



# A study of freezing behavior of cementitious materials by poromechanical approach

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## ABSTRACT

The freezing behavior of cementitious materials is investigated in this paper through poromechanical approach after the Biot–Coussy theory. The material is taken as a porous medium saturated with water and subject to freezing. The involved thermodynamic laws are recalled to establish the constitutive equations for the phase change, mass transport and heat transfer processes. As a result, the pore pressure arising from freezing is converted to macroscopic effective stress through homogenization scheme. The established model is applied to predict the macroscopic freezing strain of a saturated cement paste and the theoretical prediction is compared to observed experimental results in (Powers and Helmuth, 1953). The results show that the poromechanical model can reasonably capture the freezing behaviors from pore pressure accumulation, pore pressure relaxation as well as the thermal shrinkage associated with the freezing process.

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## 1. Introduction

Cementitious materials, after hydration reactions, have extremely intricate microstructure, containing C–S–H gels, mineral crystals and pores fully or partially occupied by water. The phase change of confined pore water to ice can build up important pore pressure and cause material deterioration at macroscopic scale. For freezing behavior of cementitious materials, the hydraulic pressure theory (Powers and Helmuth, 1953) was the first systematic modeling dedicated to the mechanical effects of freezing water in pores: it attributed internal pore pressure accumulation to the viscous flow of liquid water driven by around 9% volumetric increase during water freezing. By this theory, the safety air void spacing has been correctly predicted for air-entrainment techniques (Powers, 1949). However, the experiments conducted in (Hodson and McIntosh, 1960; Beaudoin and MacInnis, 1974) showed clearly that porous materials could also be damaged by freezing liquid without volumetric increase during solidification. A micro-ice-lens model has been developed by Setzer (2001) to take into account the water and heat transport during micro-ice-crystal formation. Also based on thermodynamic equilibria of phase change, Penttala derived material freezing deformation by effective freezing stress arising from crystallization pressure (Penttala, 2006). The crystallization pressure of freezing water in pores was detailed by Scherer (1993, 1999). Coussy and Fen-Chong (2005) proposed a pore model, taking into account both viscous water flow and thermodynamic equilibrium between ice and

capillary supercooled water, to describe the pore water cryosuction and stress relaxation during freezing. This model was later developed into a comprehensive thermoporoelastic model for freezing cementitious materials (Coussy, 2005; Coussy et al., 2008).

However, there is not direct experimental verification for this theory. We here try to address the poromechanical framework to the freezing behavior for cementitious materials with specific and defined porosity presented in (Powers and Brownyard, 1947) and compare the predicted results with the experiment ones presented in (Powers and Helmuth, 1953). This paper follows the same thermoporoelastic approach established so far (Coussy, 2005, 2010; Fabbri et al., 2008; Zuber and Marchand, 2004) and investigates particularly the freezing strain of saturated cementitious materials with and without entrained air. To this aim, this paper starts with the thermodynamic descriptions for phase equilibria and phase change for water confined in pores, mechanical constitutive equations are derived from standard poromechanics, and then the mass conservation for water and heat transfer are expressed in terms of pore water pressure and temperature. Using the established model, the freezing strain measurements on cement paste presented in (Powers and Helmuth, 1953) are simulated and concluding remarks are drawn on the basis of the comparison between the simulated and measured strains.

## 2. Poromechanical modeling

### 2.1. Ice-water equilibrium in pores

As a saturated porous material is exposed to freezing, the solidification temperature of pore water depends on the “throat” size

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percolating the pore (Scherer, 1993, 1999). This temperature is often depressed since the potential of water in small pores is lower than that of bulk ice at icing-point, i.e. 0.1 °C at atmospheric pressure. For a certain throat size  $r$ , the potentials of water and ice are in equality only when the temperature reaches some depressed degrees (supercooling)  $\Delta T = T - T_f$ . At this supercooling, it can be assumed that ice occupies all the pores with curvature radius larger than  $r$  and that ice is not to penetrate further to smaller pores unless the supercooling  $\Delta T$  breaks the ice-water equilibrium. This principle can be deduced firstly from Gibbs (chemical) potential equilibrium for bulk water and ice crystal, then the capillary pressure in freezing pore, difference between ice and water pressures  $P_i - P_l$ , can be expressed as:

$$P_i - P_l = -S_f \Delta T + \left( \frac{\rho_i^0}{\rho_l^0} - 1 \right) (P_l - P_m), \quad (1)$$

where  $S_f = S_l^0 - S_i^0$  is the melting entropy of ice,  $\rho_l^0$  and  $\rho_i^0$  are the initial water and ice density at triple point ( $T = 273.16$  K,  $P_l = P_i = P_m$ ) and  $P_m$  is the atmospheric pressure (101.325 KPa).

As the freezing water is not confined in small pores, the liquid pressure, second term in left hand of Eq. (1), can be rather low and be neglected. However, as water and ice are confined in cementitious materials with low permeability or in undrained condition, the liquid pressure due to viscous flow of water in pore spaces may reach the magnitude of 100 MPa (Coussy and Monteiro, 2008). This high pressure can have a significant impact on the liquid water content in such material because of 9% volume increase during phase change from water to ice (Coussy and Monteiro, 2009).

In a freezing pore, the mechanical equilibrium between liquid water and ice crystals can be described by Young-Laplace's law:

$$P_i - P_l = \frac{2\gamma_{il}}{r}, \quad (2)$$

where  $\gamma_{il}$  stands for the interface energy between ice and liquid water ( $\text{J/m}^2$ ). For a drying process of liquid-saturated porous materials like soil and rock, the van Genuchten equation is well accepted to express the relationship between pore capillary pressure and liquid saturation  $S_l$  (van Genuchten, 1980),

$$P_g - P_l = \mathcal{N}^m \left[ S_l^{1/m} - 1 \right]^{1-m}, \quad 0 < m < 1, \quad (3)$$

where  $P_g$  is the gas pressure and  $\mathcal{N}^m$  and  $m$  are adjustable constants related to material pore structure. Again, mechanical equilibrium between vapor and liquid water obeys to Young-Laplace's law,

$$P_g - P_l = \frac{2\gamma_{gl}}{r}, \quad (4)$$

where  $\gamma_{gl}$  stands for the interface energy between gas and liquid water ( $\text{J/m}^2$ ). Combining Eqs. (2)–(4) provides,

$$P_i - P_l = \mathcal{N} \left[ S_l^{1/m} - 1 \right]^{1-m}, \quad 0 < m < 1 \quad (5)$$

with definition  $\mathcal{N} = \gamma_{il}/\gamma_{gl} \times \mathcal{N}^m$ . We can rewrite Eq. (5) as,

$$S_l = \left[ 1 + \left( \frac{P_i - P_l}{\mathcal{N}} \right)^{\frac{1}{1-m}} \right]^{-m}, \quad 0 < m < 1. \quad (6)$$

As water crystallizes in pores, a liquid like layer is assumed to exist at the interface between ice and solid skeleton (pore wall) and this part of liquid phase is reported to be crucial for pore water solidification process (Takamuku et al., 1997). If this unfrozen liquid layer, noted by its pore saturation  $S_r$ , is included into pore liquid phase, the above equation can be extended as,

$$S_l = S_r + (1 - S_r) \left[ 1 + \left( \frac{P_i - P_l}{\mathcal{N}} \right)^{\frac{1}{1-m}} \right]^{-m}, \quad 0 < m < 1. \quad (7)$$

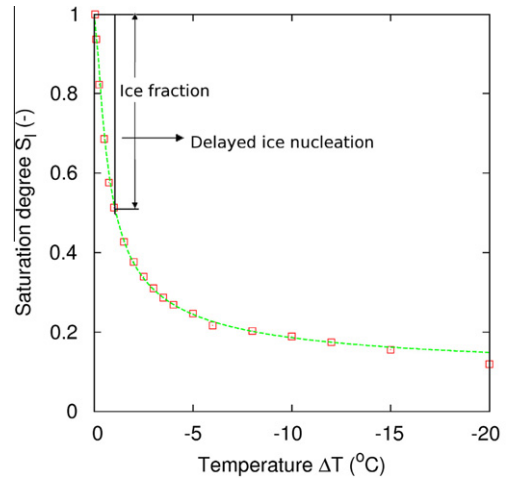


Fig. 1. Liquid saturation degree during freezing vs temperature. The void square is profiled with data from Powers and Brownyard (1947), pp: 955–956, Table 8.6–8.7.  $W/C = 0.62$ , 28 day aged; the dash line is fit by Eq. (7) with  $P_l = P_m$ .

The validity of the above equation can be supported by experimental observation on cement pastes in (Powers and Brownyard, 1947) that there is unfrozen water in pores until  $-78$  °C. The authors estimated furthermore that the maximum amount of unfreezeable water  $w_n = 4V_m$  with  $V_m$  as the quantity of water required to cover the pore internal surface with a single layer of water molecules ( $\text{m}^3/\text{g}$ ) (Powers and Brownyard, 1947). Fig. 1 presents the saturation degrees  $S_l$  in terms of depressed temperature  $\Delta T$  from the experimental data in Powers and Brownyard (1947) and Eq. (7). Note that the liquid saturation can be determined in other ways, such as in (Fen-Chong et al., 2004, 2006; Fen-Chong and Fabbri, 2005; Fabbri et al., 2006, 2009). To use Eq. (7), the following parameters are retained:  $P_l = P_m$ ,  $S_f = 1.2227$  MPa  $\cdot$  K $^{-1}$ ,  $\gamma_{il} = 0.0409$  J  $\cdot$  m $^{-2}$  (Brun et al., 1977),  $S_r = 0.085$ ,  $\mathcal{N} = 0.45$  MPa,  $m = 0.41$ . It can be found that Eq. (7) can fit Powers and Brownyard's results reasonably well. However, in most cases ice forms by heterogeneous nucleation in porous medium at some depressed temperature rather than immediately at triple point due to energy barrier (Scherer, 1993; Shaw et al., 2005). As schematically shown in Fig. 1, when ice nucleation is delayed to  $-1$  °C, a large amount of ice is to form instantaneously at this delayed nucleation temperature and may create high pressure. This nucleation delay is to be discussed further in Section 3.

## 2.2. Freezing strain and stress

Consider a deformable porous medium with total porosity of  $\phi$  initially saturated with water. The porosity  $\phi$  excludes the volume of entrapped and/or entrained voids. Under freezing the pores are progressively invaded by ice nucleation and occupied by two phases: the wetting liquid phase (with subscript  $l$ ) and the non-wetting ice (with subscript  $i$ ). The relative volumes of the two phases satisfy:

$$\phi = \phi_l + \phi_i, \quad S_l + S_i = 1; \quad (8a)$$

$$\phi_{J=li} = \phi_0 S_J + \phi_J, \quad (8b)$$

where  $\phi_0$ ,  $\phi$  stand for initial and current porosities and  $\phi_J$  for partial porosity changes due to deformation of the porous volume occupied by the phase  $J$ . According to the standard unsaturated poroelasticity developed by Coussy (2004, 2005, 2010), the linearized form of constitutive equations for an isotropic porous medium under freezing writes,

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