Are Deicing Salts Necessary to Promote Scaling in Concrete?
Antonin Fabbri, Ph.D.¹; Olivier Coussy²; Teddy Fen-Chong³; and Paulo J. M. Monteiro⁴

Abstract: The main purpose of the present study is to investigate the role of the material parameters such as permeability, thermal diffusivity, and pore size distribution on the mechanical behavior of cementious structures submitted to frost action, such as surface scaling. An experimental device, in which a cement paste specimen is exposed to freezing-thawing cycles under a thermal gradient, has been developed. The experimental results show that, under high thermal gradient (up to 1.5°C/mm), skin damage can occur without a saline layer in contact with the frozen surface. This can be explained and quantified in the framework of poromechanics. The model is based on the coupling between liquid-ice crystal thermodynamic equilibrium, liquid water transport, thermal conduction, and elastic properties of the different phases that form the saturated porous material. It eventually predicts that a less permeable sample is more susceptible to damage by surface defacement, which explains the observed experimental result.

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Introduction
When concrete structures are exposed to freezing and thawing cycles, two types of damage can occur: internal frost damage and surface scaling (Pigeon 1984). The former takes place and generates microdamage within the whole medium. Theoretical study of concrete behavior at low temperature at the material scale started with the work of Powers in 1949 (Powers 1949; Powers and Helmuth 1953). In this seminal work, he attributed the expansion of concrete to the hydraulic pressure originated by the expulsion of liquid water from the freezing pores due to the liquid-to-ice volumetric expansion. Early attempts at evaluating frost performance of concrete were based on the comparison between the tensile stress induced by the hydraulic pore pressure and the tensile strength of the material. However, the picture was not so simple as demonstrated by the fact that expansion is observed in cement paste saturated with benzene, whose density increases with solidification (Beaudoin and MacInnis 1974). Nowadays, it has been recognized that the mechanical response of a saturated or partially saturated porous material at freezing temperatures is the result of the volumetric increase of water during its solidification, the transport of unfrozen liquid water through the porous network, and the thermomechanical properties of all the phases of the composite material. Physico-mechanics-based models have been developed to capture and quantify all these phenomena both at the pore scale (Vigues and Dijkema 1974; Coussy and Fen-Chong 2005) and at the material scale (Coussy 2005; Zuber and Marchand 2004; Bazant et al. 1988).

On the other hand, scaling is the result of a local flaking or peeling of the concrete surface. Generally, it starts as localized small patches which later often merge and extend to larger areas. Moderate and severe scaling expose the coarse aggregate from the concrete surface and may involve losses up to 3–10 mm of the surface, which is harmful as it reduces the cover of the steel reinforcement. The discovery of scaling in the early 1950s prompted a series of experimental studies (Verbeck and Klieger 1957; Sellevold and Farstad 1991; Pigeon et al. 1996; Valenza and Scherer 2005; Penttala 2006). The results indicate that scaling is largely enhanced by the presence of deicing salts and that any surface drying prevents the specimen from scaling. Despite numerous studies, the mechanisms responsible for surface damage, and especially the action of deicing salts, have not been clearly identified. Indeed, while according to many studies scaling only happens when a saline layer is in contact with the surface submitted to frost action (Sellevold and Farstad 1991; Valenza and Scherer 2005), in others (Verbeck and Klieger 1957; Penttala 2006), scaling can happen even when the saline surface is not present, albeit not often.

This work investigates the role of the material parameters such as permeability, thermal diffusivity, pore radii distribution, and connectivity (which determines the ice content as a function of temperature at the scale of the representative volume element) on the mechanical behavior of saturated cementitious materials submitted to frost action. Let us emphasize that its goal is not to predict in situ scaling but to understand how these material parameters may influence the mechanical response of a cementitious structure submitted to frost action and to determine if the action...
of deicing salts is the only phenomenon that produces surface deterioration.

It is first shown experimentally that scaling can occur without the presence of deicing salts. This experimental result is then explained by a poromechanical-based approach at a scale where the importance of the permeability and the amount of ice formed on frost durability is indubitable.

**Experimental Evidence of Scaling without Salts**

Samples of hardened cement paste, with 0.4 water-cement ratio (W/C) by mass, were prepared in a 5-L mortar mixer, and cast in 150 mm high cubic molds. Ordinary Portland cement similar to ASTM Type I and distilled water were used. One day after casting, the specimens were removed from their mold and stored in moist conditions (relative humidity = 95 ± 5%) for 6 months, when they were cored and cut into 20-mm-thick slices with 40 mm-diameter and remained in water until tested. Some specimens (index d) were dried in an oven at 55°C then saturated with degassed distilled water at 3 kPa air pressure before being tested.

The tested sample was inserted between two hollow pistons, each filled with a fluid from a cryostat. Their temperature was controlled by a PT100 sensor. The piston in contact with the bottom side of the specimen was held at a constant temperature of 10°C. The other one was subjected to 56 cycles ranging from 0.1 ± 0.1°C to −20 ± 0.1°C. As sketched in Fig. 1, the temperature rate was 10°C/h. Freezing was stopped at −20°C and the sample was thawed to 0.1°C. At the end of freezing, the temperature was held constant for 1 h and at the end of thawing the temperature was held constant for 2 h. Let us recall that the purpose of this paper is not to simulate and/or to predict in situ frost scaling, but to investigate if scaling can occur without deicing salt. In this context, in order to enhance the effect of structural gradients, a large thermal gradient through the sample was intentionally imposed.

The thermal insulation of the lateral surfaces of the specimen was achieved by an expanded polystyrene ring. In order to avoid surface drying during freezing-thawing cycles, each specimen was wrapped by a moisture resistant Parafilm sheet. Thus, the surface submitted to frost action is not in contact with a frost layer (i.e., a water or brine layer). A picture of the experimental device is shown in Fig. 2.

After each 14 cycles, the specimen was weighed in order to verify that no water supply nor evaporation have occurred during the test. Then, the Parafilm sheet was removed and scales were collected, dried at 55°C during 4 days, and weighed.

Table 1 shows the evolution of the mass of scales collected per unit of surface. As it can be seen, no scaling occurs on previously dried P4-E-3d and P4-E-4d samples. Indeed, these two specimens were totally disintegrated by internal cracking during the first 14 cycles (see Fig. 3). On the other hand, a significant scaling occurred on P4-E-1 and P4-E-2 samples (Fig. 4). This result clearly indicates that scaling can occur without a frozen brine layer in contact with the surface submitted to frost action. The lack of scaling without free liquid on the surface commonly observed (Verbeck and Klieger 1957) may be due to a surface drying during the test, which is not possible in this study, thanks to the presence of the Parafilm sheet.

**Table 1. Experimental Results of Scaling Tests**

<table>
<thead>
<tr>
<th>Scales mass (g/m²)</th>
<th>P4-E-1</th>
<th>P4-E-2</th>
<th>P4-E-3d</th>
<th>P4-E-4d</th>
</tr>
</thead>
<tbody>
<tr>
<td>14 cycles</td>
<td>4</td>
<td>27</td>
<td>Crumbled</td>
<td>Crumbled</td>
</tr>
<tr>
<td>28 cycles</td>
<td>117</td>
<td>145</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>42 cycles</td>
<td>152</td>
<td>154</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>56 cycles</td>
<td>168</td>
<td>182</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

**Fig. 1.** Freezing-thawing cycle imposed at sample top surface

**Fig. 2.** Picture of experimental device

**Fig. 3.** Picture of P4-E-3d cement paste after first 14 cycles
In all cases, the solicitation was the same and the differences only relied on the cure of the specimen (predried or not). The next step is then to identify the material characteristics which are significantly changed by a drying-imbibition process and to investigate their actions on frost-thaw behavior.

Characterization of Material Properties

It is established that drying strongly affects the intrinsic permeability ($k_0$) of concrete (Hearn and Morley 1997) and the amount of ice formed during freezing (Fabbri et al. 2006; Kaufmann 1999). The permeability of the predried sample is evaluated through the Katz–Thompson–Garboczi relation based on mercury injection experiments (MIE) (Katz and Thompson 1986; Garboczi and Bentz 1996) (see Appendix I). This is not possible for virgin specimens because MIE can only be made on dried samples. Consequently, their permeability is estimated from the predried one according to the study performed by Hearn and Morley (1997), where two orders of magnitude are observed between the permeability of a virgin and a predried sample. This can be explained by the formation of microcracks produced by oven drying that noticeably increases connectivity and the size of capillary pores and thus causes the liquid transport easier (Shafiq and Cabrera 2004). Results lead to $k_0=4.3 \times 10^{-20}$ m$^2$ for predried samples and $k_0=4.3 \times 10^{-22}$ m$^2$ for virgin ones. The porosity ($\Phi_0$) was determined through the mass loss between the saturated ($m_{sat}$) and the oven-dried states at 55°C ($m_{ov}$): $\Phi_0=(m_{ov}-m_{sat})/V$, where $\rho_l$ is the mass density of liquid water and $V$ is the sample volume. This leads to $\Phi_0=0.29$ for predried samples and $\Phi_0=0.28$ for virgin ones. The dependency of the volumetric ratio of unfrozen water ($S_l$) as a function of temperature ($\theta$) was determined by a capacitive sensor apparatus developed at the Navier Institute. The full description of the experimental setup and its calibration are reported in Fen-Chong et al. (2004) and Fabbri et al. (2006). As shown in Figs. 5 and 6, in the [−30; 0°C] temperature range, both $S_l(\theta)$ curves vary linearly, except for two particular temperatures on cooling, around −5 and −20°C, and one, around −5°C on heating, where the slope changes significantly. However, the amount of ice formed in predried hardened cement pastes appears to be significantly higher than in virgin ones.

Assuming that the in-pore ice formation results from the propagation of ice crystals through the connected porous network (Scherer 1993), the mechanical (Young–Laplace’s law) and chemical equilibria between ice crystal and surrounding water provide a relation between the water to ice transition temperature $\theta_{f-c}$ and the ice crystal mean curvature $C^*$ (Brun et al. 1977)

$$\theta_{f-c} = -\frac{\gamma C^*}{\Sigma J}$$

where $\gamma=$liquid-ice surface tension while $\Sigma J=$entropy of fusion.

As $C^*$ increases with decreasing pore radius in which the water is confined, pores with larger radius will freeze at higher temperature. From studies made with low-temperature calorimetry (Sellevold and Bager 1980) and nuclear magnetic resonance (Jehng et al. 1996), a maximum of three distinct types of pores, associated with the three freezing peaks, was observed in a freezing test: large capillaries ($r_c > 50$ nm, $\theta_{f-c} > -1\,\text{°C}$), small capillaries ($r_c = 2$–5 nm, $\theta_{f-c} = -25\,\text{°C}$), and open gel pores ($r_c < 1$ nm, $\theta_{f-c} < -40\,\text{°C}$). In our experiment, the lowest temperature is −30°C, so only the water confined in large and small capillaries can freeze. This is why only two freezing peaks are
presented in Figs. 5 and 6. As a consequence, the larger amount of ice formed in P4-E-3d and 4d cement paste samples can be explained by the damage caused by microcracks produced by oven drying that reduces the proportion of open gel pores and raises the proportion of small and large capillary pores.

The characteristics of the hardened cement paste samples are summarized in Table 2. At this point, strong differences on permeability and the amount of ice formed between the two kinds of specimens have been quantified. Now, in order to evaluate and predict the consequence of these differences on the frost-thaw behavior, theoretical modeling is necessary.

### Table 2. Hardened Cement Pastes Characteristics. \( S_{c,-0\degree C}=\)Ice Saturation at \( x \degree C \)

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \kappa_0 ) (m²)</th>
<th>( \phi_0 ) (%)</th>
<th>( S_{c,-10\degree C} ) (%)</th>
<th>( S_{c,-20\degree C} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>( 4.3 \times 10^{-22} )</td>
<td>28</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>Predried</td>
<td>( 4.3 \times 10^{-20} )</td>
<td>29</td>
<td>46</td>
<td>52</td>
</tr>
</tbody>
</table>

Assuming that the entropy \( s_j \) of the phase \( j \) per unit of porous media volume does not depend on pressure, standard thermodynamics leads to

\[
s_j = s_j^0 + c_{pj}^0 \ln \frac{T}{T_0} \quad (5)
\]

where \( s_j^0 \) and \( c_{pj}^0 \)=bulk specific entropy and the specific heat capacity, both constant and associated with the reference state; while \( T_0=\)freezing temperature of bulk liquid water.

Let us define the capillary pressure as \( p_{cap}=p_c-p_l \). The integration of Eq. (3) from the reference state, while using Eqs. (4) and (5), the hypothesis of small density variations, and neglecting second-order terms, but taking into account variations, of temperature from 253.15 to 273.15 K leads to (see Fabbri 2006 for more details)

\[
p_{cap} = \Sigma(T_0-T) - C_j \left( \frac{(T-T_0)^2}{2T_0} \right) \quad (6)
\]

where \( \Sigma_j=p_j^0(s_j^0-s_c^0) \) and \( C_j=p_j^0(c_{pj}^0-c_{pc}^0)=\)respectively, entropy of fusion and heat capacity difference between water and ice per unit of volume.

### Unsaturated Poroelasticity

Let us consider the initial state to be \( [\sigma](x,0)=0, [\varepsilon](x,0)=0, p_j(x,0)=p_j(x,0)=0, T(x,0)=T_{ref}, \Sigma(x,0)=\Sigma_0, \) and \( \varepsilon_j(x,0)=0 \) where \( [\sigma], [\varepsilon], \) and \( \Sigma=\)respectively, stress tensor, strain tensor, and entropy of the empty porous medium (solid matrix and empty porous network) while \( \varepsilon_j=\)deformation of the porosity occupied by phase \( j \). The relationship between the related porosity of the phase \( j \) (noted \( \phi_j \)), the saturation ratio of the phase \( j \), and \( \varepsilon_j \) is given by (Coussy 2005)

\[
\phi_j = \varepsilon_j + \phi_0 \Sigma_j \quad (7)
\]

The lowest temperature reached in the scaling experiments is \(-20\degree C\). As indicated in Figs. 5 and 6 and in Table 2, less than 60% of water is solidified in the tested samples at this temperature. Consequently, the interfacial liquid-ice energy remains small enough to be negligible in the expression of the pressure actually transmitted to the solid matrix by the crystal and liquid phases (Fabbri 2006). In this case the complete set of constitutive equations of the empty porous medium (Coussy 2004, 2005) are then found to simplify to (Fabbri 2006; Coussy and Monteiro 2007)

\[
[\sigma] = \left( K - \frac{2}{3} G \right) \varepsilon + 2G[\varepsilon] - \left( \sum_{j=l,c} (b_j p_j) + \alpha K(T-T_0) \right) \quad (8a)
\]

\[
\varepsilon_j = b_j \varepsilon + \frac{1}{N_{jl}} p_j + \frac{1}{N_{jc}} p_c - \alpha_{lj}(T-T_0); \quad j = l \text{ or } c \quad (8b)
\]

\[
\Sigma = -\Sigma_0 - \alpha K \varepsilon - \sum_{j=l,c} (\alpha_{lj} b_j p_j) + C_m \ln \frac{T}{T_0} \quad (8c)
\]

where \( \varepsilon=\)tr([\varepsilon])=volumetric dilatation; \( K, G, C_m, \) and \( \alpha=\)respectively, bulk modulus, shear modulus, heat capacity, and thermal volumetric dilatation coefficient of the empty porous medium; \( b_j \) and \( N_{jl} \)=generalized Biot coefficients and the generalized Biot coupling moduli; while \( \alpha_{lj}=\)coefficient related to the thermal dilatation of the pore volume occupied by phase \( j \). They depend upon the elastic properties of the solid matrix and the saturations of liquid and ice according to...
\[
\frac{1}{N_{ij}} + \frac{1}{N_{ik}} = \frac{b_{j} - \phi_{0} S_{j}}{K_{m}}; \quad b_{j} + b_{l} = 1 - \frac{K_{m}}{K_{n}}
\]

and \(\alpha_{ij} = \alpha_{ij}(b_{j} - \phi_{0} S_{j})\) where \(j = l\) or \(c\) \(\tag{9}\)

where \(K_{m}\) is the bulk modulus of the solid matrix.

The generalized Biot coefficients \(b_{j}\) can be estimated from the Biot coefficient \(b = 1 - K/K_{m}\) by use of the so-called iso-deformation hypothesis expressing that there is no morphological difference between the forming ice crystal and the liquid water domains (they are both bounded by pores having the same shape). This yields (Chateau and Dormieux 2002)

\[
b_{j} = S_{j} b; \quad j = c, l \tag{10}\]

Let us assume a one-dimensional problem without any external mechanical load. The momentum balance (\(\text{div}(\sigma_{ij}) = 0\) and the geometric compatibility of the strain tensor \(\sigma_{ij} = [\text{grad}(u)] + [\text{grad}(u)]^{T}\), where \(u\) = displacement vector, require \(\sigma_{ij} = 0\) and \(\sigma_{xx} = \frac{\partial u_{x}}{\partial x}\); \(\sigma_{ij} = 0\) for \(ij \neq xx\) \(\tag{11}\)

Then, the substitution of Eqs. (6), (9), and (11) in the constitutive Eq. (8a) allows for the computation of volumetric strain

\[
\varepsilon = \frac{b\rho_{l} + b_{1}\left(C_{l}(T - T_{0}) - m_{l}(T - T_{0})\right) + \alpha K(T - T_{0})}{K + 4G/3} \tag{12}\]

Due to the temperature gradient across the specimen, the pressure field is not uniform and a liquid flow is created. Assuming that it is governed by Darcy’s law, we write

\[
w = -\rho_{l}^{0} \frac{\kappa(S_{l})}{\eta_{l}(T, p_{l})} \text{grad}(p_{l}) \tag{13}\]

where \(w\) = relative flow vector of mass fluid; while \(\kappa(S_{l})\) and \(\eta_{l}(T, p_{l})\) = respectively, permeability of the porous medium and viscosity of liquid water. The expression of the permeability has been extensively studied in the case of drying, as reviewed in Baroghel-Bouny et al. (2007). In the case of freezing/thawing, the nuclear magnetic resonance (NMR)-based paper (Kleinberg and Griffin 2005) concludes that ice forms from the pore centers. Within this picture, it can be assumed that water flow is possible even for very low saturation values, by means of the unfreezable water layer between ice and the pore walls. Such a situation can be taken into account by the usual self-consistent differential scheme yielding (Dormieux and Bourgeois 2003)

\[
\kappa = \kappa_{0}(S_{l})^{3/2} \tag{14}\]

where \(\kappa_{0}\) = constant intrinsic permeability, while the term \((S_{l})^{3/2}\) = relative permeability accounting for the change in porous volume due to the solidification of liquid water (since no liquid flow can occur through ice crystal).

Because the flow of ice is significantly slower than the usual cooling timescales, it will be neglected. In this case, the overall mass conservation of water \((m = m_{l} + m_{c})\), in both liquid and crystal forms, requires

\[
\frac{\partial m}{\partial t} = -\text{div}(w) \tag{15}\]

Using Eq. (7), the global mass of liquid and crystal per unit of porous medium volume can be expressed as

\[
m_{j} = \rho_{j} \phi_{j} = \rho_{j}(\phi_{j} S_{j} + \psi_{j}); \quad j = l \text{ or } c \tag{16}\]

Finally, due to the small density difference between liquid and crystal phases of water \((|\rho_{l} - \rho_{c}| = 0.1, 0.09 < 1\)), the combination of Eqs. (4), (8b), (9), (10), (12), (13), (15), and (16) under the assumption of small perturbation allows us to express the overall mass conservation according to the only unknown variables \(p_{j}\) and \(T\)

\[
\text{div}
\begin{bmatrix}
\rho_{j}^{0} \frac{\kappa(S_{j})}{\eta(T, p_{j})} \text{grad}(p_{j})
\end{bmatrix}
= \frac{\partial}{\partial t}(A p_{j}) + \dot{r}_{\Delta p} + \dot{r}_{T} + \dot{r}_{\text{cryo}} \tag{17}
\]

with

\[
A = \phi_{j}^{0} S_{l}\left(\frac{1}{K_{l}} - \frac{1}{K_{c}}\right) + \frac{b_{1}^{2}}{K + 4G/3} + \frac{b - \phi_{0}}{K_{m}} + \frac{\phi_{0}}{K_{l}} \tag{18a}\]

\[
\dot{r}_{\Delta p} = \phi_{j}^{0} \left(\rho_{j}^{0} - 1\right) \frac{\partial S_{j}}{\partial t} \tag{18b}\]

\[
\dot{r}_{T} = \left(\phi_{j}^{0} \alpha_{l}^{0} + S_{l} (\alpha_{c}^{0} - \alpha_{l}^{0})\right) - \alpha_{l}^{0} \frac{24G/3}{K + 4G/3} \frac{\partial T}{\partial t} \tag{18c}\]

\[
\dot{r}_{\text{cryo}} = \phi_{j}^{0} S_{l}\left(\frac{1}{K_{m}} - \frac{1}{K_{c}}\right) - b_{1}\left(\frac{b}{K + 4G/3} + 1\right) \frac{\partial p_{\text{cryo}}}{\partial t} \tag{18d}\]

The source term of liquid pressure in Eq. (17) is made of three distinct contributions. The first contribution, \(\dot{r}_{\Delta p}\), is a positive term originating from the expansion that occurred when liquid water freezes. It is the only contribution considered in Power’s hydraulic theory (Powers 1949). The term \(\dot{r}_{T}\) accounts for the pressure in the liquid caused by the relative thermal contraction between the solid matrix and the in-pore constituent. And finally, \(\dot{r}_{\text{cryo}}\) accounts for the pressure in the liquid caused by flows at the microscopic scale. The physical understanding of the driving force of these flows, which drives liquid water to the already frozen sites in order to meet the liquid-crystal equilibrium condition Eq. (6), was previously discussed in Vignes and Dijkema (1974) and Vignes-Adler (1976).

**Equation of Heat Transfer**

The second law of thermodynamic applied to the porous medium for a reversible evolution leads to

\[
T \left(\frac{\partial S_{l}}{\partial t} + m_{l} \frac{\partial S_{l}}{\partial t} + m_{c} \frac{\partial S_{c}}{\partial t}\right) = T_{0}(s_{l} - s_{c}) \frac{\partial m_{l}}{\partial t} - \text{div}(q) \tag{19}\]

where \(\Sigma_{l}\) = entropy of the skeleton which, in the present study, is assumed to be equal to the entropy of the empty porous medium \(\Sigma\). The term \((s_{l} - s_{c}) (\partial m_{l}/\partial t)\) = heat source due to the latent heat of liquid to ice phase change. The heat flow \(q\) is unidirectional and the medium is assumed to be isotropic. Applying Fourier’s law

\[
q = -\lambda(S_{l}) \text{grad}_{l}(T) \tag{20}\]

where \(\lambda(S_{l})\) = isotropic thermal conductivity. Assuming that ice crystal is growing from the center of the pore in which it is confined, \(\lambda\) can be estimated using the \((n+1)\)-phases multiscale scheme developed by Hervé (2002) for isotropic composite media. Thus
\[
\lambda(S, T) = \lambda_m(T) \left( 1 + \frac{\phi_0}{3} - \frac{\lambda_m(T)}{\lambda_m(T) - \lambda_m(T)} \right)
\]

with

\[
\lambda(S, T) = \lambda(T) \left( 1 + \frac{1 - S_l}{\lambda(T)} \right)
\]

(21)

where \(\lambda_m\), \(\lambda_s\), and \(\lambda_t\) = isotropic thermal conductivity of matrix, liquid water, and ice crystal, respectively.

Moreover, assuming that the entropy of the skeleton \(S_t\) does not depend on pressure and strain, and under the small transformation hypothesis, Eqs. (8c) and (16) give the following approximation for \(\partial S_t / \partial t\) and \(\partial m_t / \partial t\):

\[
\frac{\partial S_t}{\partial t} = C_m \frac{\partial T}{\partial t}
\]

(22a)

\[
\frac{\partial m_t}{\partial t} = -p_0 \phi_0 \frac{\partial S_l}{\partial t}
\]

(22b)

Let \(C_m = C_{p,w} = \text{heat capacity of water per volume unit. The substitution of Eqs. (20) and (22) into Eq. (19) leads to}

\[
\text{div}(\lambda \text{grad}(T)) = \frac{\partial T}{\partial t} \left( \text{C}_m + \phi_0 (C_{pl} - S_c C_c) \right) - T \phi_0 \left( \sum f + C \ln \frac{T}{T_0} \right) \frac{\partial S_l}{\partial T}
\]

(23)

where \(-T \phi_0 \left( \sum f + C \ln \frac{T}{T_0} \right) \frac{\partial S_l}{\partial T} = \text{latent heat of solidification (respectively, fusion) of water and } C_m + \phi_0 (C_{pl} - S_c C_c) = \text{average heat capacity of the porous medium.}

**Numerical Application**

The specimen is modeled as a one-dimensional structure made up of an isotropic medium, of length \(L\) and lateral surface \(S\), ideally insulated on its lateral surfaces. The Cartesian coordinate system \((O, x)\) is used, with \(O\) the node of the surface which is submitted to frost action and \(x\) following the symmetry axis from the top to the bottom of the specimen. In this case, at the macroscopic scale the flow of heat and liquid only occurs in the \(x\) direction. As a consequence, the elementary volume is given by \(d\Omega = S dx\).

At the initial condition, the temperature of the sample is \(T(x, t=0) = T_0 = 273.15\) K with no water overpressure \((p_w(x, t=0) = 0\) MPa) where \(T\) stands for absolute temperature in Kelvin \([\text{K}]=0[\text{°C}]+273.15\) and \(t\) stands for time in seconds. At \(t=0\), the \(x=0\) surface is submitted to a progressive decrease of temperature while the \(x=L\) surface is increased to \(T_0 = 283.15\) K

\[
T(0, t) = T_s(t); \quad T(L, t) = T_p
\]

where \(T_s(t)\) follows the same time evolution as the experimental protocol, thus

\[
T_s(t) = 273.15 - 0.002792 \times t; \quad t \in [0, 7, 200]
\]

(25)

\[
T_s(t) = 253.15; \quad t \in [7,200, 10,800]
\]

(26)

\[
T_s(t) = 253.15 + 0.002792 \times (t - 10,800); \quad t \in [10,800, 18,000]
\]

(27)

In this study, no external loading is applied to the structure, which leads to: \([\sigma] \cdot n_L = 0\) where \(n_L = \text{outward unit vector of the bottom surface.}\)

The Parafilm sheet used to wrap the specimen should not be sufficient to prevent the in-pore water from being expelled from the \(x=L\) surface. Consequently, the most realistic liquid pressure boundary condition is

\[
p_L(L, t) = 0
\]

(28)

Similarly, we may assume that the water which solidifies at the \(x=0\) surface during the first freezing-thawing cycles will play the role of an impermeable frost layer. In this case, no flow \((w)\) through the frozen surface has to be prescribed as the boundary condition

\[w \cdot \mathbf{n} = 0 \quad \text{for } x = 0\]

(30)

where \(\mathbf{n}\) = outward unit vector perpendicular to the frozen surface.

In the following, the influences of each of Eqs. (29) and (30) boundary conditions on frost behavior are studied.

At last, the poromechanical-based approach of the problem can be summarized by Eqs. (17)–(23) where \(p_L\) and \(T\) stand for the main unknown variables. This system is solved using the Newton–Raphson method on a structure discretized according to the finite volume method implicit scheme (Eymard et al. 2000). Mathematical functions used to implement the \(S_d(\theta)\) experimental curves on the model are reported in Appendix II and the thermo-physical property values used for the calculation are reported in Appendix III.

The predicted liquid and ice pressure profiles at the end of the cooling stage, for the predried and virgin hardened cement pastes and the Eqs. (29) and (30) boundary conditions, are in Fig. 7.

**Discussion**

Whatever the permeability and the boundary condition used, the maximum ice pressure (round to 25.5 and 41.0 MPa for the less permeable cement paste and round to 8.5 and 32.0 MPa for the more permeable one) is close to or higher than the usual tensile elastic limit of an ordinary Portland cement paste \((f_t)\), which is between 5 and 10 MPa (Taylor 1997). In the case of the \(p_L(0, t)=0\) boundary condition, the ice pressure peak of the virgin sample is localized at 2.7 mm beneath the surface, which is inappropriate with the depth of scaling commonly observed under lower thermal gradients. On the contrary the ice pressure peak of the predried sample is broad and localized in the sample core (8 mm beneath the surface). In case of the \(w(0, t) \cdot \mathbf{n} = 0\) boundary condition, the profiles shape are also noticeably different. Indeed, for the predried sample, the \(p_L(x)\) curve is quite homogenous all over the specimen, while for the virgin specimen a great peak of overpressure is observed near the frozen surface.

However, the knowledge of the ice pressure is not sufficient to estimate the susceptibility of the solid matrix to be crushed. To do so, we rather use the stress in the solid matrix, \(\sigma_{m,x}\). As reported in Chateau and Dormieux (2002), neglecting the influence of the interfacial tension between liquid water and pore walls, it can be linked to the porous medium stress and the pressures of liquid and
The permeability of the solid matrix is constant over the temperature cycle, assuming that the thermophysical properties of the solid matrix are not submitted to frost action. Moreover, only the boundary conditions give a matrix stress close to or higher than $p_c$, with a $\omega(0, t) \cdot n_0 = 0$ boundary condition while dashed line is for $\omega(0, t) \cdot n_0 = 0$

crystal by the relation $(1 - \phi_0) \sigma_{m,zz} = \sigma_{zz} + \phi_0 p_l + \phi_c p_c$. Then, assuming that the thermophysical properties of the solid matrix are constant over the temperature cycle, $\sigma_{m,zz}$, can be expressed through Eqs. (6) and (11) as

$$\sigma_{m,zz} = \frac{\phi}{1 - \phi_0} p_l - \frac{\phi_c}{1 - \phi_0} \left[ \sigma_0 (T - T_0) + C_f \frac{(T - T_0)^2}{2T_0} \right]$$

The $\sigma_{m,zz}$ profiles are in Fig. 8.

For the predried specimen, whatever the boundary condition used, no peak of tensile stress is predicted near the surface submitted to frost action. Moreover, only the $\omega(0, t) \cdot n_0 = 0$ boundary condition results in a significant risk of frost damage through the structure ($\sigma_{m,zz}$ is higher than 5 MPa until 8 mm depth). Then, the hypothesis of the existence of an impermeable frozen film on the skin surface leads to a better suitability between experimental results and theoretical calculations. For virgin samples, both boundary conditions give a matrix stress close to or higher than $f_c$ only within the first millimeters depth (until 3 mm). This fact, enhanced by a poor surface quality of the material and an increasing number of freezing-thawing cycles, can explain the observed damage on the skin surface.

The explanation of the behavior difference between the two types of samples is pointed up by the $p_c(x)$ profiles. Indeed, liquid overpressure appears to be easily dissipated through the porous network for a predried sample than in a virgin one, where liquid overpressurization peaks are observed. This is why, while the amount of ice formed in predried samples is significantly higher than in virgin ones (at $-20^\circ$C, $S_c$ is about 0.1 for a virgin sample and $S_c$ is about 0.5 for a predried one), the maximum ice pressure of the virgin sample is higher: a higher permeability allows for a more efficient in-pore overpressure relaxation.

Actually, in the case of too low permeable cement pastes, the liquid flow expulsion is not important enough to relax the whole local overpressure caused by thermal stresses, cryogenic aspiration, and liquid-ice difference of density. Thus, this pore overpressure, which produces a local tensile stress in the matrix, remains localized near the $x=0$ surface where the ice formation is most important. This fact is illustrated in Fig. 9 where a decrease of the maximum tensile stress in the matrix is predicted during the 1 h temperature step at $-20^\circ$C. This decrease is clearly due to the pore relaxation due to slow water transport from the overpressurized zone to the bottom and/or the top of the specimen.

This explanation leads to the conclusion that scaling is enhanced by the inability of the frozen porous network to relax local overpressure from the skin surface. This is consistent with the experimental data from Baroghel-Bouny et al. (2002) where a concrete with a compressive strength equal to 50 MPa exhibits a better frost durability than a less permeable but higher resistance concrete (with a compressive strength equal to 75 MPa). In addition, the common lack of efficiency of an air-entraining agent in a high resistant concrete (LCPC 2003) can then be attributed to the difficulty of the liquid water to migrate from the porous network to air voids in the case of too low permeable material.

To sum up, similarly to the experimental observations, the poromechanical model rather predicts an internal frost damage for predried samples and scaling for virgin samples even though they are submitted to the same solicitation. The observed difference between the two mechanisms seems to be caused by the contrast between permeability and the amount of ice formed. Indeed, in the case of initial and boundary conditions which force the top surface temperature to be lower than the bottom one, water will first freeze near the skin surface. If the amount of ice formed is high enough and the permeability is too small to relax pore over-
pressure, scaling will occur. Thus, it appears to be an internal frost-like damage localized at the \( x=0 \) surface.

According to a recent work performed by Valenza and Scherer (2005), the increase of scaling due to the presence of salts is a consequence of mechanical interaction between the skin surface and the frozen brine layer. This effect can be taken into account in the present model by changing the boundary conditions at the top surface \( (x=0) \). For this case, all components of the strain tensor have to be taken into account. It leads to lengthy three-dimensional calculations but the global analysis remains the same.

### Conclusion

An experimental device, in which initially water-saturated hardened cement paste specimens are submitted to freezing-thawing cycles under a thermal gradient, has been developed. This study reveals the occurrence of scaling without a brine layer in contact with the frozen surface. To explain this behavior, a poroelastic model has been worked out. The model predicts that scaling can occur without salts due to the localization of pore overpressure near the skin surface, caused by the low permeability of cementitious material. Finally, a link is established between the frost behavior at the structural scale and the two key material parameters toward frost durability: the permeability and the amount of ice formed as a function of temperature. The permeability influences tensile matrix stress localization while the amount of formed ice rather acts on its global amplitude.

### Appendix I: Permeability of Saturated Porous Specimen

The permeability is estimated using a mercury injection experiment and the Katz–Thompson relation (Katz and Thompson 1986)

\[
\kappa = \frac{1}{226} \frac{l^2}{C} \frac{C_o}{C} \quad (32)
\]

where \( l \) = threshold pore diameter in MIE; \( C \) = sample conductivity; and \( C_o \) = conductivity of the water in the pore space. The relative conductivity \( C/C_o \) is also estimated by a mercury injection experiment through a relationship reported in Garboczi and Bentz (1996), based on a three-dimensional (3D) electrical analogy of the cement paste and assuming that the relative conductivity of capillary water is 1 while all the other constituents ones are null

\[
\frac{C}{C_o} = 0.001 + 0.07\phi^2 \left[ \phi_{\text{MIE}} - \phi_{\text{c}} \right] + 1.8 \left[ \phi_{\text{MIE}} - \phi_{\text{c}} \right]^2 \quad (33)
\]

where \( \phi_{\text{MIE}} \) = porosity estimated by MIE while \( \phi_{\text{c}} \) = capillary porosity under which the pore space becomes nonpercolated and is commonly estimated to be approximately 0.18 (Powers 1959; Garboczi and Bentz 1996) and \([\ldots]\) = Heaviside function. As reported in Garboczi and Bentz (1996); and Cui and Cagayani (2001), a good agreement is found between Eq. (33) and experimental data for ordinary cement pastes by many authors.

### Appendix II: Fit of Freezing-Thawing Curves

The freezing-thawing curve shapes, quite similar to water retention capillary curves, are well described by the following Van Genuchten-like (Van Genuchten 1980) sigmoidal functions:

\[
S_{i,\text{frost}}(\theta) = \sum_{j=1}^{k} \phi_j \left[ 1 + n_i \left( \frac{\theta}{\theta_i} \right)^{1/(1-n_i)} \right] + \left( 1 - \sum_{j=1}^{k} \phi_j \right) \quad (34a)
\]

\[
S_{i,\text{thaw}}(\theta) = \phi_T \left( 1 - \phi_T \right) + n_i \left( \frac{\theta}{\theta_i} \right)^{1/(1-n_i)} \quad (34b)
\]

where \( S_{i,\text{frost}}(\theta) \) and \( S_{i,\text{thaw}}(\theta) \) = liquid saturation ratio on freezing and thawing, while \( k \) = number of freezing peaks; \( \theta^* \) = temperature at which each of them happens; and \( \theta^* \) = temperature at which the thawing peak happens. These coefficients can be evaluated from the analysis of the \( S(\theta) \) derivative curve.

Let \( \theta_{bh} \) be the temperature at which thawing begins. Because the liquid saturation ratio is a continuous function, \( S_{i,\text{frost}}(\theta_{bh}) \) and \( S_{i,\text{thaw}}(\theta_{bh}) \) are equal. As a consequence, the coefficient \( \phi_T \) must be

\[
\phi_T = \frac{S_{i,\text{frost}}(\theta_{bh}) - f_{n,\theta^*}(\theta_{bh})}{1 - f_{n,\theta^*}(\theta_{bh})} \quad (35)
\]

with

\[
f_{n,\theta^*}(\theta) = \left( 1 + n \left( \frac{\theta}{\theta^*} \right)^{1/(1-n)} \right)^{-n}
\]

Finally coefficients \( \phi_n \), \( n \), and \( \theta^* \) are estimated with the shape of the \( n \)th freezing sigmoidal function and the shape of the thawing curve, need to be fitted from experimental data. It must also be emphasized that \( \theta^* \) and \( n \) appear to be independent of \( \theta_{bh} \) on the two kind of cement pastes tested (virgin or pre-dried). Thus, the fit of only one thawing curve is sufficient to estimate the amount of ice within the porous network whatever the lower temperature reached during the freezing stage. Figs. 5 and 6 show a comparison between the experimental data and the fitted curves using Eq. (34) for different thawing temperatures, keeping \( \theta^* \) and \( n \) constant for each thawing curve.

### Appendix III: Thermophysical Properties

Numerical application is made with \( p_i^0 = 9.97 \times 10^{-3} \) MN/m\(^3\), \( \rho_i^0 = 9.17 \times 10^{-3} \) MN/m\(^3\), \( \alpha_i = -68.7 \times 10^{-6} \) K\(^{-1}\), and \( \Delta \alpha_i = 24.732 \times 10^{-6} \) K\(^{-2}\), \( \alpha_i = 160 \times 10^{-6} \) K\(^{-1}\), \( K_i = 1.970 \) MPa, \( K = 4.310 \) MPa, \( \lambda_i = 0.56 + 0.017(T-T_0) \) W/(mK), \( \lambda = 2.15 + 0.0123(T-T_0) \) W/(mK) (Lide 2001), \( \Sigma_j = 1.2 \) MPa/K, \( C_j = 2.14 \) MPa/K, \( C_{pl} = 4 \) MPa/K (Brun et al. 1977), \( C_{m} = 1.36 \) MPa/K (de Schutter and Taerwe 1995), \( \alpha = \alpha_m = 30 \times 10^{-6} \) K\(^{-1}\), \( K_i = 14.100 \) MPa, \( K_m = 31.800 \) MPa, \( b = 0.55 \) (Ulmm et al. 2004), \( \gamma_{\text{air}} = 36 - 0.25(T - T_0) \) mN/m (Zuber and Marchand 2004), \( \lambda_{\text{m}} = 1.9 \) W/(mK) [deduced from the experimental values of saturated and a dried cement pastes conductivity given by Kim et al. (2003)].

There is an evolution of the viscosity of supercooled water with temperature and liquid pressure by numerous empirical relationships. In this study, one of the most recent proposed by Harris and Woolf (2004) is chosen \( (p_i \) in MPa and \( T \) in K)
\[
\eta(T,p) = \exp\left( a_1 + a_2 p_1 + a_3 p_1^2 + a_4 p_1^3 + a_5 was \right)
\]

(36)

with

\[
\begin{align*}
 a_1 &= 0.411011 \text{ mPa s}, & a_2 &= 0.00854113 \text{ mPa s/MPa} \\
 a_3 &= -2.67340 \text{ mPa s K/MPa}, & a_4 &= -1.35750 \text{ mPa s/MPa}^2 \\
 a_5 &= 0.00525404 \text{ mPa K/MPa}, & a_6 &= -5.15042 \text{ mPa s/MPa}^3 \\
 a_7 &= -2350.32 \text{ mPa s K}, & a_8 &= 654.401 \text{ mPa s K}^2 
\end{align*}
\]

Let us emphasize that the cement paste did not have an air-entraining agent so there was no relief on the hydraulic pressure by the air voids.

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