THERMO-PORO-ELASTIC ANALYSIS OF FREEZING BEHAVIOR OF POROUS MATERIALS SATURATED WITH SALINE SOLUTION

Qiang Zeng*,** a), Kefei Li*, Teddy Fen-Chong** & Patrick Dangla**
* *Department of civil engineering, Tsinghua University, Beijing, 100084, China*
** *Université Paris-Est, Laboratoire Navier (UMR 8205 ENPC / IFSTTAR / CNRS) 2 allé Kepler Champs-sur-Marne, 77420, France*

Summary Thermo-poro-elastic behavior of porous materials saturated with saline solution subjected to freezing is studied in the present work. The pore water mixed with salts can lower the capillary pressure and retard the ice penetration into thinner pores according to the thermodynamic equilibrium. Two additional terms of strain induced by adding salts into pore liquid are explicitly addressed. The extra strain $|\epsilon_a|$ due to water activity change when mixed with salts increases with the augmentation of salt concentration c_0, the strain ϵ_c induced by density change of liquid phase when solution is concentrated with freezing, however, is negligible small.

INTRDUCTION

When porous materials subjected to freezing, the induced large internal pressure as water crystallizes in pores may cause severe deteriorations. From the comprehensive poromechanical work [1, 2], it is now clear that the deformation can be attributed to the density change, interfacial energy, fusion entropy change and thermal dilation discrepancy between pore fluid and solid phase when porous materials initially saturated with pure water are subjected to freezing . It is also clear that, for the bulk solution, the lowering of the activity of water when mixed with solutes retards the ice formation. However, when the salt solution is confined in porous materials, the freezing process and the induced deformation are still debatable. Following the thermo-poro-elasticity framework, we thus aim to evaluate the contribution of salt solutions to the freezing process and the volumetric strains of porous materials under the undrained freezing. Owing to its extensive use, and its well evaluated physico-chemical properties, the NaCl solution is selected as saturating liquid.

POROMECHANICAL ANALYSIS

During cooling, ice first forms in big pores, then penetrates into smaller pores depending on the percolated "throat" size under thermodynamic equilibrium [3]. From the Gibbs (chemical) potential equilibrium between bulk pore solution and ice crystals, the capillary pressure, which equates to the difference between ice and water pressures $P_{cap} = P_c - P_l$, can be expressed as:

$$P_{cap} = P_{\Delta\rho} + P_{\mathcal{S}} + P_a \tag{1}$$

The term $P_{\Delta\rho} = (\rho_c/\rho_l - 1)(P_l - P_0)$, represents the effect of liquid pressure, with ρ_c and ρ_w denoting the density of ice crystals and liquid phase respectively. Because $\rho_c < \rho_l$, ice tends to melt or water tends to keep the liquid state under the high liquid pressure [4]. The term $P_{\mathcal{S}} = \rho_c[\mathcal{S}_f(T_0 - T) + \mathsf{C}_f((T - T_0) + T\ln(T_0/T))]$, represents the effect of fusion energy, where $\mathcal{S}_f$ is the melting entropy of ice at reference state, C_f is the heat capacity difference between the liquid phase and ice crystals at current temperature T. The term $P_a = RT\ln a_w/\mathsf{V}_c$, represents the effect of salt, with R the ideal gas constant, V_c the molar volume of ice, and $\ln a_w$ the water activity. This term can be evaluated by Lin and Lee's model [5]. Owing to the fact that the water activity represents the deviation of water from ideal behavior, this contribution thus increases with salt concentration. For the same reason, ice formation is retarded in pores, see Figure 1(a). Under the free surface loading $\boldsymbol{\sigma} = \mathbf{0}$, the strain tensor $\boldsymbol{\epsilon}$ of a porous material can be given by [1, 2],

$$\boldsymbol{\epsilon} = \sum_\alpha \mathbb{C}^{-1} : b_\alpha P_\alpha \mathbf{I} + \alpha_s(T - T_0)\mathbf{I} \tag{2}$$

where $\mathbb{C}$ is the fourth order stiffness tensor, b_α is the Biot's coefficient of phase α, α_s is the thermal expansion coefficient of solid matrix, $\mathbf{I}$ is the unit second order tensor. Under the undrained freezing, the mass conservation of total solution currently contained in the porous materials allows us writing the equation:

$$m_l = \rho_l^0\phi_0 + \rho_l^0(\varphi_{\Delta\rho} + \varphi_v + \varphi_s) \tag{3}$$

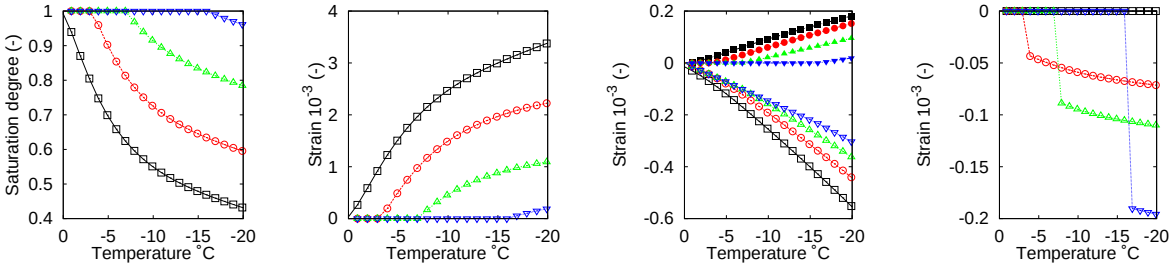
where m_l is the total mass of pore solution in a representative volume element, ϕ is the porosity under Lagrangian framework. The superscript 0 denotes the initial state. The term $\varphi_{\Delta\rho} = (\rho_c^0/\rho_l^0 - 1)\phi_0(1 - S_l)$, captures the pore volume change by density difference between solution and ice as ice forms, where S_l is the liquid saturation degree. The term $\varphi_v = b\epsilon + \sum_\alpha [P_\alpha/M_\alpha + 3(\phi_0 S_\alpha\alpha_\alpha + \alpha_{\phi\alpha})](T - T_0)$, represents the pore volume change due

a) Corresponding author. E-mail: ceng-q08@mails.tsinghua.edu.cn.

to the thermo-mechanical loading, where M_α denotes the pressure coefficient related to the Biot's modulus N_α and saturation degree S_α, and $\alpha_{\phi\alpha}$ denotes the the coefficient related to the thermal dilation of the pore volume occupied by phase α [1]. The terms $\varphi_{\Delta\rho}$ and φ_v are identified as the constitutive expressions of the deformation sources for unsaturated case [2]. The term $\varphi_s = 1/\rho_l^0 \cdot [(\mathsf{M}_s - \mathsf{M}_w/\mathsf{V}_w \cdot \mathsf{V}_\phi) \cdot c_0 S_c/S_l]$, captures the extra pore volume change when pore water is initially mixed with salt at c_0, where M and V denote the molar mass and molar volume, and the subscript s and w represent the NaCl and water respectively. For undrained freezing without salt crystallization, $m_l = \rho_l^0 \phi_0$, one has, $\varphi_{\Delta\rho} + \varphi_v + \varphi_s = 0$. Combining this relation and eqs(1) and (2), one obtains the volumetric strain of porous materials ϵ as:

$$\epsilon = \epsilon_{\Delta\rho} + \epsilon_{th} + \epsilon_{\mathcal{S}} + \epsilon_a + \epsilon_c \tag{4}$$

The first term, $\epsilon_{\Delta\rho} = \phi_0 bM/K_u \cdot S_c(1 - \rho_c^0/\rho_l^0)$, is the volumetric freezing strain due to density differences between ice and liquid solution, where $1/M = 1/M_l + 1/M_c$ and $K_u = K + b^2 M$ with K the bulk modulus of skeleton. $\epsilon_{\Delta\rho}$ decreases with the augmentation of initial salt concentration c_0 due to the lowered ice saturation degree S_c, see Figure 1(b). The second term, $\epsilon_{th} = 3[\alpha_s + bM/K_u \cdot (\phi_0 S_c \alpha_c + \phi_0 S_l \alpha_l + \alpha_{\phi,l} + \alpha_{\phi,c} - \alpha_s)](T - T_0)$, gives the hydrothermal strain induced by the mismatch of thermal expansion coefficients. The third term, $\epsilon_{\mathsf{S}} = [M/K_u \cdot (b_c/M_l - b_l/M_c)]P_{\mathcal{S}}$, indicates the contribution of energy change as water crystallizes, which is also known as the effect of micro-cryo-suction [2]. This term also accounts for the freezing strain when using benzene as saturating liquid [1]. Both $|\epsilon_{th}|$ (the absolute value) and ϵ_{S} decrease with c_0 due to, again, the decreases of S_c, see Figure 1(c). The fourth term, $\epsilon_a = bM(bb_c M_c + K)/(K_u K M_c) \cdot P_a$, addresses the contribution of the water activity when mixed with solutes. Lowering water activity leads to the increase of $|\epsilon_a|$ with c_0, see Figure 1(d). The last term, $\epsilon_c = -\phi_0 bM/(K_u \rho_l^0) \cdot (\mathsf{M}_s - \mathsf{M}_w/\mathsf{V}_w \cdot \mathsf{V}_\phi) c_0 S_c$, presentes the contribution of liquid density variation when saline solution is concentrated as freezing occurs. The increase of $(\mathsf{M}_s - \mathsf{M}_w/\mathsf{V}_w \cdot \mathsf{V}_\phi) S_c$ with c_0 leads to the augmentation of ϵ_c, which depicts the reduction of the density difference between water and NaCl. However, the values are so small, i.e. $|\epsilon_c| < 10^{-6}$ for all the calculated cases, that can be neglected.



(a) (b) (c) (d)

Figure 1. (a) Variation of saturation degree with temperature; (b) the volumetric strain $\epsilon_{\Delta\rho}$ induced by density difference as ice forms, (c) the hydrothermal strian ϵ_{th} (open symbols) and the micro-cryo-suction strian ϵ_{S} (closed symbols); and (d) the extra strian ϵ_a induced by water activity change when mixed with salts. □: $c_0 = 0$ mol/l, ◯: $c_0 = 1$ mol/l, △: $c_0 = 2$ mol/l, ▽: $c_0 = 4$ mol/l. The required parameters for calculation can be found in [4].

CONCLUSIONS

The present work attempts to address the undrained freezing behaviors of porous materials saturated with NaCl solution by thermo-poro-elasticity. For a given porous material, it can be concluded that: the volumetric strain $\epsilon_{\Delta\rho}$ induced by density difference when phase freezing occurs, the hydrothermal strain $|\epsilon_{th}|$ and the micro-cryo-suction strain ϵ_{S} decrease with the augmentation of initial salt solution c_0; the extra strain $|\epsilon_a|$ induced by water activity change when mixed with salts, however, increases with c_0; the strain ϵ_c induced by density change when solution is concentrated with freezing is negligible small.

References

[1] Coussy O.: Poromechanics of Freezing Materials. *J. Mecha Phys Solids* **53**:1689–1718, 2005.

[2] Coussy O., Monteriro P.J.M.: Poroelastic Model for Concrete Exposed to Freezing Temperature. *Cem Concr Res* **38**:40–48, 2008.

[3] Scherer G.W.: Crystallization in Pores. *Cem Concr Res* **29**:1347–1358, 1999.

[4] Zeng Q., Fen-Chong T., Dangla P., Kefei Li.: A Study of Freezing Behaviour of Cementitious Materials by Poromechanical Approach. *Int J. Solids Struct* **48**:3267–3273, 2011.

[5] Lin C.L., Lee L.S.: Estimations of Activity Coefficients of Constituent Ions in Aqueous Electrolyte Solutions with the Two-ionic-parameter Approach. *Fluid Phase Equilibria* **237**:1–8, 2005.