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Analysis of damage development in cement paste due to ice nucleation at different temperatures

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ABSTRACT

From the thermodynamic considerations and from a virtual microstructure of cement paste, a quantitative assessment of the internal damage of cement paste due to hydraulic pressure is investigated by 3D lattice fracture model. Two issues are solved in this study: (1) the capillary pores related to the penetration of ice crystals are characterized by a multi-step digitalization algorithm. (2) The hydraulic pressure P_L is achieved through an iterative fracture process simulation where the creation of micro-cracks is taken into account. The iterative fracture process simulation then is verified by a benchmark test. Simulations indicate that randomly distributed micro-cracks are formed at a low ice crystal saturation degree S_C (defined as the molar percentage of water transformed into ice crystals), while local propagation of micro-cracks occurs and transverse cracks can be formed at high S_C. Comparison of S_C and cracks pattern by simulation and by experiments are finally discussed.

1. Introduction

The freezing behavior of concrete is a complex physical phenomenon and is an important issue with regard to the durability of concrete structures in cold and wet climates. So far, debate about the mechanism of frost damage is still ongoing [1–5]. Harmful stresses during freezing process could result from hydraulic pressure, ice crystallization pressure and the mismatch of thermal effects between ice and solid phases [1]. According to the well-known hydraulic pressure model, proposed by Powers [2], as the temperature decreases, ice is formed in the capillaries of cement paste, and in order to accommodate the volume increase associated with ice formation, excess water is expelled from the freezing sites causing a hydraulic pressure. If the matrix does not have enough tensile strength to resist the resulting pressure, cracks develop and the long-term performance of the structure is compromised [3]. Subsequently, experiments from Beaudoin and MacInnis [4] gave the evidence for the importance of crystallization pressure. Concrete specimen expands at the freezing point of benzene after its pore water had been exchanged with benzene. Since the volume of benzene decreases during freezing, no hydraulic pressure is created in this case. In order to maintain the equilibrium of chemical potentials between crystals of ice and liquid water, stresses may be exerted on pore walls due to the ice crystallization pressure. Scherer and Valenza [5] indicated that a tensile hoop stress exerted by ice crystals on the pore wall could approach the tensile strength of concrete at low temperatures.

In fact, besides thermal effect, either hydraulic pressure or ice crystallization pressure would play a dominant role for the frost damage of cement-based materials, depending on saturation degree of specimens, temperature decreasing rate, the lowest temperature, freezing environments, boundary conditions of specimens and so on. For water-saturated cement-based materials, under the condition that excess water can be driven out and the crystals of ice grow slowly into small pores as temperature drops, ice crystallization pressure may be the main source of frost damage. Damage due to ice crystallization pressure may become more significant at a very low temperature [5]. In contrast, under an undrained condition (e.g. surface sealed) and no free space is available for the extra water (e.g. in a non-air-entrained specimen), hydraulic pressure may be the main contribution to frost damage. If heterogeneous nucleation occurs at a temperature much lower than the freezing temperature of bulk ice, a large amount of ice is formed at the nucleation point and immediate damage is caused due to the sudden built up of hydraulic pressure. Air entraining agent is usually utilized in cement-based materials to avoid the

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frost damage due to hydraulic pressure. Hydraulic pressure model is often used and quoted because it is the only major theory capable of providing an order of magnitude of the stress and of the critical spacing factor for entrained air bubbles [3].

Using different simulation methods, many models were established to simulate the freezing behavior of cement-based materials in the last several decades [3,6–14]. By a poromechanical approach, Coussy and Monteiro [3] studied the influence of pore size distribution and gave a recommended spacing factor between adjacent air-voids. Zeng et al. [6,7] predicted the macroscopic strain of a water-saturated cement paste. By mathematic models, the deterioration of cement-based materials was investigated in literature [8–10]. In the poroelastic models or mathematic models, since the pore pressure was converted to a macroscopic effective stress through homogenization scheme, the micro-damage of cementitious materials cannot be captured. In addition, using high-performance computing, the micro-internal damages of cement-based materials due to frost action were simulated by finite element analysis [11–13] or by 3D lattice fracture analysis [14]. By these computer models, the penetration of ice crystals in pores, the internal stresses on pore walls and the creation of micro-cracks in the microstructure as a function of freezing temperature can be obtained.

From the aspect of frost damage sources, averaged pore pressures, respectively from liquid water and from ice crystals, were employed in the calculation of the strain-temperature response [3,6–12], and local pressures from ice crystallization were utilized in the fracture simulations of Dai et al. and Liu et al.'s work [13,14]. Nevertheless, few models provide the internal damage assessment of water-saturated cement-based materials attributed to hydraulic pressure. Continuing previous simulation work of authors [14], this paper studies the freezing behavior of water-saturated cement paste at different nucleation temperatures where hydraulic pressure is dominant.

On the basis of thermodynamics of in-pore crystallization, coupled with a virtual microstructure of cement paste, the internal damage (in terms of creation of micro-cracks) of cement paste attributed to hydraulic pressure is going to be evaluated by 3D lattice fracture analysis. Two issues are to be solved in this study. One is the characterization of capillary pores which is related to the penetration of ice crystals in pores, the other one is the determination of hydraulic pressure which changes with the changed capillary pores and the created micro-cracks. In order to capture all the capillary pores larger than 10 nm (frozen at −18 °C), a multi-step digitalization algorithm is proposed, by which the pore structure extracted from the microstructure of cement paste can be digitalized as voxels of different sizes. Then, the freezing of ice crystals in the multi-sized pore voxels can be simulated. In the 3D lattice fracture analysis, an iterative fracture simulation process is proposed where an initial guess of hydraulic pressure is used as input and the real hydraulic pressure is approached by considering the response of lattice structure to the input value. A benchmark test is carried out to verify the iterative fracture simulation process. Simulations about crack patterns and the propagation of micro-cracks, volume expansions and hydraulic pressure at stable state at different nucleation temperatures are clarified.

2. Thermodynamics of in-pore crystallization

The thermodynamics of crystallization within porous materials provides fundamental understanding of ice growth and stress development on pores. In the case of the liquid–crystal transition, at temperature T, the pressure in liquid P_L and in crystal P_C satisfies with the Thomson equation [15],

$$P_C - P_{atm} - (P_L - P_{atm})\overline{V}_L^0/\overline{V}_C^0 = (T_m - T)\Delta S_m \quad (1)$$

where P_{atm} is the atmospheric pressure. T_m is the freezing temperature where both liquid and crystal phases are at atmospheric pressure, i.e., the freezing point of bulk ice. ΔS_m is the melting entropy per unit volume of crystal, MPa/K. For ice, $\Delta S_m \approx 1.2$ MPa/K at 273 K [3,5]. $\overline{V}_L^0$ and $\overline{V}_C^0$ are molar volumes of liquid water and ice. For $\overline{V}_L^0/\overline{V}_C^0$, 1/1.09 is used. At temperature T, crystals of ice can penetrate into pores with a small entry larger than $2r_p$,

$$r_p = \frac{2\gamma_{CL}}{(T_m - T)\Delta S_m} + \delta \quad (2)$$

where γ_{CL} is the energy of the crystal/liquid interface, $\gamma_{CL} \approx 0.0409$ J/m^2 [3,16–18]. δ represents the thickness of the liquid film between the crystal and the pore wall. In cement paste, $\delta \approx 1.0–1.2$ nm [18]. The threshold of pores where crystals of ice can penetrate into (see Eq. (2)) is obtained on the assumption that crystals of ice have a hemispherical end [5,16]. Therefore, at a given temperature, the amount of ice in a porous material is closely related to its pore structure. For a water-saturated material, define the molar percentage of water transformed into ice as crystal saturation degree S_C, and liquid saturation degree S_L equals to $1 - S_C$. The hydraulic pressure is given in literature [15],

$$P_L = S_C(1 - \overline{V}_L^0/\overline{V}_C^0)\frac{K_L K_C}{S_L K_C + S_C K_L} \quad (3)$$

where K_L and K_C are the bulk modulus of water and ice, respectively. $K_L \approx 1.79 \times 10^3$ MPa at 263 K for supercooled water [19] and $K_C = 7.81 \times 10^3$ MPa at 263 K for crystals of ice [20].

3. Simulation of freezing in capillaries and calculation of hydraulic pressure

The computational procedure for simulation of freezing in capillaries and generation of hydraulic pressure in cement paste consists of the following steps: (1) generation of the microstructure of cement paste; (2) pore structure characterizing; (3) freezing in pores; (4) calculation of hydraulic pressure.

3.1. Microstructure simulation

A virtual microstructure of cement paste is generated by a numerical model HYMOSTRUC3D [21,22]. By HYMOSTRUC3D model, 51,072 cement particles with a Blaine surface area value of 420 m^2/kg and a discretized particle size distribution between 1 μm and 50 μm with an interval of 1 μm, are randomly distributed in a 3D body with the dimension of 100 × 100 × 100 μm^3 before hydration. Periodic boundary conditions are utilized during the particle placement. CEM I 42.5N with a potential Bogue phase composition of 64% C_3S, 13% C_2S, 8% C_3A, and 9% C_4AF by mass is used. For cement paste with a water-to-cement ratio (w/c) of 0.4 at the hydration degree (α) 0.69, a cube of 50 μm in length cut from the microstructure is shown in Fig. 1. The microstructure of cement paste is represented by vectors which give the x, y, z values of each spherical hydrated cement particle in the 3D coordinate. Unhydrated cement and hydration products (i.e., inner and outer CSH) are represented by concentric spherical shells.

3.2. Pore structure charactering

Pores in cement paste range from nanometers to millimeters, include gel pores, capillary pores, hollow-shell pores and air voids [23]. It is a big challenge to characterize these pores due to their microstructure features (e.g. irregular shape, isolated pores, dead-end pores and critical necks), wide pore size distributions and limitation of computer memory. According to Eq. (2), the crystals of ice can grow from large pores into small pores with an entry