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.

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 thermoporo mechanical approach established so far (Coussy, 2005, 2010; Fabbrì 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
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:

\[
P_i - P_l = -S_l \Delta T + \left( \frac{\rho_l^0}{\rho_i^0} - 1 \right) (P_i - P_m),
\]

where \( S_l = S_l^0 - S_l^i \) 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, \( P_i = P_m = P_m \)) 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:

\[
P_l - P_i = \frac{2 \gamma_{li}}{r},
\]

where \( \gamma_{li} \) stands for the interface energy between ice and liquid water (J/m²). 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),

\[
P_l - P_i = N^c \left[ S_l^{1-m} - 1 \right]^{1-m}, \quad 0 < m < 1,
\]

where \( P_l \) is the gas pressure and \( N^c \) and \( m \) are adjustable constants related to material pore structure. Again, mechanical equilibrium between vapor and liquid water obeys to Young-Laplace’s law,

\[
P_g - P_l = \frac{2 \gamma_{lg}}{r},
\]

where \( \gamma_{lg} \) stands for the interface energy between gas and liquid water (J/m²). Combining Eqs. (2)-(4) provides,

\[
P_l - P_i = N^c \left[ S_l^{1-m} - 1 \right]^{1-m}, \quad 0 < m < 1
\]

with definition \( N = \gamma_{il} / \gamma_{li} \times N^c \). We can rewrite Eq. (5) as,

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

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 \( S_J \), is included into pore liquid phase, the above equation can be extended as,

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

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 unfreezable water \( w_0 = 4V_m \) with \( V_m \) as the quantity of water required to cover the pore internal surface with a single layer of water molecules (m²/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: \( P_l = P_m \), \( S_l = 1.2227 \) MPa K⁻¹, \( \gamma_{il} = 0.0409 \) J m⁻² (Brun et al., 1977), \( S_l = 0.085 \), \( N = 0.45 \) 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:

\[
\phi = \phi_l + \phi_i, \quad S_l + S_i = 1:
\]

\[
\phi_{l-i} = \phi_l S_l + \phi_i:
\]

where \( \phi_{l-i} \) stand for initial and current porosities and \( \phi_{l} \) 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,
\[ \begin{align*}
\sigma &= \left( K - \frac{2}{3}G \right) \epsilon I + 2Ge - [b(P_l + bP_i) + \alpha_s(T - T_f)] I, \\
\varphi_i &= b_i \epsilon + \frac{P_l}{N_{l}} + \frac{P_i}{N_{i}} - \alpha_{\varepsilon}(T - T_f), \\
\varphi_s &= b_s \epsilon + \frac{P_l}{N_{l}} + \frac{P_i}{N_{i}} - \alpha_s(T - T_f).
\end{align*} \] (9a-c)

Here \( \sigma, \epsilon, I \) are stress, strain and unit tensors of second order, \( \epsilon = \text{tr}(\epsilon) \) is the trace of strain tensor, \( b_i, N_{l}, N_{i} \) are respectively the generalized Biot coefficients and Biot coupling coefficients, \( K, G \) are bulk and shear moduli of porous medium, and \( \alpha_{\varepsilon}, \alpha_s \) denote respectively the thermal dilatation (volumetric) coefficient of skeleton and coupling dilatation coefficients. The bulk moduli \( K, G \) can be evaluated in terms of the bulk modulus of solid skeleton \( k_s \), its shear modulus \( G_s \), and initial porosity \( \varphi_0 \) by adopting the Mori–Tanaka homogenization scheme (Mori and Tanaka, 1973), see Appendix A.

Consider now a stress-free freezing case, i.e. the applied external stress is null. The volumetric strain can be evaluated from Eq. (9a) as,

\[ \epsilon = \frac{1}{K} (b(P_l + bP_i) + \alpha_s(T - T_f)). \] (10)

where strains from two origins are identified: mechanical strain from pore effective pressure \( \varphi_i = b_i \epsilon + \frac{P_l}{N_{l}} + \frac{P_i}{N_{i}} \) and thermal strain from temperature change \( \alpha_s(T - T_f) \). If the strain is measured only in one direction, e.g. along \( x \) axis, the measured linearized strain \( \epsilon_{xx} \) is,

\[ \epsilon_{xx} = \frac{1}{3} \epsilon = \frac{1}{3K} [(b(P_l + bP_i) + \alpha_s(T - T_f)]. \] (11)

If, furthermore, the temperature profile \( T(x) \) and pore pressure profile \( \varphi_i(x) \) are not uniform in the measured domain \( x \in [0, L] \), the average strain over \( L \) can be evaluated as:

\[ \bar{\epsilon}_{xx} = \frac{AL}{L} \int_{0}^{L} \epsilon_{xx} \, dx. \] (12)

More deepened analysis about the pore pressure \( \varphi_i \) contribution to cryo-deformation can be found in (Coussy, 2005; Coussy et al., 2008), and the viscous flow pressure is identified as an important contribution to cryo-swellling of freezing porous medium. That confirms the mechanism of air entainment to increase the freezing resistance of porous medium since the air voids provide shorter distance for viscous flow leading to lower flow pressure. Freezing strain analysis on cement pastes with and without air entrainment cases is presented in Section 3.2.

2.3. Mass and heat conservations

As a saturated porous medium is subject to freezing, the volume change by almost 9% due to water–ice phase change in pores creates viscous water flow from nucleation sites to unfrezen pores while the lower potential of ice than water makes liquid water flow to nucleation sites. The liquid water flux by both driving sources can be described in Darcy’s law,

\[ w_l = -P_i \frac{D_{li}}{\eta_l} \nabla P_i, \] (13)

where \( D_{li}, D_i \) are respectively the intrinsic and relative permeabilities of material, and \( \eta_l \) the viscosity of liquid. \( D_{li} \) depends on the pore structure while \( D_i \) is highly dependent on the liquid saturation degree. For cementitious materials, a semi-empirical power law is usually assumed for relative permeability, i.e. \( D_i = S_{li}^{m} \). Powers adopted \( m = 3.6 \) for cement pastes (Powers, 1949). The water viscosity \( \eta_l \) is temperature dependent, and the relevant literature provides the following expression, \( \eta_l = 7.934 \times 10^{-5} \exp(2608.075/T) \text{Pa.s} \) (Abdulagatov and Azizov, 2006).

The total water mass includes the solid part \( m_s \) and liquid part \( m_l \), i.e. \( m_{hi,0} = m_s + m_l \). Note that the ice crystals are often assumed to be not transportable (Setzer, 2001). Hence, the mass change of water is solely due to liquid water transport, flow and/or ice nucleation. Accordingly, the mass conservation for total water \( m_{hi,0} \) can be written as,

\[ \frac{\partial m_{hi,0}}{\partial t} = -\nabla \cdot w_l. \] (14)

Taking into account the porosity definition in Eq. (8a), the total water mass in freezing porous medium writes,

\[ m_{hi,0} = \rho_l(\varphi_i S_l + \varphi_s) + \rho_s(\varphi_0 S_l + \varphi_s). \] (15)

Substitution of Eq. (13), (15) and Eq. (B.2) into Eq. (14) provides the water mass conservation equation in terms of liquid water pressure \( P_i \) and temperature \( T \):

\[ -\nabla \frac{D_i}{\eta_l} \rho_l \nabla P_i = \frac{\partial}{\partial t} \left\{ \rho_l \left[ \frac{1}{K} \left[ \varphi_i S_l + \frac{1}{N_l} \right] \right] \right\} + \rho_s \frac{d}{dr} \left\{ \left( 1 - \frac{\rho_s}{\rho_l} \right) \varphi_i S_l - S_l \Gamma(T(T_f - T) - \varphi_0 \tilde{W}(T(T_f - T)) \right), \] (16)

where \( D_i = D_{li}D_l^2 \) is the effective permeability of porous material, the item \( 1/K \) is the liquid storage coefficient of a porous medium originally defined in soil and rock mechanics (Detournay and Cheng, 1994). The item \( \Gamma(T) \) accounts for the coefficient of volume change of ice by liquid pressure, see also (Boukpeti, 2008), and \( \tilde{W}(T) \) stands for the pore volume change by thermal effects. The detailed mathematical derivation given in Appendix B.

The heat conservation for a freezing porous medium states that the change rate of material entropy is equal to the addition of convection heat storage by liquid water flow and conduction heat storage, that is,

\[ \frac{\partial S}{\partial t} = -\nabla \cdot w_l \tilde{Q} - \frac{1}{T} \nabla \cdot \tilde{Q}, \] (17)

where the conduction heat flux \( \tilde{Q} \) can be depicted by Fourier’s law, \( \tilde{Q} = -\lambda \nabla T \) with \( \lambda \) as bulk heat conductivity of material. Note that in Eq. (17), the fluid dissipation has not been considered due to its negligible contribution since the liquid pressure \( P_i \) is found to be at low level for cases in Section 3.2, see Appendix C for details. The total entropy \( S \) is composed of the entropy of solid skeleton \( S_{nk} \), entropy of pore liquid water and ice \( \sum_{j=-1}^{0} S_{j} m_j \) and the fusion heat of ice (if formed) \( S_f m_f \). After the mathematical derivation given in Appendix C, the entropy rate can be evaluated as,

\[ \frac{1}{T} \left[ \left( \sigma^0_{ijkl} + \phi_0 \phi_l \sigma^0_{ipq} C_{ipq}^0 - \phi_0 S_l \rho_l \sigma^0_{ipq} C_{ipq}^0 (\tilde{S}_{l}) \right) \right] \frac{\partial T}{\partial t} + \phi_0 \left[ \tilde{S}_{l} \left( \frac{\sigma_{li}}{\rho_l} (T(T_f - T)) - 1 \right) \right] - C_f \ln \left( T(T_f) + \left( \frac{S_l}{C_l} \right) \left( P_l - P_m \right) \right) \frac{\partial S_l}{\partial t} \frac{\partial T}{\partial t} - \frac{1}{T} \nabla \cdot \lambda \nabla T, \] (18)

where \( S_{j} C_{j} \) are the entropy and heat capacity differences of water and ice, \( C_{ipq} = C^0_{ipq} - C_{ipq} \). The bulk heat conductivity \( \lambda \) takes into account the contribution of all phases in freezing porous medium, and if the heat capacities are constant, \( C = C^0 \) the equation reduces to

\[ \lambda = \lambda_{s} + \left( 1 - \frac{\phi_0}{\lambda_{s}} \right) \frac{\phi_0}{\lambda_{s}} \left( S_{l} \lambda_{s} + S_{f} \lambda_{f} - \lambda_{i} \right), \] (19)

with \( \lambda_{s}, \lambda_{f} \) standing for heat conductivities of solid skeleton, pore liquid phase and pore ice phase respectively.
3. Numerical analysis

3.1. Numerical solution of thermoporoelastic problem

For a saturated deformable porous medium, the freezing behaviors can be described completely by the above equations. The mechanical constitutive relation is expressed by Eq. (9a) and the freezing case by Eq. (12) with \( \varepsilon, P, P_s, T \) as basic variables; the water mass conservation is expressed in Eq. (16) with \( S, P_s, T \) as basic variables; the heat conservation is depicted by Eq. (18) with \( S, T \) as basic variables. The Eq. (7) gives the fundamental relation between saturation degree \( S \) and capillary pressure \( P - P_s \), which is correlated with the basic variables \( P, T \) by Eq. (1). Thus, totally five equations are available with five variables: \( \varepsilon, P, P_s, S, T \), and the equations are mathematically closed.

For the numerical solution, an algorithm by finite volume method is developed for these coupled partial differential equations. The involved equations, together with the relevant initial and boundary conditions, are discretized both in spatial domain and temporal domain.

3.2. Case study: saturated cement pastes with and without air entrainment

The established model is applied to calculate the freezing strains of saturated cement pastes published in Powers and Helmuth (1953) and compare the model prediction with the experimental data. Since the pore structure of samples were not available in (Powers and Helmuth, 1953), the pore structure data with a similar mixing (W/C = 0.62) from the same author is retained in our analysis (Powers and Brownyard, 1947). Using Eq. (7), the relation between pore liquid saturation and temperature is calculated and presented in Fig. 1.

Freezing strains are calculated for samples with and without entrained air for one dimensional case. The parameters retained for the thermoporoelastic model are recapitulated in Table 1. The initial conditions and boundary conditions for both cases are listed for the thermoporoelastic model are recapitulated in Table 1. The length retained for air-entrained sample is the half distance of two adjacent air voids measured by the authors, i.e., \( L = 0.016 \) in \( \approx 0.4 \) mm while for the sample without air entrainment the length is taken as the half of sample length, i.e. \( L = 0.125 \) in \( \approx 3.2 \) mm. The observed and predicted freezing strains are presented in Fig. 2.

It can be seen that the numerical results reproduce reasonably well the experimental observations in (Powers and Helmuth, 1953). As the cooling process starts from about 4 °C, material begins to shrink for both samples due to thermal contraction, followed by an expansion peak at \( t = 12 \) min (\( \sim -1 \) °C) due to relatively important quantity of ice formation. To simulate this expansion peak, the nucleation point is delayed to \(-1 \) °C in Fig. 1, hence the numerical simulation also gives the expansion peak at this moment. This reflects in fact the energy barrier to overcome for liquid water in pores to nucleate. After this point, the pore pressure is simultaneously controlled by viscous pressure by liquid flow and crystallization pressure by ice formation, of which the relative importance depends on the ice formation rate and pore structure.

For air-entrained case, this expansion behavior in Fig. 2 ends at \( t = 15 \) min. One can assume that both effects are present during this period. As cooling suddenly stops at \( t = 30 \) min, the contraction of material does not stop simultaneously but presents a transitional contraction. That is an obvious evidence for pore pressure relaxation by viscous flow. The pore pressure relaxation time lasts about 8 min, which can be estimated by viscous flow: \( t = \frac{\eta L^2}{4D_l} \approx 420 \) s with \( \eta \approx 1.63 \times 10^{-10} \) Pa - s, \( L \approx 16 \times 10^{-6} \) m, \( D_l \approx 3.11 \times 10^{-26} \) m². \( \Delta P \approx 5 \times 10^6 \) Pa. As cooling restarts from \( t = 52 \) min, the numerical prediction gives firstly a small expansion followed by a contraction. In Fig. 3 are illustrated separately the thermal shrinkage and pore pressure-induced strain, showing that the thermal contraction is relatively small compared to the contribution of pore pressure. For air-entrained sample, the pore pressure is the main contraction source, and this negative pore pressure arises from the capillary equilibrium of liquid water and ice crystals as entrained air voids provide an atmospheric pressure to ice.

For non-air-entrained case, the sample undergoes significant expansion from \( t = 12 \) min to \( t = 30 \) min, due to viscous flow pressure as well as pore crystallization pressure. As the cooling stopped at \( t = 30 \) min and the temperature was kept constant for 22 min, the sample was observed to expands slightly, probably due to the diffusion process of gel water to ice nucleation site according to (Powers and Helmuth, 1953). Our model predicts a continuous expansion from \( t = 10 \) min to \( t = 30 \) min, a slight contraction during the cooling platform and an expansion afterwards, see Fig. 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
<th>Significance</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \phi )</td>
<td>0.45</td>
<td>–</td>
<td>Porosity</td>
<td>(Powers and Helmuth, 1953)</td>
</tr>
<tr>
<td>( \rho_l )</td>
<td>999</td>
<td>kg/m³</td>
<td>Water density</td>
<td>(Speedy, 1987)</td>
</tr>
<tr>
<td>( \rho_i )</td>
<td>917</td>
<td>kg/m³</td>
<td>Ice density</td>
<td>(Speedy, 1987)</td>
</tr>
<tr>
<td>( k_l )</td>
<td>1.75</td>
<td>GPa</td>
<td>Water compressibility</td>
<td>(Speedy and Angell, 1978)</td>
</tr>
<tr>
<td>( k_i )</td>
<td>8.65</td>
<td>GPa</td>
<td>Ice compressibility</td>
<td>(Nagornov and Chizhov, 1990)</td>
</tr>
<tr>
<td>( C_{P, l} )</td>
<td>2110</td>
<td>J/(kgK)</td>
<td>Heat capacity of water</td>
<td>(Lide and Frederikse, 2003-2004)</td>
</tr>
<tr>
<td>( C_{P, i} )</td>
<td>4218</td>
<td>J/(kgK)</td>
<td>Heat capacity of ice</td>
<td>(Lide and Frederikse, 2003-2004)</td>
</tr>
<tr>
<td>( a_l )</td>
<td>(-298 \times 10^{-6})</td>
<td>K⁻¹</td>
<td>Water dilatation coefficient</td>
<td>(Speedy, 1987)</td>
</tr>
<tr>
<td>( a_i )</td>
<td>(154 \times 10^{-6})</td>
<td>K⁻¹</td>
<td>Ice dilatation coefficient</td>
<td>(Nagornov and Chizhov, 1990)</td>
</tr>
<tr>
<td>( D_l )</td>
<td>(30 \times 10^{-15})</td>
<td>m²</td>
<td>Skeleton dilatation coefficient</td>
<td>(Powers and Brownyard, 1947)</td>
</tr>
<tr>
<td>( k_s )</td>
<td>31.8</td>
<td>GPa</td>
<td>Water permeability</td>
<td>(Powers and Helmuth, 1953)</td>
</tr>
<tr>
<td>( g_s )</td>
<td>19.1</td>
<td>GPa</td>
<td>Bulk modulus of skeleton</td>
<td>(Ulm et al., 2004)</td>
</tr>
<tr>
<td>( s )</td>
<td>154</td>
<td>GPa</td>
<td>Shear modulus of skeleton</td>
<td>(Ulm et al., 2004)</td>
</tr>
</tbody>
</table>
According to our modeling, the continuing ice formation between $t = 12$ min to $t = 30$ min supports the expansion, during the cooling platform the pore pressure relaxes very slowly due to much longer distance between (natural) air voids and lower permeability of partially ice filled pores ($\approx 10^{-24} \text{m}^2$). As the cooling resumes from $t = 52$ min, the ice formation compensates both the contraction by pressure relaxation and the thermal shrinkage.

### 3.3. Further discussion

Form the above case study, it is showed that the freezing strain is largely controlled by the pore pressure accumulated during the freezing, which is intimately related to one intrinsic property of porous medium: pore structure. Pore structure or pore size distribution, intrinsic property of porous material, is a basis for ice or water content determination under freezing. According to the Gibbs–Thomson equation, the equilibrium temperature or depression of liquid water can be frozen under small depressed temperature, the freezing expansion peak, consequently, is significant even for cement pastes with air entrainment. If, on the contrary, the pore distribution is more centered on small pores, the freezing expansion peak is to be delayed to larger supercooling degrees, the freezing peak will even not appear since the thermal contraction can dominate the pore pressure effect. Pore structure determines another fundamental property of porous medium: permeability. Pore structure with high percolation degree gives large permeability. The pore pressure relaxation directly depends on the permeability of porous medium to liquid water. Larger permeability gives shorter relaxation time, thus more freezable water can be transported to nucleation sites, giving more important ice formation and usually more detrimental to material durability.

### 4. Concluding remarks

1. The freezing behavior of porous medium saturated with water is described in this paper through a thermoporoelastic approach. The established model includes mass conservations of water (pure liquid water and ice), heat conservation of saturated porous medium as well as the fundamental relation between liquid saturation and pore capillary pressure. In fact, it is this relationship that globalizes the detailed progressive freezing process of liquid in a specific pore structure of cementitious materials as shown in Gibbs–Thomson equation. With liquid pressure, temperature as independent variables, the involved coupled partial differential equations are solved by finite volume method and the numerical model is available for further study on the freezing behavior in saturated porous materials.

2. By the numerical application to cement pastes in freezing, the numerical results reasonably agree with the freezing strains measured in experiments. The freezing expansion is captured by the model through pore hydraulic pressure and ice formation pressure. The hydraulic pressure has an important relaxation property related to viscous flow during freezing and ice formation, which is well verified by the experiment and captured by the numerical results for both samples with/without air entrainment.

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Appendix A. Moduli and parameters in Section 2.2

For a porous materials with assumption that pores are statistically isotropic and embedded in solid phase, the effective bulk modulus and shear modulus can be estimated by Mori–Tanaka homogenization scheme (Mori and Tanaka, 1973) (equal to Hashin–Strikman upper bound, cf. Hashin and Shtrikman (1962), Hashin (1983):

\[
K = \frac{4g_k(1-\phi_0)}{3\phi_k} + 4g \quad \text{(A.1a)}
\]

\[
G = \frac{g(8g_k + 9k_k)(1-\phi_0)}{5\phi_k(4g_k + 3k_k) + (8g_k + 9k_k)(1-\phi_0)} \quad \text{(A.1b)}
\]

In case of isodeformation hypothesis, the Biot’s tangent modulus \(b_i\) generalized Biot coupling modulus \(1/N_f\) and the thermal coupling dilatation coefficient \(\alpha_{jd}\) of the partial pore volume occupied by phase \(j\) observe Coussy (2005, 2010):

\[
b = b_i + b_t = 1 - \frac{K}{K_k}, \quad b_{i,j} = b_S; \quad \text{(A.2a)}
\]

\[
\frac{1}{N_f} + \frac{1}{N_i} = b_i (b_t - \phi_S S_j); \quad \text{(A.2b)}
\]

\[
\alpha_{jd} = \alpha_j (b_t - \phi_S S_j), \quad \text{(A.2c)}
\]

Appendix B. Derivation of mass conservation equations

The water mass conservation equation, Eq. (16), is derived firstly by recalling Eqs. (13)–(15). Substitution of Eqs. (13), (15) into Eq. (14) gives,

\[
\frac{\partial}{\partial t} (\rho_i (\phi_S S_i + \varphi_i) + \rho_i (\phi_S S_i + \varphi_i)) = \nabla \cdot \left( \rho_i \frac{D_i D_P}{\eta_i} \nabla P_i \right). \quad \text{(B.1)}
\]

The density \(\rho_t\) and entropy \(S_j\) for unfrozen water and ice crystals are functions of pressure \(P_j\) and temperature \(T\) (Coussy, 2005; Fabbrini et al., 2008), given by:

\[
\rho_{i,j} = \rho_i^0 \left[ 1 - z_j (T - T_j) + \frac{1}{k_j} (P_j - P_m) \right] \quad \text{(B.2a)}
\]

\[
S_{i,j} = S_j^0 + C_j^0 \ln \left( \frac{T}{T_j} - \frac{1}{k_j} \frac{P_j - P_m}{P_t} \right) \quad \text{(B.2b)}
\]

with \(\rho_i^0, S_i^0\) for density and entropy in reference state \(T = T_j, C_j^0, k_j, z_j\) for heat capacity, compressibility modulus and thermal dilatation coefficient of phase \(j\) respectively. Substitution of density defined in Eq. (B.2a), deformed porosities in Eqs. (9b),(9c) and volume strain in Eq. (10) into Eq. (15) yields:

\[
\rho_i (\phi_S S_i + \varphi_i) + \rho_i (\phi_S S_i + \varphi_i) = \rho_i^0 \phi_S S_i + \rho_i^0 \phi_S S_i + \rho_i^0 \left( \frac{\phi_S S_i}{k_i} + \frac{1}{k_i} \frac{b_i b_t}{K_k} + \frac{1}{N_i} \right) \rho_t + \rho_i^0 \left( \frac{\phi_S S_i}{k_i} + \frac{1}{k_i} \frac{b_i b_t}{K_k} + \frac{1}{N_i} \right) \rho_t + \rho_i^0 \left[ (\phi_S S_i - b_i \varphi_i) + (\phi_S S_i - b_i \varphi_i) \right] (T - T_j)
\]

\[
- \rho_i^0 \left( \frac{\phi_S S_i}{k_i} + \frac{1}{k_i} \frac{b_i b_t}{K_k} + \frac{1}{N_i} \right) S_j (T - T_j). \quad \text{(B.3)}
\]

Note that in deriving this equation some first order approximations are adopted to simplify the expression: \(\rho_t^0 \approx \rho_i^0\) and \(1 - \rho_i^0/\rho_t^0 \approx 0\). Substitution of Eq. (B.3) into Eq. (B.1) gives finally the Eq. (16),

\[
- \nabla \cdot D_i \frac{\rho_i}{\eta_i} \nabla P_i + \frac{\partial}{\partial t} \left( \rho_i^0 \left[ \frac{1}{C_k} + \phi_0 (1 - K_k) \right] \right) = \rho_i^0 \left( \frac{1}{K_i} b_i \frac{\rho_i}{\rho_t} \right) \phi_S S_i - S_j (T - T_j) - \phi_0 \hat{N}(T - T_j),
\]

where the term \(1/C\), the liquid storage coefficient of a porous medium is given by:

\[
\frac{1}{C} = \frac{1}{M} + \frac{1}{N_i} + \frac{1}{N_i} \frac{\phi_0}{k_i} \quad \text{(B.4)}
\]

and the volume change coefficient of ice by liquid pressure \(\Gamma(T)\) and pore volume change coefficient by thermal effect \(\hat{N}(T)\) are, respectively, expressed as:

\[
\Gamma(T) = b_{bJ} + \frac{1}{k_i} \frac{\phi_0 S_i}{\phi_0 S_i}; \quad \text{(B.5a)}
\]

\[
\hat{N}(T) = (x_i - x_i) + S_i (x_i - x_i); \quad \text{(B.5b)}
\]

Appendix C. Derivation of heat conservation equations

The overall heat conservation of a porous material can be given by (see for instance, Coussy, 2005; Coussy, 2010):

\[
T \frac{\partial S_i}{\partial t} + \nabla \cdot (S_i W_i) + \nabla \cdot Q + w_i \frac{\partial P_i}{\partial t} - \nabla P_i = 0, \quad \text{(C.1)}
\]

where, the term \(D_i = T \cdot (S_i W_i)\) is defined as the intrinsic dissipation of pore fluid, the term \(D_s = V \cdot Q\) is the dissipation of heat, and the term \(D_{ij} = w_i \rho_i \cdot \nabla P_i\) is the dissipation of fluid due to Darcean flow. Systematic calculations indicate that the contribution of the fluid dissipation due to Darcean flow is relatively small, see Fig. 4. When neglecting the term \(D_s\) the Eq. (17) is obtained.

Let us now consider a representative elementary volume (REV). The total material entropy defined on this volume, \(S\), is the sum of entropy of three phases: solid skeleton, liquid water and ice crystals.

\[
S = S_{sk} + S_{wl} + S_{il}; \quad \text{(C.2)}
\]

where \(m_{i,j}\) is the mass of phases occupying pore space, i.e., \(m_{i,j} = \rho_i \rho_j \phi_0\). The entropy change rate can thus be deduced as,

\[
\frac{\partial S}{\partial t} = \frac{\partial S}{\partial t} (S_{sk} + S_{wl} + S_{il}) = \frac{\partial}{\partial t} S_{sk} + m_0 s_{sk} + S_{wl} + m_i s_i + S_{il} + m_0 s_0 + S_{il} / \partial t \quad \text{(C.3)}
\]

Fig. 4. Ratio \(D_i/(D_{sk} + D_{wl})\) with respect to distance to surface. The material without air entrainment is used, and the same initial and boundary conditions as presented in bottom half of Table 2.
We rewrite the first term of right side of Eq. (17) by neglecting the entropy gradient of liquid water, since \( |w_l \nabla S_l| \ll |S_l \nabla \cdot w_l| \), which gives

\[
- \nabla \cdot (S_l w_l) = -w_l \cdot \nabla S_l - S_l \nabla \cdot w_l \approx -S_l \nabla \cdot w_l \quad (C.4)
\]

Substituting Eqs. (C.4) and (C.3) into Eq. (17), and considering Eq. (14) one can obtain the following expression,

\[
\frac{\partial}{\partial t} S_{ak} + m \frac{\partial S_i}{\partial t} + m \frac{\partial S_j}{\partial t} + (S_i - S_l) \frac{\partial m_l}{\partial t} = \frac{1}{T} \nabla \cdot \lambda \nabla T \quad (C.5)
\]

In infinitesimal transformation, the ice formation rate is assumed to be proportional to rate of ice content,

\[
\frac{\partial m_l}{\partial t} \approx \rho_i^0 \phi_0 \frac{\partial S_i}{\partial t} = \rho_i^0 \phi_0 \frac{\partial S_i}{\partial t} \frac{\partial T}{\partial t} \quad (C.6)
\]

A simplified relation adopted for \( dS_j/dT \) and heat capacity \( C_r(T) \):

\[
\frac{dS_j}{dT} = C_r(T) \quad (C.7)
\]

Substitution of Eqs. (1), (C.6) and (C.7) into Eq. (C.5) can give Eq. (18),

\[
\frac{1}{T} \left[ \left( \epsilon_0 + \phi_0 \rho_i^0 C_r(T) \right) \frac{\partial T}{\partial t} + \phi_0 \rho_i \left[ (1 - \rho_i^0) (T - T_j) - 1 \right] \right] - C_r \ln \left( (I/T_j) \right) + \rho_i^0 \rho_i \left( P_l - P_m \right) \frac{\partial S_i}{\partial T} \frac{\partial T}{\partial t} = \frac{1}{T} \nabla \cdot \lambda \nabla T.
\]

References


