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Numerical investigation of the effects of freezing on micro-internal damage and macro-mechanical properties of cement pastes

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ABSTRACT

It is of significance to investigate the deterioration of cement-based systems subjected to freezing temperatures including intrinsic microstructure change and reduction in mechanical resistance. From the microstructure of materials in question, few computer models take the coupled effects of water expulsion, in-pore crystallization and cryosuction into account to assess the realistic internal damage due to frost action. By considering the coupled effects of thermal action, hydraulic pressure and crystallization pressure, this study has established a microstructure-based model to investigate the effects of freezing on micro-internal damage and the macro-mechanical property changes of cement-based systems. Two parts of work are carried out: (1) by coupling a microstructure model HYMOSTRUC3D with a 3D lattice fracture model, the freezing of water in pores and the response of cement paste to the water freezing are captured. Changes in the microstructure of cement paste, represented by the creation of microcracks, are illustrated. (2) Changes in the mechanical properties of cement paste after freezing/thawing are estimated, and the estimated Young's modulus and volume deformation during freezing are compared with those by experiment. In the discussion chapter, from the aspects of thermodynamic considerations, damage sources, crack pattern and deformation, the hydraulic pressure model, ice crystallization pressure model and the newly established model in this study are discussed.

1. Introduction

Frost action (freeze–thaw cycles) is one of the major causes of the deterioration of concrete in cold wet climates, especially for hydraulic concrete. Concrete in some service environments can be subjected to freezing/thawing cycles coupled with exposure to deicer (Shi et al., 2010) or sulfate attack (Miao et al., 2002). To mitigate the premature deterioration of such concrete, enhanced understanding of frost action would also be very beneficial. Investigations on the deterioration of cement-based materials exposed to freezing/thawing have revealed a reduction in the mechanical resistance and an increase in the permeability, which are associated with the intrinsic changes of the microstructure (Diao et al., 2013; Liu and Wang, 2012; Liu et al., 2013; Shang and Song, 2013; Wardeh et al., 2010; Yang et al., 2013). The microstructure changes in hardened cement-based systems after freeze–thaw cycles have been studied by using a variety of experimental techniques, such as scanning electron microscope (SEM) (Skripkiūnas et al., 2013), X-ray diffraction (XRD) (Skripkiūnas et al., 2013), X-ray computed tomography (X-ray CT) (Liu, 2012), ultrasonic imaging (Molero et al., 2012) and so on. In addition, instead of obtaining the microstructure images of cement-based materials, Li and Weiss et al. (Li et al., 2012) have evaluated the internal damage of mortar during freezing–thawing processes by acoustic emission.

Studies (Powers, 1949; Scherer, 1999; Scherer and Valenza, 2005; Zeng, 2012) on the mechanisms governing frost damage of hydrated cement-based systems for several decades have consistently found that harmful stresses could result from: a) hydraulic pressure due to a 9% expansion in volume accompanying ice formation; b) crystallization pressure, induced by the growth of crystals in pores and their interaction with pore walls; c) the mismatch of thermal effects between ice and solid phases, etc. According to the above frost damage mechanisms, numerous recent papers have attempted to simulate the freezing behavior and to predict the deterioration of cement-based materials (Bazant et al., 1988; Coussy and Monteiro, 2008; Dai et al., 2013; Duan et al., 2013; Hain and Wriggers, 2008; Liu et al., 2011, 2014; Wardeh and Perrin, 2008; Zeng et al., 2010, 2011; Zuber and Marchand, 2000). By linking thermodynamics to poromechanics, the macroscopic deformation during freezing (Zeng et al., 2010, 2011), the influences of pore size distribution and air-void spacing (Coussy and Monteiro, 2008) have been analyzed. By mathematical models, the deterioration of cement-based materials has been investigated in the literature (Bazant et al., 1988; Wardeh and Perrin, 2008; Zuber and Marchand, 2000). By coupling a microstructure of cement-based materials with a fracture model, the micro-internal damage of cement-based materials

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due to frost action has been captured in the literature (Dai et al., 2013; Duan et al., 2013; Hain and Wriggers, 2008; Liu et al., 2011, 2014). Although these microstructure-based models, in which the microstructure of cement-based materials is taken into account, can provide the internal damage assessment, the damage sources are assumed too simplistic where either crystallization pressure (Dai et al., 2013; Liu et al., 2011) or hydraulic pressure (Liu et al., 2014) is playing a dominant role. Few models take the coupled effects of hydraulic pressure and crystallization pressure into account to assess the realistic internal damage due to frost action.

By considering the coupled effects of thermal action, hydraulic pressure and crystallization pressure, this study is going to establish a microstructure-based model to assess the micro-internal frost damage, and to estimate the mechanical property changes of cement-based systems after freezing/thawing. In the following, based on thermodynamic and porous medium considerations, theoretical backgrounds are first presented, including a description of in-pore phase transition, a conceptual explanation for the freezing behavior of porous solids and a discussion about hydraulic pressure model and crystallization pressure model. Then, two parts of work are carried out: (1) by coupling a microstructure model HYMOSTRUC3D with a 3D lattice fracture model, the freezing of water in pores and the response of cement paste to the water freezing are captured. Changes in the microstructure of cement paste, represented by the creation of microcracks, are illustrated. (2) Freezing effects on the mechanical properties of cement paste are investigated, and the simulated Young's modulus and volume deformation is compared to experiments. Moreover, the micro-internal damage of cement paste under different frost mechanisms is discussed.

2. Theoretical background

The thermodynamics of in-pore crystallization can provide us a fundamental understanding for the freezing behavior of porous solids. Therefore, a description of in-pore crystal–liquid phase transition is first presented in this chapter. A conceptual explanation for the freezing behavior of porous solids is followed by the presentation about hydraulic pressure model and crystallization pressure model.

2.1. In-pore crystal–liquid phase transition

The in-pore crystal–liquid phase transition is totally different from that between bulk water and ice. At low temperatures, in order to maintain the equilibrium of chemical potential between ice crystals and liquid water, the Thomson equation (Coussy, 2010) is satisfied with,

$$P_{\mathrm{C}}-P_{\mathrm{atm}}-(P_{\mathrm{L}}-P_{\mathrm{atm}})\overline{V}_{\mathrm{L}}^{0}/\overline{V}_{\mathrm{C}}^{0}=(T_{\mathrm{m}}-T)\Delta S_{\mathrm{m}} \tag{1}$$

where P_{L} and P_{C} are the pressure in the liquid and in the crystal, MPa. P_{atm} is the atmospheric pressure, MPa. T_{m} is the freezing temperature where both liquid and crystal phases are at the atmospheric pressure, K. ΔS_{m} is the melting entropy per unit volume of crystal, MPa/K. $\overline{V}_{\mathrm{L}}^{0}$ and $\overline{V}_{\mathrm{C}}^{0}$ are molar volumes of liquid water and ice.

For a crystal of ice confined in a small pore (see Fig. 1), at its free end, it satisfies with the Laplace equation's (Liu et al., 2011; Scherer, 1999; Scherer and Valenza, 2005),

$$P_{\mathrm{C}}=P_{\mathrm{L}}+\gamma_{\mathrm{CL}}\kappa_{\mathrm{f}} \tag{2}$$

where γ_{CL} is the energy of the crystal/liquid interface, J/m^2. κ_{f} is the curvature of the crystal/liquid interface at the free end of the crystal, m^{-1}. At the non-free sides of the crystal where its curvature κ_{n} is far smaller than that at the free end κ_{f}, the mechanical equilibrium of the crystal and liquid interface is maintained by involving a disjoining pressure P_{D},

$$P_{\mathrm{C}}=P_{\mathrm{L}}+\gamma_{\mathrm{CL}}\kappa_{\mathrm{n}}+P_{\mathrm{D}}. \tag{3}$$

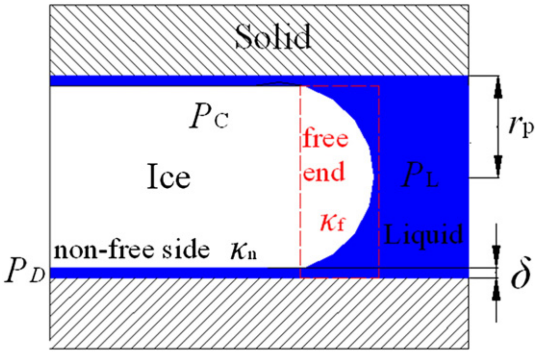

Fig. 1. In-pore phase transition of ice and water. r_{p} — the radius of a pore entry. δ — thickness of the liquid film between the crystal and the pore wall. κ_{f} — curvature of the crystal/liquid interface at the free end of the crystal. κ_{n} — curvature of the crystal/liquid interface at the non-free sides of the crystal. P_{D} — disjoining pressure.
Reproduced after Liu et al. (2011).

Owing to the presence of intermolecular forces, the disjoining pressure P_{D} is introduced by a layer of liquid film between the crystal and the pore wall with a thickness of δ. Combining Eq. (2) with Eq. (3), P_{D} can be obtained,

$$P_D=\gamma_{\mathrm{CL}}(\kappa_{\mathrm{f}}-\kappa_{\mathrm{n}}). \tag{4}$$

On the assumption of $P_{\mathrm{L}}=P_{\mathrm{atm}}$, the well-known Gibbs–Thomson equation is given by (Scherer, 1999),

$$r_{\mathrm{c}}=-\frac{2\gamma_{\mathrm{CL}}\cos\theta}{\Delta S_{\mathrm{m}}(T_{\mathrm{m}}-T)} \tag{5}$$

where r_{c} is the radius of the crystal at its free end at temperature T. θ is the contact angle between the crystal and the pore wall. The Gibbs–Thomson equation provides a scientific basis for calculating the freezing order of pores as temperature decreases. Assuming that the contact angle is 180° and by considering the thickness of the liquid film between the crystal and the pore wall δ, Eq. (5) can be rewritten as:

$$r_{\mathrm{p}}=\frac{2\gamma_{\mathrm{CL}}}{(T_{\mathrm{m}}-T)\Delta S_{\mathrm{m}}}+\delta \tag{6}$$

where r_{p} is the radius of a pore entry. Eq. (6) gives the penetration threshold of ice crystals at temperature T. The lower the temperature is, the smaller the pore will be which ice crystals can grow into, and a more significant surface energy cost is required with regard to the volume to be frozen.

2.2. Freezing behavior of porous solids

For water-saturated porous solids, besides the thermal effect, their freezing behavior could be involved in the coupled effects of expulsion (i.e., the buildup of hydraulic pressure) and cryosuction during temperature decreasing.

As illustrated in Fig. 2a, when ice crystal nucleates at the temperature T_{a} ($T_{\mathrm{a}}<T_{\mathrm{m}}$), a hydraulic pressure P_{L} is built up ($P_{\mathrm{L}}>0$) because a crystal of ice is formed in the biggest pore accompanying a 9% volume expansion of water-to-ice. The unfrozen water is expulsed from the freezing site to unfrozen sites. The pore wall which is in contact with the ice crystal is subjected to stress σ_1 with,

$$\sigma_1=P_{\mathrm{L}}+P_{\mathrm{D}}. \tag{7}$$

The pore wall remaining unfrozen is subjected to stress σ_2 with,

$$\sigma_2=P_{\mathrm{L}}. \tag{8}$$