. 3 and 4 are obtained by letting dry samples of cement mortar with a water-to-cement ratio of 0.8, be subjected to saturated air at 30 °C on one side only. During the experiment, the water content in the sample in various sections was measured by means of gammametry. A rectangular beam of cross-section measuring

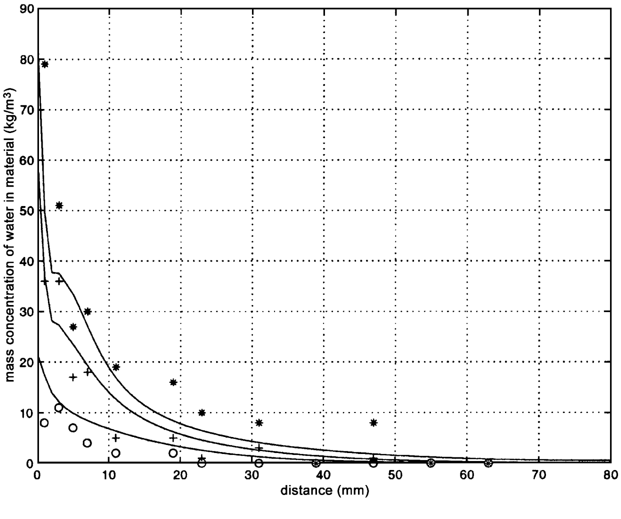

Fig. 3. Comparison between measured water concentration profiles [1] and calculated profiles (solid lines). Experimental profiles are shown by circles, plus signs, and stars at 20, 100, and 300 h, respectively, after exposing the dry sample to saturated air at 30 °C. Linear absorption kinetics are assumed in the simulation.

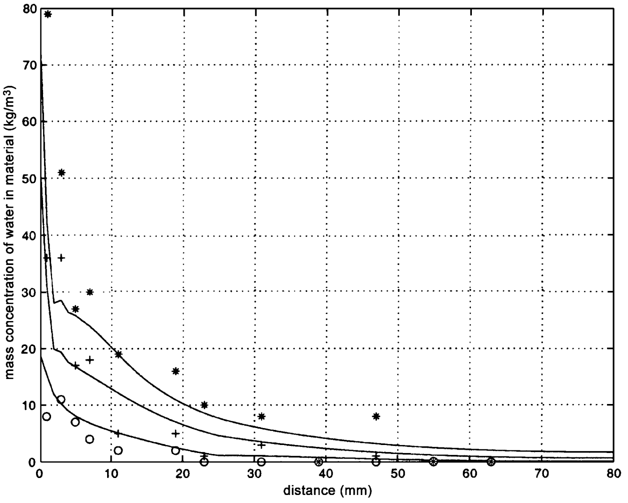

Fig. 4. Comparison of experimental values and simulation (solid lines) using an assumption of nonlinearities in the parameter describing the absorption kinetics. Experimental profiles are shown by circles, plus signs, and stars at 20, 100, and 300 h, respectively, after exposing the dry sample to saturated air at 30 °C.

2 × 10 mm was used, in order to get fine definition of sharp water content profiles [1].

The equilibrium condition between the vapor mass concentration and liquid water mass concentration is described with the polynomial in Eq. (9), using $\alpha_1 = 0.776 \times 10^4$ (−), $\alpha_2 = -1.117 \times 10^{-6}$ m^3/kg, and $\alpha_3 = 0.576 \times 10^8$ (m^3/kg)^2. The diffusion coefficient for water vapor in bulk air is $D_v^0 = 25 \times 10^{-6}$ m^2/s. This value is scaled in order to account for the influence of liquid water clogging the pore system with respect to vapor diffusion and due to the porosity of the material. The scaling constants involved in describing the effective mass diffusion velocity of vapor in Eq. (7) are $k_a = 0.5$ (−) and $k_w = 30 \times 10^{-3}$ (m^3/kg)^2. The porosity of the material is estimated to $a = 0.2$. The constant used to describe the kinetics of sorption in Eq. (13) is set to the value $r_1 = 3.42 \times 10^{-6}$/s.

The initial condition for ρ_v and ρ_w is zero and the boundary condition used at the left-hand side of the one-dimensional geometry is a description of the mass concentration of water vapor, which is 0.030 kg/m^3. This corresponds to saturation at 30 °C, which is the condition in the test to which the simulation is compared. At the right-hand side of the one-dimensional domain, the mass flow is set to zero since the specimens were sealed on all sides except the side exposed to humid air. No boundary condition is specified for the mass concentration of liquid water since these values are determined by the model at all locations in the domain of interest.

The results of the simulation, using the material constants shown above, are given in Fig. 3.

A second simulation of the same problem is shown in Fig. 4, in which the sorption kinetics were assumed to be described by a nonlinear function, as defined in Eq. (15). The best fit for this calculation was obtained by using the constants $k_w = 27 \times 10^{-3}$ (m^3/kg)^2 and $r_2 = 5 \times 10^{-8}$ m^3/kg/s. The rest of the constants are the same as for the first calculation, presented in Fig. 3, excluding r_1 and Eq. (13), which are replaced by r_2 and Eq. (15), respectively.

8. Possible future developments of the model

In this paper, only the principal way of treating diffusion and transient condensation and vaporization during wetting was examined. The experimental values performed on the sorption kinetics were, further, not explicitly used when comparing with the measurements presented in Ref. [1]. The parameters used for describing the kinetics and the diffusion, in the example presented in Section 7, were rather chosen to fit the experimental data given in Ref. [1] without using a direct measure of the kinetic behavior of condensation. In that sense, the experiments performed on the sorption kinetics, in this study, should only be seen as an instrument to show that transient condensation and vaporization exist and that this will affect the strategies to evaluate the measurements on moisture profiles. A natural extension to this work is, therefore, to fit the material constants involved to describe the sorption kinetics by using the described model together with the type of measurements described in Section 7. This will mean that the specific choice of the function $D_v(\rho_w,a)$ must be significantly changed in order to get a good match of the experimental data presented in Fig. 3. This approach seems to be significant since the sorption kinetics can be measured with a minimum of experimentally involved assumptions in an explicit manner. It is also realized that the function $D_v(\rho_w,a)$ is extremely difficult to evaluate in a direct and systematic way.

One of the aims was to develop a stringent physical model for wetting by diffusion and transient condensation in cement mortar using the concepts developed in Ref. [1]. Another important purpose was to open up for possibilities to include nonisothermal conditions without necessarily modeling this by making the diffusion parameter D_v a function of temperature. The experimental values obtained for vapor diffusion in the air are shown to have a weak dependence on temperature, e.g., see Ref. [10]. Hence, the marked difference in response in terms of moisture content in porous materials due to diffusion and transient condensation at different temperatures cannot be a consequence of D_v being a function of temperature alone, as this dependence is very small. However, assuming the sorption kinetics and its equilibrium conditions, i.e., the sorption isotherms, to be affected by temperature, should result in a more physically sound explanation for the different measured responses obtained at different temperatures. Furthermore, these properties can be measured explicitly by using the technique described in Section 2.

The capillary suction of water was ignored in this investigation by assuming zero velocity of the liquid water in pore system. The phenomena can be incorporated by introducing a separate constitutive assumption for the mass density flow of liquid water as done for the water vapor constituent, i.e., see Eq. (7). In such a case, Darcy's law can be used in which the gradient of the capillary pressure is used as the driving potential for liquid water flow in the pore system. It is very likely that the liquid water flow plays a dominant role at high water contents and should therefore not be excluded in a consistent model describing moisture transport in porous materials such as concrete. In this work the focus is on local transient condensation and diffusion of vapor in cement mortar and the liquid water flow phenomena is excluded by simplicity reasons.

Yet another experimental fact must be considered in making the presented model more general. The problem referred to is the hysteresis in the sorption. This phenomenon can also be incorporated into the format of constitutive equations as described in Section 4. A natural approach is to let the equilibrium conditions, as given in Eq. (9), also be dependent on the history of the process in terms of wetting and drying conditions.

9. Conclusions

The main conclusion is that the kinetics of sorption in mature cement mortar is a relevant phenomenon which can be measured very accurately using the sorption balance instrument. The experiments showed that the equilibration process needed for reaching a point in the sorption isotherm is far from being instantaneous, as assumed in most models dealing with moisture transport in porous materials.

The constitutive equation was established in a way that makes an extension of including temperature and hysteresis effects straightforward. This is due to treating diffusion and transient sorption as truly separate phenomena.

The time scale for the sorption kinetics obtained by the sorption balance instrument and the kinetics obtained by evaluating the measurements in Ref. [1] on moisture profiles showed a marked diversity. The reason for this observed difference may be a slow equilibration process at very high liquid water content in the pores of the material. These high values cannot be tested in the sorption balance that runs in the range of 0–96% relative humidity, which should be compared with the experiment performed in Ref. [1] where the relative humidity at the exposed material surface was very close to 100%. At these high relative humidities, the slope of the sorption isotherm is very steep. Hence, a small increase in relative humidity corresponds to a high increase in liquid water content. Another possible reason for obtaining a slower equilibration process when evaluating the sorption kinetics from the indirect measurements presented in Ref. [1], compared to the direct measurements presented in Section 2, can be that the pore system is not properly accounted for in the sorption balance measurements. That is, the sorption behavior can be affected by the sample being finely divided.

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