PRESSURE INDUCED BY SALT CRYSTALLIZATION IN BUILDING MATERIALS - EXPERIMENTAL AND NUMERICAL ANALYSIS

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Abstract

MIP tests of the cement mortar saturated with NaCl, CaCl₂, Na₂SO₄ solutions were performed. The changes of porosity, pore size distribution and pore shape were investigated by two intrusion-extrusion cycles. The crystallization pressure bursts the meso-pores. The model of coupled heat, moisture and salt transport considering the salt crystallization is presented. During salt crystallization an additional heat is released, which must be considered in the energy conservation equation of multiphase domain. The key factor while modeling the salt crystallization is the kinetics of salt phase change, which is approximated in the presented research by means of Freundlich non-equilibrium isotherms. In order to calculate the solution supersaturation ratio the short and long range ions interaction was taken into account applying the Pitzer model. The mathematical model was solved using FEM and FDM and some numerical examples were calculated and discussed. It was proved that the higher rate order is assumed in the kinetic law the higher crystallization pressure is obtained from simulations.

1. INTRODUCTION

Salt crystals, which grow on the surface, are responsible for the optical and chemical damage of the historical finishing layers. The growing crystals produce an additional crystallization pressure [1, 2]. Generally salt exists in two phases in pore system: salt dissolved in pore water and salt crystals. Salt strongly influences the properties of the multiphase domain: sorption isotherms [3], properties of liquid [4], pore structure. Additional heat is released during the salt crystallization [5]. Therefore salt affects the moisture and energy transport as well. Two different processes might induce the salt crystallization: drying and cooling. During drying water occupying the pores evaporates. Salt is transported together with water toward the surface, but cannot evaporate, hence its concentration strongly increases. Solution becomes supersaturated and the salt crystallization starts. The second process (cooling) concerns only those salts, whose solubility decreases during cooling e.g.: Na₂SO₄. In such a case the solution supersaturation is referred to the fact that the colder solution, the lower solution solubility. Therefore the coupling between salt, moisture and energy transport must be taken into
account while analyzing the salt crystallization and its influence on the moisture and energy transport as well as on the durability of porous materials.

Although a lot of experimental and theoretical research was devoted to salt crystallization there is still lack of commonly accepted, coherent mathematical model describing the heat, moisture and salt transport in porous materials considering the salt crystallization, accounting for the long and short-range ion interaction, and its influence on the transfer phenomena. The salt crystals change the inner pore structure of the porous material. Hence it influences on the basic properties e.g.: porosity and intrinsic permeability, which determines the transfer phenomena. The brick and cement mortar containing different salts have been investigated using the mercury intrusion porosimetry. The mathematical model of energy, moisture and salt transfer in porous materials and its numerical solution is presented in the paper. The moisture and salt flow is described by means of the Fick (diffusion, salt dispersion) and Darcy's (capillary flow) laws. The additional, heat is released during the crystallization and the energy is consumed during the crystals dissolution of salt, e.g. Na$_2$SO$_4$ are considered. The driving force of the crystal formation is the solution supersaturation ratio. The pore water is a concentrated electrolyte, so the non-ideal behavior of the solutions must be taken into account. Apart from the long-range interaction between the ions the short-range must also be considered, otherwise the calculations might be erroneous. The Pitzer ion interaction model is taken into account in the present formulation.

The developed model was verified against experimental data concerning salt, moisture and heat transport without salt crystallization, (capillary suction) [3]. Although one can notice the effects of salt crystallization in everyday life (damage of surface, salt efflorescence), the exact measurement of salt crystals content is very difficult due to the fact that the process is very fast and influenced by many environmental factors as temperature or relative humidity.

2. **INFLUENCE OF CRYSTALLIZING SALT ON THE CEMENT MORTAR POROSITY**

The mercury intrusion porosimetry (MIP) tests were performed in order to investigate the effect of salt crystals on the cement mortar porosity. The material samples dimensions were: 4x4x16cm. The samples were fully filled with the saturated solutions of three salts: Na$_2$SO$_4$, NaCl or CaCl$_2$, then they were dried: one week in relative humidity of 40% and temperature of 25$^\circ$C, then two weeks in the oven, at temperature of 70$^\circ$C. After this procedures the samples of 1cm$^3$ volume were taken from the vicinity of the surface. The salt was expelled from the surface using a brush. Then the samples were tested in the MIP porosimeter (Micrometrics, AutoPore IV 9500). Two cycles of mercury intrusion-extrusion were applied for cement mortar and brick, in order to assess the amount of ink-bottle type pores [8]. After first extrusion large amount of mercury is entrapped. This is the consequence of the pore system structure, which is built of the large chambers interconnected by smaller capillary or gel pores. After the first intrusion-extrusion cycle all ink-bottle type pores remain saturated with mercury. During the second mercury intrusion only the empty pores are filling according to the pressure that corresponds to their radius. Figure 1a shows the mercury cumulative volume during two intrusion-extrusion cycles. One can notice considerable hysteresis of the loops. The thicker lines denote intrusions, while the thin ones describe extrusions. The difference between the first and the second intrusion might be a measure of the ink-bottle type pores contribution to the whole pore volume expressed as a function of the mercury pressure.
Figure 1b shows the contribution of ink-bottle type pores in cement mortar. Cement mortar initially saturated with salts solution has porosity about 20% higher than the pure cement mortar. It is a proof that the crystallizing salt causes the burst of the solid skeleton. This process proceeds in meso- and macro-pores. All the analyzed salts cause a decrease of the amount of ink-bottle type pores in cement mortar. In pure cement mortar about 57% of pores are interconnected by smaller capillary or gel pores, what prevents mercury from escaping during the first extrusion. The salt crystallization changes the shape of pores and it lowers the fraction of ink-bottle type pores to about 45-50%.

Figure 1. The results of two cycles of mercury intrusion-extrusion tests a) versus mercury pressure, b) the relative volume of ink-bottle like pores of cement mortar containing the Na$_2$SO$_4$, NaCl and CaCl$_2$ salts.

3. MATHEMATICAL MODEL

3.1 Ion interaction model

The pore water containing dissolved salt is an electrolyte (M means cation, X-anion). Ions behave as the independent reagents in any kind of physical or chemical reaction. Therefore the ion interaction must be taken into account while analyzing the salt phase change. The dissociation of solution compounds might be described by the equation:

\[ M^{z_+}_v X^{-}_v \leftrightarrow v_+ M^{z_+} + v_- X^{z_-}. \]

In the Pitzer ion interaction model [9] the excess Gibbs energy of an electrolyte solution incorporates an extended Debye-Huckel term and a power (virial) series, representing short-range ions interaction. The virial coefficients account for all binary interactions between anions and cations, binary interactions between ions for the same sign but different charges, and all possible interactions between groups of three ions. In the presented approach it is assumed that only one salt might be dissolved in the pore water hence the ternary interactions parameters are neglected. The entire set of Pitzer model equations might be found in e.g. [9, 10]. The osmotic coefficient and the activity coefficients of cation $M$ and anion $X$ equals:
\[(\phi - 1) = \sum_{i} \frac{2m_i}{1 + bI^{0.5}} \left[ -A^e I^{1.5} + m_a m_c (B_{ca}^e + ZC_{ca}) \right] \quad (1)\]

\[\ln \gamma_M = z_M^2 F + m_a (2B_{Ma} + ZC_{Ma}) + \left| z_M^2 \right| m_a C_{ca} \quad (2)\]

\[\ln \gamma_X = z_X^2 F + m_c (2B_{cX} + ZC_{cX}) + \left| z_X^2 \right| m_m C_{ca} \quad (3)\]

Figure 2 presents the mean activity coefficient and the water activity of Na\(_2\)SO\(_4\) solutions, calculated based on the Pitzer model. The function \(F\) depends on the ionic strength according to the equation:

\[F = -A^e \left[ \frac{I^{0.5}}{1 + bI^{0.5}} + \frac{2}{b} \ln(1 + bI^{0.5}) \right] + m_c m_a B'_{ca} \quad (4)\]

The subscripts \(c, a\) refer to cation and anion respectively and \(A^e\) is the Debye-Huckel parameter for the osmotic coefficient, \(b\) is a universal parameter equals 1.2 kg\(^{0.5}\)mol\(^{-0.5}\).

Water activity is given by the equation:

\[\ln a_w = -\frac{M_w}{1000} \sum_{i} m_i \phi \quad (5)\]

Assuming the equilibrium, the water activity \(a_w\) of an aqueous solution can be given by the equation

\[a_w = \frac{p_w}{p_w^0} = RH \quad (6)\]

where \(p_w\) is the water vapour pressure above the salt solution and \(p_w^0\) is the saturation vapour pressure of pure water. At equilibrium the water activity equals the relative humidity, RH. Based on eq. (6) the water activity of solution of various salt solutions, at different concentrations can be measured and utilized for the model parameters determinations.

Having all above parameters one is able to calculate the ion activity of any salt \(M_{sH_2O} X_{sX} \cdot nH_2O\):

\[\ln a = v_M \ln(m_M) + v_X \ln(m_X) + v_M \ln(\gamma_M) + v_X \ln(\gamma_X) + v_0 \ln(a_w) \quad (7)\]
The solution saturation is given by means of the ion activity product and equilibrium constant \( K \) as follows:

\[
S = \frac{a}{K}
\]  

(8)

### 3.2 Kinetics of salt crystallization

The driving force of salt crystallization is the solution supersaturation ratio, written in terms of the ion activity product, - eq. (8). The crystals grow when the solution is supersaturated. The rate of crystal growth might be described by the non-equilibrium isotherms [11]. The rate of crystal growth in the supersaturated solution and crystal dissolution might be described by the non-equilibrium Freundlich isotherms:

\[
\frac{dS_p}{dt} = \begin{cases} 
S_w F (S - A')^\gamma, & S \geq A' \land S_p < 1 \\
-S_w F |S - 1|^\gamma, & S < 1 \land 0 < S_p < 1 
\end{cases}
\]

(9)

The process order \( p \), and the constant \( F \) depend on the kind of salt and the properties of porous material. The rhs is greater than zero, when the solution supersaturation ratio exceeds \( A' \) (for secondary crystallization \( A'=1.0 \) hence it describes the crystallization process. When there are crystals in the solution and the solution supersaturation ratio is lower than 1.0, the dissolution process proceeds. \( A' \) is the primary crystallization coefficient. It was experimentally proved that for salt primary crystallization, much higher solution supersaturation is needed than for the secondary ones, which proceeds usually by \( A'=1.0 \). The primary crystallization coefficient depends on the kind of salt and porous materials and might vary from 1.7 up to 10 [12].

The crystallization pressure, which is exerted on the pore wall by the growing crystal can be described as [6, 7]:

\[
\Delta p = \frac{RT}{V_m} \ln \left( \frac{a}{K} \right) = \frac{vRT}{V_m} \left( \ln \frac{m}{m_0} + \ln \frac{\gamma_\|}{\gamma_{z,0}} + \frac{v_0}{v} \ln \frac{a_w}{a_{w,0}} \right)
\]

(10)

where \( a \) can be described by the equation (7) and \( K \) is the equilibrium constant.

### 3.3 Governing equations

The mass balance equation of dry air includes both diffusive (the third term on the lhs) and advective (the last term on the lhs) components of the mass fluxes, the influence of the precipitated salt is also considered [13, 14]:

\[
n \frac{\partial}{\partial t} \left( S_g \rho^a \right) - \beta S_g \rho^a \left( 1 - n \right) \frac{\partial T}{\partial t} + \nabla \cdot \left( J^a \right) + \nabla \cdot \left( n S_g \rho^a \mathbf{v}^{gv} \right) = 0
\]

(11)

where \( S_g = 1 - S_w - S_p \).

The moisture mass balance equation was derived by summing up the water vapour and liquid water mass balance equation, which are linked together by source terms, related to evaporation-condensation or adsorption-desorption process. The final form of moisture balance equation is [13, 14]:


Salt influences the density and dynamic viscosity of the liquid phase. The more salt is contained in the porous material, the more moisture is adsorbed by the material at the same relative humidity. This relation might be modeled using the artificial neural networks [3]. The sources or sinks of dissolved salt due to the crystallization/dissolution process are taken into account by means of kinetics approach (the third term on the lhs). The mass balance of the salt dissolved in the fluid phase is expressed as, [13 14]:

\[
\begin{align*}
&n \frac{\partial}{\partial t} \left( S_w \rho^w \right) + n \frac{\partial}{\partial t} \left( S_e \rho^e \right) - \beta_s (1 - n) \left( S_e \rho^e + S_w \rho^w \right) \frac{\partial T}{\partial t} + \\
&+ \text{div}(n S_w \rho^w \mathbf{v}^w) + \text{div}(n S_e \rho^e \mathbf{v}^e) + \text{div}(\mathbf{J}^\text{disp}) = 0
\end{align*}
\] (12)

The enthalpy conservation equation of the multiphase medium, obtained by summing the appropriate balance equations of the constituents, includes the heat effects due to phase change of water and heat released during the salt precipitation process (the terms on the rhs), as well as the convectional and latent heat transfer, [13, 14]:

\[
\begin{align*}
&\left( \rho C_p \right)_\text{ef} \frac{\partial T}{\partial t} + \left( \rho^w C_p^w \mathbf{v}^w + \rho^e C_p^e \mathbf{v}^e \right) : \text{grad} \, T - \text{div} \left( \lambda_\text{ef} \text{grad} \, T \right) = \\
&= -\dot{m}_\text{vap} \Delta H_\text{vap} - \dot{m}_\text{prec} \Delta H_\text{prec}
\end{align*}
\] (13)

where \( (\rho C_p)_\text{ef} \) is effective thermal capacity of the multiphase domain.

4. SIMULATION RESULT

The numerical example concerns the cooling and warming process of the 25 cm brick assuming the following material properties: \( n = 0.20 \), \( k = 3.0 \times 10^{-16} \text{ m}^2 \), \( C_p = 880 \text{ J/(kg·K)} \), \( \lambda_\text{dry} = 0.77 \text{ W/(m·K)} \), \( \rho^f = 1700 \text{ kg/m}^3 \). Sodium sulphate solubility strongly varies with the temperature and the composition of crystals - Figure 5a. Salt crystallization analysis was performed assuming that the process order \( r \) equals: 1.5 (case a), 3.5 (case b). The ambient temperature varies according to the formula:

\[
T = \begin{cases} 
303.15 - 5t, & t \in [0, 4] \\
283.15, & t \in (4, 6) \\
303.15 + 5t, & t \in (6, 10) \\
303.15, & t \in (10, 12)
\end{cases}
\]

Two such temperature loops were analyzed during the simulations. The initial conditions are: \( p^g = 101325 \text{ Pa} \), \( S_{w,0} = 1 \) (fully saturated state), \( T_0 = 303.15 \text{ K} \), \( \omega_0 = 0.25 \text{ kg/kg} \). It is assumed that the initial dissolved salt concentration is lower than the solution solubility and no solid salt is initially present in the pores, \( S_{p,0} = 0 \). The boundary conditions are symmetrical, therefore all results will be presented only for one half of the analyzed material. For all the considered cases the rate constant in eq. (9) was the same and equal to \( F = 0.005 \). The time step \( \Delta t = 10 \text{ s} \) was assumed. The salt crystallization causes the temperature increase. It is a
The crystallization pressure is observed close to the surface, where the changes of temperature appear firstly - Figure 10d. The maximum crystallization pressure on the surface varies from 0.5 MPa (case 1) up to 2.6 MPa (case 2), what may cause the damage of the surface layer. It can be noticed that the lower rate order is assumed, the lower crystallization pressure in the sample was obtained. This observation is opposite to the one concerning the degree of saturation with the crystallized salt. It can be explained by the fact that the slower crystals growth the higher solution supersaturation ratio can be achieved, which is on the other hand the driving force of crystallization pressure.

Figure 10. The profiles of maximum crystallization pressure for a) case 1, b) case 2.

5. CONCLUSIONS AND FINAL REMARKS

The mathematical model describing salt crystallization in non-isothermal condition in fully and partly saturated state is presented in the paper. The key point in the salt crystallization modeling is the kinetics of salt phase change. The rate law was described using Freundlich non-equilibrium isotherms. In order to calculate the ion activity coefficient and the water activity the Pitzer ion interaction model is employed, which takes into account both the long and short-range interaction between ions.

Based on the mathematical model the computer code was developed. Using the software the cooling-warming experiment was simulated. Based on the simulation results one of these experiment one can conclude that the higher rate order of the kinetics equation the slower salt crystals growth. But on the other hand the higher rate order the higher solution supersaturation is reached and the higher maximum crystallization stress might be generated.

The mercury intrusion porosimetry of brick and cement mortar saturated with NaCl, Na₂SO₄, CaCl₂ solutions were performed. Two intrusion cycles were tested for this materials in order to investigate the ink-bottle type pores. The measure of ink-bottle type pores was proposed. Salt crystals influence not only the porosity and the pore size distribution but also the shape of pores (the participation of ink-bottle type pores), hence they determine the transport processes in porous materials.
Growing crystals exert considerable expanding pressure on solid skeleton. Majority of building materials have good resistance for compression but rather poor for tension. Therefore the additional tension due to salt crystallization might cause the damage of material microstructure and development of cracks. These phenomena accelerate the transport processes, what was not taken into account in the presented research. Further study must be devoted to modeling the damage of materials caused by crystallizing salt.

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