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Salt transport and crystallization in non-isothermal, partially saturated porous materials considering ions interaction model

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ABSTRACT

Crystallizing salt changes the inner pore structure of materials. MIP tests of cement mortar and brick saturated with NaCl, $CaCl_2$, Na_2SO_4 solutions were performed. The changes of porosity, pore size distribution and pore shape (ink-bottle type pores) were investigated by performing two intrusion–extrusion cycles. The crystallization pressure bursts the mezopores. During salt crystallization the additional heat is released, which must be considered in energy conservation equation of multiphase domain. The model of coupled heat, moisture and salt transport considering the salt crystallization is presented. 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 practical examples were calculated and discussed. It was proved that the higher rate order appears in the kinetic law the higher crystallization pressure might be generated. The approximation procedures were tested numerically.

1. Introduction

The salt crystallization is recognized as one of the major cause of the damage of porous building materials as: concrete, brick, stone. One can distinguish two main phenomena accompanying the presence of salt in pore water which limit the service life of buildings: salt crystallization and corrosion of steel bars. The first damage mechanism is under the investigation in the presented paper. Salt crystals, which grow on the surface, are responsible for the optical and chemical damage of the historical finishing layers. Moreover growing crystals produce the additional crystallization pressure [1,2]. There are various techniques used to detect and analyze the presence of salt crystals in pore structure: scanning electron microscope [3], nuclear magnetic resonance [4]. Generally salt exists in two phases in pore system: salt dissolved in pore water and salt crystals. Only the first form is mobile. Salt strongly influences the properties of the multiphase domain: sorption isotherms [5], properties of liquid [6], pore structure. Additional heat is released during the salt crystallization [7]. 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 to those salts, whose solubility depends on the temperature e.g. Na_2SO_4. In this case solution supersaturation is referred to the fact that the warmer solution, the higher 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.

There exist some models, which might be used for simulation of the energy, moisture and salt transfer in porous materials. The first models proposed by Hassanizadeh and Leijnse [6] are limited only to salt and moisture transfer and coupling between them. In most of his works the focus is paid on the dispersive salt flow rather than salt crystallization. The formulation proposed by Nguyen et al. [8] does not take into account the energy balance equation. For some salt (Na_2SO_4) salt crystallization generates additional heat. Moreover the solution saturation depends on the temperature. Therefore negligence the coupling between energy and salt transport might generate severe errors and strongly limit the application of the model. Grunewald [9] assumed the equilibrium between salt phases: salt dissolved in pore water and solid salt. The solution concentration can never exceed the solution saturation therefore the crystal growth, which starts when the solution supersaturation ratio exceeds one, cannot be foreseen.

Correns and Steinborn first derived equation for the maximum crystallization stress. They defined the solution supersaturation in

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Nomenclature

A'	supersaturation parameter [–]
a	ion activity [–]
a_w	water activity [–]
C_p	effective specific heat of porous medium [J/(kg K)]
$\mathbf{D}^d$	tensor of hydrodynamic dispersion [m^2/s]
$\mathbf{D}_v^g$	effective diffusivity tensor of vapor in the air [m^2/s]
D^{mol}	molecular diffusivity [m^2/s]
$\mathbf{g}$	acceleration of gravity [m/s^2]
ΔH_{vap}	enthalpy of vaporization per unit mass [J/kg]
ΔH_{prec}	enthalpy of crystallization per unit mass [J/kg]
I	ionic strength [mol/kg]
$\mathbf{J}^{dysp}$	dispersive flow of salt [kg/(m s)]
$\mathbf{J}_g^a$	diffusive flux of dry air [kg/(m s)]
$\mathbf{J}_g^v$	diffusive flux of water vapor [kg/(m s)]
$\mathbf{j}^{ws} = [j_1^{ws}, j_2^{ws}]$	Darcy velocity of water [m/s]
$\mathbf{j}^{gs}$	Darcy velocity of air [m/s]
F	rate constant (rate law) [–]
k	intrinsic permeability scalar [m^2]
$k^{r\pi}$	relative permeability of Π – phase ($\Pi = w$, g – liquid, gas) [–]
M_Π	molar mass of $\Pi = a, w, g$ – dry air, water, gas [kg/k mol]
$m_\pm$	mean molality [mol/kg]
$\dot{m}_{\mathrm{vap}}$	rate of mass due to evaporation [kg/(m^3 s)]
$\dot{m}_{\mathrm{prec}}$	rate of mass due to crystallization [kg/(m^3 s)]
n	porosity (pore volume/total volume) [–]
p_Π	pressure of ($\Pi = w, g, p, v$ – liquid, gas, precipitated salt, water vapor) [Pa]
p^c	capillary pressure [Pa], $p^c = p^g - p^w$
Δp	crystallization pressure [Pa]
R	gas constant (8314.41 J/(kmol K))
RH	relative humidity [–]
r	process order (rate law) [–]
S	solution supersaturation ratio [–]
S_Π	saturation degree of the Π – phase (volume occupied by the phase/volume of the pores), $\Pi = w, g, p$ – liquid, gas, precipitated salt [–]
T	absolute temperature [K]
t	time [s]
V_m	molar volume of salt [m^3/mol]
$\mathbf{v}^{\pi s}$	relative velocity Π – phase ($\Pi = w$, g – liquid, gas) [m/s]
v_{+-}	stoichiometric coefficient
x_s^{ws}	solid surface fraction in contact with the wetting film [–]
$\mathbf{y}$	primary variables nodal values vector
z^{+-}	charge of ions

Greek symbols

α_L, α_T	longitudinal and transverse dispersivity
β_c	convective mass transfer coefficient [m/s]
β_s	cubic thermal expansion coefficient of the solid [1/K]
$\gamma_\pm$	ion activity coefficient [–]
ϕ	osmotic coefficient
λ_{ef}	effective thermal conductivity [W/(m K)]
μ^π	dyn. viscosity of Π – phase ($\Pi = w$, g – liquid, gas) [Pa s],
μ	chemical potential, [J/mol]
ρ_Π	density of Π – phase ($\Pi = w, a, g, s, p$ – liquid, dry air, gas, solid skeleton, precipitated salt) [kg/m^3]
ρ^v	mass concentration of water vapor in gas phase [kg/m^3]
ω	salt mass concentration in the solution [kg/kg]
ω_{sat}	salt mass concentration in the saturated solution [kg/kg]

terms of solution concentration. Scherer [10] analyzed also the effect of the curvature on the crystallization pressure and the phenomena related with the crystal growth: nucleation of crystals, growth of a flaw, etc. Steiger [11], by comparing the chemical potential on the different faces of the crystal, derived in a consistent way the equation describing the pressure exerted on the pore wall. The solution supersaturation is defined by means of the ion activity product.

Although a lot of experimental and theoretical research was devoted to salt crystallization there is still lack of one 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 they influence on the basic properties e.g. porosity and intrinsic permeability, which determines the transfer phenomena. The brick and cement mortar containing various salt have been investigated using the mercury intrusion porosimetry. The mathematical model of energy, moister 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_2SO_4. Therefore the fully coupled and complex model is needed in order to simulate the salt crystallization in porous materials. The driving force of the crystal formation is the solution supersaturation ratio. The pore water is the 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 presented formulation.

The developed model was verified against experimental data concerning salt, moisture and heat transport without salt crystallization, (capillary suction) [5]. Although one can notice the effects of salt crystallization in everyday life (damage of surface, salt efflorescence) the exact measurement of salt crystals is very difficult due to the fact that the process is very fast and influenced by many environmental factors as temperature or relative humidity. There exist results giving an evidence of salt crystallization [4], but no quantitative data are available in the literature. Therefore, concerning salt crystallization, only the numerical procedures were validated and are presented in the paper.

2. Influence of salt crystals on the pore structure

To investigate the effect of salt crystallization on the pore structure of cement mortar and brick the mercury intrusion porosimetry (MIP) tests were performed. Although some scientists are rather skeptical about the method [12], it is still widely used and might be applied to measure the changes of the pore structure due to some physical or chemical processes or to compare two different materials. Samples dimensions were: $4 \times 4 \times 16$ cm – cement mortar, $6 \times 6 \times 12$ cm – brick. Samples were fully filled with the saturated solutions of three salts: Na_2SO_4, $NaCl$, $CaCl_2$. Then the samples were dried: one week in relative humidity 40% and temperature 25 °C, then two weeks in the oven, temperature 70 °C. After this procedures the samples of 1 cm^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 Micrometrics, AutoPore IV 9500. Two cycles of mercury