Coupled heat and water transport in deformable porous materials considering phase change kinetics

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ABSTRACT

The paper considers water solidification in porous materials. The cement mortar microstructure and the content of ink-bottle type pores evolution due to cyclic water freezing was analyzed by means of mercury intrusion porosimetry. The influence of pressure, temperature and the size of pores on the equilibrium between solid and liquid water was investigated using Gibbs free energy. Mathematical model describing heat and water transport in deformable porous materials considering water phase change kinetics was proposed. The numerical code was developed using finite element, finite difference and Newton–Raphson methods. The model and the code was validated using experimental data considering the hysteresis of water freezing-ice thawing. The influence of water freezing in the squared concrete column on strain field was investigated as a second problem. It was shown that water solidification induces the swelling, which counteracts the thermal shrinkage. The comprehensive approach allows to investigate the transport processes together with the related phenomena and asses the durability of porous materials exploited in cold regions.

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1. Introduction

Cyclic freezing of water in porous materials is very destructive. The main reason of the damage is the increase of molar volume of ice when compared to the one of water. Ice growth induces additional pressure acting on the skeleton but it also increase liquid water pressure, which is even more sever for the material skeleton [1–4]. Majority of porous materials, e.g. rocks, cement based materials, etc, are brittle. Low permeability restricts water migration. Therefore the water solidification is extremely dangerous when the material is fully or close to fully saturated with water. The pressure which is exerted on the skeleton walls by both ice and liquid water cause the tensile stress, which might initiate cracks and the damage of microstructure. When sufficient volume of air is contained in the pore system it might be pushed away by water moving from the freezing zone. In such a case the liquid pressure is relaxed by the possible migration of water to the empty pores. Subsequently, the water migration from unfrozen zone to the freezing sites was reported by numerous researchers [5–9]. The driving force for this phenomenon, called cryo-suction, was linked to the existence of a free energy difference between ice and liquid water.

A similar mechanism is often proposed to explain heaving problems in frozen soils [10,11].

The Gibbs free energy concept was employed to investigate the thermodynamics of phase change, which accounts for the temperature variation, liquid pressure and interaction between the solid and liquid phase [10–12]. Ice growing induced by temperature drop consists of two phenomena: the nucleation and the growth of the crystals volume. The kinetic approach was introduced for the process of ice growth in porous materials, which takes into account the nucleation, the consumption of some nuclei by growing ice volume, etc. [13–15].

The freezing temperature of various liquids depends on the size of pore, where the solidification takes place. The experimental research investigating the heat released during water phase change, which might serve as a measure of pore size distribution and the shape (spherical or cylindrical) of pores is known as thermoporometry [11,16]. Fen-Chong and coworkers further utilized the sensor-based and oscillator circuit-based capacitive method to study the ice-water phase change in porous materials. These techniques relies on the dielectric properties of water, ice and solid skeleton in the radio-frequency range [17,18]. Strain accompanied with the water phase change are measure in order to assess the macroscale effects and materials resistance to the low temperature [3].

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Water solidification in porous materials is very complicated and complex. It has an essential impact on the durability of porous materials exploited in the continental, moderate and arctic climate. Numerous of mathematical models and computer codes were developed to describe that phenomenon [19,20]. None of the proposed theories covers all phenomena related to water and heat transport in deformable porous materials induced by water freezing. The proposed formulation deeply investigates the thermodynamics of water phase change with the special emphasis on the role of materials microstructure. Such an approach together with water phase change kinetic model allows to simulate the hysteresis during water freezing-ice thawing. Poroelasticity, originally developed by Biot [21], expanded in the context of continuum thermodynamics by Coussy [22], is employed to investigate the strain induced by water freezing. Finally, using the standard numerical techniques, the computer code was developed to simulate the phenomena related to water freezing.

2. Microstructure change caused by cyclic water freezing

To investigate the influence of cyclic freezing of water on microstructure of cement mortar fully saturated with water (water/cement ratio equaled to 0.5) the mercury intrusion porosimetry tests [23,24] were performed. The samples were cured during 3 months then they were treated with the subsequent water freezing. One cycle lasted 20 h, during which temperature in the climatic chamber oscillated between 20 and −20 °C, cooling took place in the air while warming in the water. Three kind of samples were tested: first group – unaffected samples, second group – samples after 50 freezing-thawing cycles, third group – samples after 100 freezing-thawing cycles. The maximum pressure, which was applied to mercury during intrusion, equaled to 200 MPa, which allowed, according to well known Washburn equation, to analyze the smallest pores with diameter equaled to 6 nm. Three samples of each group was investigated, Fig. 1 presents average results of each kind of experiment. 50 cycles of freezing-thawing didn't caused the increase of total porosity, whereas 100 cycles of freezing-thawing caused the swelling of total porosity about 40%. Even more spectacular change was observed for pores, whose entry diameter is larger than 500 nm – Fig. 1b. By performing two mercury intrusion-extrusion cycles one is able to investigate the contribution of ink-bottle pores [25] using the following formula:

$$C_{ink-bottle}(p) = 1 - \frac{V_{por}^{2^{nd}int}(p)}{V_{por}^{1^{nd}int}(p)} \qquad (1)$$

Where $V_{por}^{1^{nd}int}(p)$, $V_{por}^{2^{nd}int}(p)$ are the volume of pores occupied by mercury at pressure p during first and second intrusion. The contribution of ink bottle type pores, whose diameter ranges between 1 μm and 20 μm decreases when the number of freezing-thawing cycles increases. The opposite situation can be noticed for pores with diameter 10–100 nm. Based on that observations one might deduce the possible scenario of cement mortar microstructure ice-induced damage. The smaller channels connecting the larger pores are bursting due to pressure which is exerted by the ice crystals, growing firstly in the larger pores, and water, which participate in the pressure transition. As a consequence the dimension of small necks connecting the larger pore increases and the contribution of the ink bottle pores decreases in the course of freezing-thawing cycles. Simultaneously, the fine pieces of the crushed material are pushed into the smaller pores, what possibly increases the contribution of small, ink-bottle pores.

The above presented curves describing cumulative pore size distribution were normalized and approximated by the polynomials to be suitable for the numerical iterative procedures:

$$V_{rel}(r) = \int_{r_{max}}^{r} \pi s^2 l(s)ds \approx \sum_{k=0}^{n} a_k(\log_{10}r)^k, \quad V_{rel}(r_{min}) = 1 \qquad (2)$$

where $a_3 = -0.024216$, $a_2 = -0.37326$, $a_1 = -1.92596$, $a_0 = -3.2101$ for the witness sample, $a_5 = 0.003375$, $a_4 = -0.094877$, $a_3 = -1.051$, $a_2 = -5.736$, $a_1 = -15.57$, $a_0 = -16.88$ for the sample after 50 freezing cycles and $a_6 = -0.0028232$, $a_5 = -0.10190$, $a_4 = -1.49696$, $a_3 = -11.446982$, $a_2 = -48.03353$, $a_1 = -1.05058e + 02$, $a_0 = -93.83096$ for the sample after 100 freezing cycles.

3. Phase equilibrium

Water freezing temperature depends on the curvature of the liquid–crystal interface, which is limited by the pore radius, where the solidification takes place. The Gibbs–Duhem law [26] defines the change of chemical potentials. It might be written for a pure substance e.g. water or ice (μ_L, μ_C) as follows:

$$d\mu_L = -S_L dT + v_L dp_L \qquad (3a)$$

$$d\mu_C = -S_C dT + v_C dp_C \qquad (3b)$$

where v_L, v_C, S_L, S_C describe molar volumes and molar entropies of liquid and ice respectively.

The transition from one equilibrium state to the other, $d\mu_L = d\mu_C$, one can find:

$$\Delta S_{fv} dT = \frac{v_L - v_C}{v_C} dp_L - d(p_C - p_L) \qquad (4)$$

where ΔS_{fv} is the entropy of fusion of crystal per unit volume. One can integrate Eq. (4) over the interval limited by two points. The first one, which is the standard triple point of large, unstressed crystal, might be described by $T = T_m$, $p = p_e$ (equilibrium pressure between liquid, crystal and vapor), $\kappa_{CL} = 0$ (flat surface). The second point is characterized by the liquid pressure, p_L, the crystal curvature, κ_{CL} and the melting temperature $\widehat{T}_m = \widehat{T}_m(p_L, \kappa_{CL})$, which is shifted compared to the standard triple point. After such integration the following formula might be derived [4,27]:

$$p_C - p_L = \Delta S_{fv}\left(T_m - \widehat{T}_m\right) - \left(\frac{v_C - v_L}{v_C}\right)(p_L - p_e) \qquad (5)$$

Molar volume of water and ice equal 18.05 cm³/mol and 19,62 cm³/mol [10] respectively, thus the swelling during water solidification is observed. The pore volume is confined by the skeleton, which acts as an obstacle reducing growth of crystals. The Laplace equation defines the mechanical equilibrium between the crystal and liquid, which reads:

$$p_C - p_L = \gamma_{CL}\kappa_{CL} \qquad (6)$$

where κ_{CL} is the curvature of the solid–liquid interface equal to: $2/r$ for spherical shape and $1/r$ for cylindrical shape. Putting the Laplace formula into Eq. (5) one can obtain:

$$\gamma_{CL}\kappa_{CL} = \Delta S_{fv}\left(T_m - \widehat{T}_m\right) - \left(\frac{v_C - v_L}{v_C}\right)(p_L - p_e) \qquad (7)$$

Assuming that the crystals are spherical one can derive the formula defining the radius of pores where water solidification takes place as a function of overcooling temperature and liquid pressure:

$$r = \frac{\gamma_{CL}}{\Delta S_{fv}\left(T_m - \widehat{T}_m\right) - \left(\frac{v_C - v_L}{v_C}\right)(p_L - p_e)} \qquad (8)$$

Let us notice that the pore radius is reversely proportional to the overcooling temperature. Ice crystals firstly occupies the largest