

PDF issue: 2025-01-09

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(Citation) Journal of Building Physics,46(6):762-788

(Issue Date) 2023-05

(Resource Type) journal article

(Version) Accepted Manuscript

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Fukui K, Iba C, Ogura D. Deformation of fired clay material during rapid freezing due to supercooling. Journal of Building Physics. 2023;46(6):762-788. Copyright © The Author(s) 2023. doi:10.1177/17442591231154010

(URL)

https://hdl.handle.net/20.500.14094/0100482055



Title

Deformation of fired clay material during rapid freezing due to supercooling

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1 1 Introduction

2 Frost action is one of the main causes of the deterioration of porous building materials. A number of 3 studies have investigated the deformation mechanisms and the resulting damage to predict 4 deteriorations, propose proper countermeasures, and create frost-resistant materials (Powers, 1945; 5 Penttala, 1998; Scherer & Valenza II, 2005). The freezing point depression of water in porous media 6 is regarded as a non-negligible phenomenon in such studies (e.g., Hokoi, et al., 2000; Kočí, et al., 7 2017) and is anticipated from the pore radius assuming thermodynamic equilibrium (Fagerlund, 1973). 8 However, liquid water in porous media can be supercooled and remain in a non-equilibrium liquid 9 state even below the predicted freezing point. Among the studies on deformation and damage due to 10 such frost action, some studies have pointed out the effects of supercooling. For instance, Grübl and 11 Sotkin (1980) observed rapid expansion of cement-based materials accompanied by a sharp rise in 12 temperature during the freezing of supercooled water. In addition, they showed that this rapid 13 expansion had a good correlation with the residual strain after thawing. They considered that ice 14 rapidly growing from the supercooled water can restrict the water movement in the material and cause 15 the development of hydraulic pressure that results in instantaneous and residual expansion, referring 16 to Powers' hypothesis (Powers, 1945). Based on their study, the freezing of supercooled water can 17 affect the mechanical behavior of a material. Moreover, ice rapidly growing from supercooled water 18 may cause more severe frost damage than relatively slow freezing near the thermodynamic equilibrium. 19 Although most of these studies investigated the supercooling effects on cement-based materials, 20 supercooling can also affect the hygrothermal behavior of other building materials. For example, a 21 delay of the start of the freezing process and rapid increase in the temperature of fired clay materials 22 have been observed in both laboratory experiments and outdoor environments (Feng, et al., 2019; Iba, 23 et al., 2016; Wardeh & Perrin, 2006, 2008), which is evidence of the presence of the supercooling 24 phenomenon under various conditions, including the actual weather conditions.

25 Currently, it is becoming more important to understand the mechanisms of the deformation and 26 damage of fired clay materials due to frost actions to deal with the increasing risks of frost damage on 27 masonry walls associated with the internal insulation intended to improve the energy efficiency (Zhou, 28 et al., 2017; Feng, et al., 2019) and preservation of ceramic bricks and tiles used for historical buildings 29 (Iba, et al., 2016). Both fired clay and cement-based materials are considered frost-sensitive. Their 30 frost resistance is highly dependent on the raw materials and manufacturing processes, e.g., mineral 31 composition and firing temperature of fired clay materials (Maage 1984; Sánchez de Rojas et al., 2011) 32 and water cement ratio and air content of cement-based materials. Similar to the concrete, Ranogajec 33 et al. (2012) showed that damage to fired clay materials is caused by mechanisms such as hydraulic 34 pressure, closed container, and ice lens mechanisms (Fagerlund, 1997); however, due to their large 35 permeability, roofing tiles sintered at normal temperatures (around 1000 °C) suffer from the ice lens

36 mechanism rather than the well-known Power's hydraulic pressure theory. In addition, owing to the 37 pressing prosses, the destruction of fired clay materials is characterized by delamination and 38 anisotropic cracks (Perrin et al., 2011).

39 However, despite the great effort to investigate the mechanisms of the deformation and frost 40 damage of fired clay materials (Iba, et al., 2016; Wardeh & Perrin, 2006, 2008, 2011; Ducman, et al., 41 2011; Sánchez de Rojas et al., 2011; Ranogajec et al., 2012), the effects of supercooling on the 42 deformation have not been examined in detail. The effects of supercooling on the deformation of the 43 fired clay materials should be investigated separately from cement-based materials because of the large 44 differences in pore structures and hygrothermal and mechanical properties. In addition, the 45 supercooled water in a fired clay material freezes much faster than that in cement-based materials 46 (Fukui, et al., 2020, 2021), which can lead more significant pressure development in a material.

47 While we examined the hygrothermal behavior of a fired clay material during the freezing of the 48 supercooled water, as presented in previous papers (Fukui, et al., 2020, 2021), we investigated the 49 effects of supercooling on the deformation, as presented herein, using both experimental and numerical 50 approaches. First, we conducted a freeze-thaw experiment to measure the strain evolution of the 51 material during freezing and thawing. Subsequently, we developed a coupled hygrothermal and 52 mechanical model of the freezing and thawing processes, including supercooling. The model was 53 based on a poromechanical approach established by Coussy (2004). Models based on poromechanics 54 have been developed in (Koniorczyk, et al., 2015; Koniorczyk, 2015; Eriksson, et al., 2018; Zeng, et 55 al., 2011; Zeng, et al., 2016) but have been validated only for small cement-based materials with 56 dimensions of several millimeters. Therefore, we validated the model by comparing the calculated 57 strain evolution with the measurement results using a relatively large specimen. Using the model, we 58 examined the processes of water movement, phase change, pressure development, and deformation during freezing, including the supercooling process, and demonstrated the decisive factors of the 59 60 magnitude of the effects of supercooling on the deformation.

61 2 Methods

62 2.1. Experiments

63 2.1.1. Material

64 In this study, the material used was made from clay produced in Aichi Prefecture, Japan, which is

65 commonly used in producing tiles in the area. The sintering temperature of clay was 1000 °C. The

66 material is plated-shaped with a thickness of approximately 20 mm and is considered as transversely

67 isotropic, similar to common roof tiles (Stolecki, et al., 1999).

68 Figure 1 shows the logarithmic differential pore volume distribution of the material measured using 69 mercury intrusion porosimetry (Fukui, et al., 2021). The figure also exhibits the freezing point of water 70 in the pores theoretically determined based on the thermodynamic equilibrium between the ice and 71 liquid water (Brun, et al., 1977). Moreover, for comparison, we showed the pore volume distribution 72 of the cement paste with the water-cement ratio of 0.4 and an age of more than 1 year. The material 73 contained pores with diameters larger than those of cement-based materials (Diamond, 1971; Cook & 74 Hover, 1999). Therefore, most of the water contained in the pores is subject to a lower capillary 75 pressure, and the freezing point depression is not significant.

76 [insert Figure 1]

77 2.1.2. Strain measurement

78 The schematic of the specimen used for strain measurement is shown in Fig. 2. We used a rectangle 79 specimen with a bottom surface of 46.4×94.7 mm and a height of 21.0 mm. The height direction of 80 the specimen corresponded to the thickness direction of the material. Strain gages and thermocouples 81 were attached with cyanoacrylate adhesive to the center of the top surface and one of the sides with a 82 dimension of 21.0×94.7 mm. The strain was measured in a direction that was parallel and normal to 83 the height direction on the side and top surfaces with a dimension of 21.0×94.7 mm, respectively, to 84 check the anisotropy of the material. The employed strain gages were KFLB-5-120-C1-11 R3M3 85 (Kyowa Electronic Instruments Co., Ltd, Japan). After the strain gages and thermocouples were 86 attached, the specimen was vacuum-saturated and then loosely covered with plastic wrap to prevent 87 evaporation from the surfaces but not to constrain the deformation, allowing the movement of liquid 88 water. It was confirmed that the thermal resistance of the plastic wrap was negligible before the experiment. The air temperature in the test chamber was maintained at 293 K (20 °C) for 30 min to 89 90 stabilize the temperature distribution in the specimen before the cooling started. Subsequently, the 91 specimen was cooled at a minimum air temperature of 253 K (-20°C) for 4 h and heated at the 92 maximum air temperature of 293 K (20°C) for 4 h. The experiment consisted of six freeze-thaw cycles. 93 The set points of the air temperature in the test chamber were changed in a stepwise manner at the 94 beginning of the cooling and heating periods. During measurement, the temperature and strain of the 95 specimen and the air temperature in the test chamber were recorded every second.

96 [insert Figure 2]

97 2.2. Coupled hygrothermal and mechanical modeling

Here, we develop a numerical model corresponding to the freeze-thaw experiment to examine thedeformation processes during the freezing of supercooled water.

100 2.2.1. Constitutive equations

Although most of the numerical simulations of the freeze-thaw processes of building materials have been conducted using an isotropic model, it is considered that the anisotropy of the properties of fired clay materials has considerable effects on its mechanical behavior. Therefore, in this study, we developed a model that considered the anisotropy (transverse isotropy) of the elastic modulus and water transfer. The constitutive equations of the saturated porous media are expressed as (Coussy, 2004):

107
$$\boldsymbol{\sigma} = \mathbf{D} \Big[\boldsymbol{\varepsilon} - \boldsymbol{\alpha} \big(T - T_r \big) \Big] - \mathbf{b} p , \qquad (1)$$

108
$$\varphi = \mathbf{b} : \mathbf{\varepsilon} + \frac{p}{N} - \alpha_{\phi} \left(T - T_r \right), \qquad (2)$$

where **b** is the Biot tangent tensor, **D** is the material elastic stiffness tensor [Pa], *N* is the Biot tangent modulus [Pa], *p* is the pressure [Pa], *T* is the temperature [K], *T_r* is the reference temperature [K], **a** is the tensor of the thermal expansion coefficient of the skeleton [K⁻¹], α_{ϕ} is the volumetric thermal expansion coefficient related to the porosity [K⁻¹], ε is the strain tensor, φ is the increment of the porosity, and σ is the total stress tensor [Pa].

For the freezing and thawing of the porous media, the ice and liquid water pressures should be considered separately.

116
$$\boldsymbol{\sigma} = \mathbf{D} \Big[\boldsymbol{\varepsilon} - \boldsymbol{\alpha} \big(T - T_r \big) \Big] - \big(\mathbf{b}_i p_i + \mathbf{b}_1 p_l \big), \qquad (3)$$

117
$$\varphi_i = \mathbf{b}_i : \varepsilon + \frac{p_i}{N_{ii}} + \frac{p_l}{N_{il}} - a_i \left(T - T_r\right) \qquad \varphi_l = \mathbf{b}_l : \varepsilon + \frac{p_i}{N_{li}} + \frac{p_l}{N_{ll}} - a_l \left(T - T_r\right), \tag{4}$$

where a_i is a coefficient related to the volumetric thermal expansion of the pore volume occupied by each phase [K⁻¹] and N_{ii} , N_{il} , N_{li} , and N_{ll} are the generalized Biot coupling moduli [Pa]. Here, the subscripts *i* and *l* represent ice and liquid water, respectively. For simplicity, **b**_i and **b**_l are expressed as proportional values for the saturation *S* of each phase, according to literature (Coussy, 2005; Coussy & Monteiro, 2008).

123
$$\mathbf{b}_i = \mathbf{b}S_i \quad j = i,l \tag{5}$$

124 The anisotropies of **b** and α are ignored in this study. They are represented by values *b* and α , 125 respectively. Therefore, the final form of the constitutive equations used in this study are expressed as

126
$$\boldsymbol{\sigma} = \mathbf{D} \Big[\boldsymbol{\varepsilon} - \boldsymbol{\alpha} \big(T - T_r \big) \mathbf{I} \Big] - b \big(S_i p_i + S_l p_l \big) \mathbf{I} , \qquad (6)$$

127
$$\varphi_{i} = b\varepsilon_{v} + \frac{p_{i}}{N_{il}} + \frac{p_{l}}{N_{il}} - a_{i}\left(T - T_{r}\right) \qquad \varphi_{l} = b\varepsilon_{v} + \frac{p_{i}}{N_{li}} + \frac{p_{l}}{N_{ll}} - a_{l}\left(T - T_{r}\right), \tag{7}$$

128 where *b* is the Biot coefficient, **I** is the second-order unit tensor, α is the thermal expansion coefficient 129 [K⁻¹], and ε_v is the volumetric strain.

130 The poroelastic parameters in Eqs. (6) and (7) to be determined are a_i , a_l , b, N_{ii} , N_{li} , N_{li} , and N_{ll} . We 131 obtained b, N_{ii} , N_{il} , N_{li} , and N_{ll} by assuming that the Young's modulus in the height direction of the specimen was much smaller than that in the normal direction ($E_t \ll E_v$, where E_t and E_v are the Young's 132 133 moduli in the direction that is parallel and normal to the height, respectively) or the strain in the 134 direction normal to the height was considerably small to obtain b, Nii, Nii, Nii, and Nii. This assumption leads to the relationship $b = 1 - E_t/E_s$, where E_s is the Young's modulus of the solid phase. Helmuth 135 136 and Turk (1966) derived the relationship $E_t/E_s = (1 - \phi)^3$ for hardened cement paste, where ϕ is the 137 porosity. Then, N_{ii}, N_{il}, N_{li}, and N_{ll} were calculated using the equations derived by Aichi and Tokunaga 138 (2011). Equation (8) is obtained using the relationship $E_t \ll E_v$.

139
$$\frac{1}{N_{ll}} \approx \frac{b - \phi_0}{E_s} S_l^2 \quad \frac{1}{N_{li}} = \frac{1}{N_{il}} \approx \frac{b - \phi_0}{E_s} S_l S_i \quad \frac{1}{N_{ii}} \approx \frac{b - \phi_0}{E_s} S_i^2$$
(8)

140 where ϕ_0 is the porosity in a reference state.

In (Coussy, 2004), the derivation of a_i and a_l for anisotropic materials were not reported. Given that the anisotropy of the thermal expansion of the solid volume was ignored in this study, we assumed that a_j did not exhibit strong anisotropy. Therefore, a_i and a_l are derived from Eq. (9) by assuming the isotropy of the material (Coussy, 2004).

145
$$a_j = 3\alpha (b - \phi_0) S_j \qquad j = i, l \tag{9}$$

Finally, the main simplifications used in the constitutive equations in this study is summarized as follows:

• The anisotropy of *b* and α was ignored.

152	•	The simplified forms of the poroelastic parameters a_i , a_l , b , N_{ii} , N_{li} , N_{li} , and N_{ll} are given.
153		This is expected since the material used in this study had strong anisotropy, and our
154		main concern was the mechanical behavior in the height direction of the specimen,
155		which is the most deformable.

156 2.2.2. Liquid-ice relationship under equilibrium and non-equilibrium conditions

157 The Clausius–Clapeyron equation derived from the equilibrium of the chemical potential of liquid and 158 ice ($\mu_i = \mu_l$, where μ is the chemical potential) is expressed in Eq. (10) (Coussy & Monteiro, 2009).

$$\frac{p_l}{\rho_l} - \frac{p_i}{\rho_i} = \frac{\Delta s}{\rho_i} \left(T - T_m\right), \tag{10}$$

160 where T_m is the melting point of bulk water [K], Δs is the melting entropy ($\Delta s=1.2$ [MPa/K]), and ρ is

161 the density [kg/m³]. The dependency of ρ_i and ρ_i on p and T is expressed in a linearized form (Coussy,

162 2005; Coussy & Monteiro, 2008).

163
$$\frac{1}{\rho_j} = \frac{1}{\rho_j^0} \left(1 - \frac{p_j}{K_j} + 3\alpha_j \left(T - T_r \right) \right) \qquad j = i, l$$
(11)

164 where *K* is the bulk modulus and ρ^0 is the density in the reference state.

165 S_l can be expected from the pressure difference between ice and liquid under thermodynamic 166 equilibrium conditions. The equation suggested by van Genuchten (1980) is as follows:

167
$$S_{l} = \left[\frac{1}{1 + \left(\beta \left(p_{l} - p_{l}\right)\right)^{n}}\right]^{m}.$$
 (12)

Models presented in (Koniorczyk, et al., 2015; Gawin, et al., 2019) consider the hysteresis during freezing and thawing caused by the difference in the shape of the interface between liquid water and ice. However, we focused on the freezing process, where the water is supercooled, in the calculation. Accordingly, the equilibrium freezing and thawing processes in the calculation were not distinguished, that is, hysteresis was not considered.

173 Under non-equilibrium states, Eqs. (10) and (12) cannot be used because they are based on 174 thermodynamic equilibrium. Therefore, the rate of the increase of ice saturation ($\partial Si/\partial t$) was derived 175 from the general kinetic equation.

$$\frac{dS_i}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f\left(S_i\right),\tag{13}$$

177 where A is a constant $[s^{-1}]$, E_a is the activation energy [J/mol], $f(S_i)$ is a function of the ice saturation $(=S_i^a(1-S_i)^b)$, where a and b are constants), R is the gas constant (= 8.314 [J/(K·mol)]), and t is time 178 179 [s]. The parameters in Eq. (13) were calibrated using the results of differential scanning calorimetry 180 as follows: $A = 9.71 \times 10^{-9} \text{ s}^{-1}$, $E_a = -36694 \text{ J/mol}$, a = 0.68, and b = 1.12 (Fukui, et al., 2021). 181 Models presented in (Koniorczyk, et al., 2015; Gawin, et al., 2019) consider non-equilibrium states 182 (relatively close to the equilibrium). In these models, the Young-Laplace equation was used to relate 183 the current liquid water saturation of a material and the pressure difference between the ice and liquid 184 water. To the best of our knowledge, there are no studies that have reported the applicability of the 185 assumption of the mechanical equilibrium for the large pressure difference and rapid penetration of 186 ice into liquid-filled pores under strong non-equilibrium states, that is, during the freezing of 187 supercooled water. Based on Eq. (6), the evolution of p_i does not significantly contribute to the stress 188 when S_i is not large. In fact, the increase in S_i during the non-equilibrium freezing was 0.11 to 0.14, 189 which will be mentioned in Section 4, and is not significant. Therefore, we used Eq. (12) even under 190 non-equilibrium conditions assuming that the calculation results were not significantly influenced by 191 the relationship between p_i and p_l .

192 *2.2.3. Conservation equations*

- 193 The momentum balance is expressed as
- 194

176

$$\nabla \cdot \mathbf{\sigma} + \mathbf{F} = 0 , \qquad (14)$$

where **F** is the body force vector $[N/m^3]$. **F** = 0 because we did not consider any sources of external force.

197 Equations for the heat and moisture mass conservation can be expressed as follows:

198
$$\frac{\partial}{\partial t} (CT - Hm_i) = \nabla \cdot (\lambda \nabla T), \qquad (15)$$

199
$$\frac{\partial}{\partial t} (m_i + m_l) = \nabla \cdot (\lambda' \nabla p_l), \qquad (16)$$

200 where

201
$$m_i = \rho_i \left(\phi_0 S_i + \varphi_i \right) \quad m_l = \rho_l \left(\phi_0 S_l + \varphi_l \right), \tag{17}$$

$$202 C = c_d \rho_d + c_i m_i + c_l m_l. (18)$$

- 203 Here, c is the specific heat $[J/(kg\cdot K)]$, H is the latent heat of solidification (= 334 × 10³ [J/kg]), λ is
- 204 the tensor of thermal conductivity $[W/(m \cdot K)]$, and λ' is the tensor of moisture permeability related to
- 205 the liquid water pressure gradient $[kg/(m \cdot s \cdot Pa)]$. The subscript *d* represents the bulk material in the
- dry state. C is the volumetric specific heat of the wet material $[J/(m^3 \cdot K)]$, and m_i and m_l are the masses
- 207 of the ice and liquid water, respectively, contained in a unit volume of the bulk material [kg/m³].

208 2.2.4. Calculation methods for freeze-thaw processes including supercooling

- We began the calculation using the temperature above the freezing point to reproduce the temperature distribution in the specimen when freezing started. Therefore, the calculation included three states: unfrozen, non-equilibrium freezing, and equilibrium freezing. The calculation method accounting for these three states was similar to that in previous studies (Fukui, et al., 2020, 2021), in which we developed a hygrothermal model including supercooling processes. However, the conditions under which the state of water changes to another state were slightly different because we accounted for the p_i evolution in this study.
- 216 Figure 3 shows the conditions under which water state changes. While the freezing of a saturated 217 material is expected to start when the temperature drops below T_m under thermodynamic equilibrium conditions, the start of freezing is delayed when the water is supercooled. We set the temperature T_f 218 219 [K] at which the supercooled water started to freeze to a value measured in the freeze-thaw experiment. 220 In addition, previous studies (Fukui, et al., 2020, 2021) reported that the solidification of supercooled 221 water in the fired clay material starts almost simultaneously in a specimen. Therefore, in the 222 calculations, the freezing of a segment is triggered when it comes into contact with a segment 223 containing ice.
- 224 [insert Figure 3]

The S_i of the material rapidly increases after the supercooled water starts freezing, as shown in Eq. (13). On the other hand, S_l decreases based on Eq. (16), and the difference between p_i and p_l changes, as expected from Eq. (12). Furthermore, *T* increases because of the released latent heat, as shown in Eq. (15). The thermodynamic equilibrium of the water in the material is achieved when Eq. (10) is satisfied.

During the heating period, the state of the water in the material changed directly from the equilibrium freezing state to the unfrozen state when S_i decreased to 0.

232 2.2.5. Calculation model, conditions, and numerical solution

233 The calculation model for the strain measurement is shown in Fig. 4. The calculation was performed

two-dimensionally on a cross-section with a size of 40×20 mm under the assumption of the plane

235 strain state. Given that the specimen was symmetric, the calculation was conducted on a quarter of the 236 cross-section, and the two axes of the rectangular coordinate system were set in the directions of the 237 40 mm and 20 mm sides (x and y axes in Fig. 4, respectively). The basic equations were discretized 238 using the Galerkin finite element method for space with 2×2 mm bilinear elements based on the 239 monolithic approach. The calculation results were confirmed to not be dependent on the mesh size by 240 comparing these results using the elements with half sides. T, p_l , and displacement vector **u** [m] were 241 expressed using vectors of the nodal values T_e, p_e, and u_e, respectively, and the shape function N and Nu.

242

243
$$T = \mathbf{NT}_{\mathbf{e}} \quad p_{l} = \mathbf{Np}_{\mathbf{e}} \quad \mathbf{u} = \mathbf{N}_{\mathbf{u}}\mathbf{u}_{\mathbf{e}} \tag{19}$$

244 After the discretization, we obtained the following system of equations:

245
$$\begin{bmatrix}
\mathbf{C}_{\mathrm{TT}} & \mathbf{C}_{\mathrm{Tp}} & \mathbf{C}_{\mathrm{Tu}} \\
\mathbf{C}_{\mathrm{pT}} & \mathbf{C}_{\mathrm{pp}} & \mathbf{C}_{\mathrm{pu}} \\
\mathbf{C}_{\mathrm{uT}} & \mathbf{C}_{\mathrm{up}} & \mathbf{C}_{\mathrm{uu}}
\end{bmatrix} \frac{\partial}{\partial t} \begin{bmatrix}
\mathbf{T}_{\mathrm{e}} \\
\mathbf{p}_{\mathrm{e}} \\
\mathbf{u}_{\mathrm{e}}
\end{bmatrix} , \qquad (20)$$

$$= \begin{bmatrix}
\mathbf{K}_{\mathrm{TT}} & \mathbf{0} & \mathbf{0} \\
\mathbf{0} & \mathbf{K}_{\mathrm{uu}} & \mathbf{0} \\
\mathbf{0} & \mathbf{0} & \mathbf{0}
\end{bmatrix} \begin{bmatrix}
\mathbf{T}_{\mathrm{e}} \\
\mathbf{p}_{\mathrm{e}} \\
\mathbf{u}_{\mathrm{e}}
\end{bmatrix} + \begin{bmatrix}
\mathbf{f}_{\mathrm{T}} \\
\mathbf{f}_{\mathrm{p}} \\
\partial \mathbf{f}_{\mathrm{u}}/\partial t
\end{bmatrix} ,$$

246 where Eq. (6) was differentiated by time. All components in Eq. (20) are presented in the Appendix. 247 The discretization in time was performed using the finite difference method. The forward difference 248 was used and the time step was set to 0.00125 s. We confirmed that the calculation was stable with no

249 oscillations. The program code was developed by the authors using programming language Fortran 90.

250 [insert Figure 4]

251 Table 1 summarizes the initial and boundary conditions. The initial temperature was assumed to be 252 uniform in the material. It was set as the average of the two temperatures measured on the top and side 253 surfaces at the beginning of the freeze-thaw experiment. Considering that the specimen was 254 completely saturated, the initial value of p_i in the material was set to 0 Pa. On the axes of symmetry (x 255 = 0 or y = 0 in Fig. 4), no heat or moisture flow was considered, and the displacement normal to the 256 direction of the axis was restricted. During the experiment, the evaporation of water through the 257 surface of the material was prevented by plastic wrap, but the wrap did not restrict liquid water 258 movement through the surfaces. Therefore, p_l on the surface of the material was set to 0 Pa. The Robin 259 boundary condition with the measured temperature of the air in the test chamber was used to calculate 260 the heat flux density on the surface of the material. The heat transfer coefficient was set to 6.5 261 $[W/(m^2 \cdot K)]$ to ensure that the calculation results of the temperature evolution is in agreement with the 262 measurement results.

	Position	Coordinate	Heat	Moisture	Stress and
		(shown in Fig. 4)			displacement
Initial	Calculation	$0 \le x \le L_x$	Measured	$p_l = 0$	$\mathbf{u} = 0$
condition	area	and $0 \le y \le L_y$	temperature		
Boundary	Axes of	x = 0 or $y = 0$	$\mathbf{Q} \cdot \mathbf{n} = 0$	$\mathbf{J} \cdot \mathbf{n} = 0$	$\mathbf{u} \cdot \mathbf{n} = 0$
condition	the symmetry				
	Material's	$x = L_x$ or $y = L_y$	Q∙n	$p_l = 0$	$\boldsymbol{\sigma} \cdot \boldsymbol{n} = 0$
	surfaces		$=h(T-T_{out})$		

263 **Table 1.** Initial and boundary conditions of the calculation.

264 *h* is the heat transfer coefficient $[W/(m^2 \cdot K)]$; J and Q are vectors of the moisture flow $[kg/(m^2 \cdot s)]$ and heat

flow $[W/m^2]$, respectively; **n** is a unit vector normal to the boundary; T_{out} is the air temperature measured

266 in the test chamber [K]

267 2.2.6 Material properties

Table 2 lists the material properties with constant values. Some of these properties were derived in our previous study (Fukui, et al., 2021). A thermomechanical analysis on an air-dried specimen was conducted to determine α . The shear modulus G_{tv} [Pa] was calculated using the following equation (Hayashi, 1954):

272
$$\frac{1}{G_{tv}} = \frac{4}{E_{45}} - \left(\frac{1}{E_t} + \frac{1}{E_v} - \frac{V_{tv}}{E_t}\right),$$
 (21)

where E_{45} is the Young's modulus in the 45° direction from the height direction [Pa] and v_{tv} is the Poisson's ratio corresponding to the loading in the normal direction. G_{tv} was obtained by assuming

that E_{45} was the average of E and E'. We adopted the value of a brick from (Kumaran, 1996) for c_d .

Property	Unit	Direction	Symbol	Value	Source
Dry density	kg/m ³		ρ_s	1800	Measurement
Water content at vacuum	m ³ /m ³		ϕ_0	0.299	Measurement
saturation					
(regarded as porosity)					
Specific heat	J/(kg·K)		C_d	840	(Kumaran,
					1996)
Young modulus	Ра	Height	E_t	3×10^{9}	Measurement
		Normal to the height	E_{v}	11 × 10 ⁹	Measurement
Shear modulus	Ра		G_{tv}	5×10^9	Equation (21)
Poisson's ratio		*1	V _{tv}	0.12	Measurement
			V_{vt}	0.44	
			$V_{\nu\nu}$	0.19	
Thermal expansion	K-1		α	2.91 ×	Measurement
coefficient				10^{-6}	

Table 2. Material properties with a constant value.

282

^{*1} A symbol v_{mn} represents the Poisson's ratio that corresponds to an expansion in direction *n* when a contraction is applied in direction *m*.

The relationship between air pressure p_a [Pa] and p_l in an unsaturated material and between p_i and p_l in a frozen material can be expressed using the Young–Laplace equation:

$$p_a - p_l = 2\frac{\gamma_{al}}{r}, \qquad (22)$$

$$p_i - p_l = 2\frac{\gamma_{il}}{r}, \qquad (23)$$

where *r* is the pore radius [m], and γ_{al} and γ_{ll} are the interfacial energies between the air and liquid water (= 73 × 10⁻³ J/m² at 20 °C) and between the ice and liquid water (= 33 × 10⁻³ J/m² at 0 °C (Ketcham & Hobbs, 1969)), respectively. The difference in p_a-p_l in Eq. (22) is the negative value of the capillary pressure p_c [Pa]. Moreover, S_l of a frozen material can be obtained from the adsorption isotherm of an unfrozen and unsaturated material using Eqs. (22) and (23).

288
$$S_{l} = \left[\frac{1}{1 + \left(\beta \frac{\gamma_{al}}{\gamma_{il}} \left(p_{i} - p_{l}\right)\right)^{n}}\right]^{m}$$
(24)

289 The adsorption isotherm of the employed material in the unfrozen state was derived in our previous

study (Fukui, et al., 2021) based on gas adsorption and pressure plate methods. The constants β , *n*, and *m* in Eq. (12) were determined to be 1.1×10^{-6} Pa⁻¹, 2.3, and 0.57, respectively. The hysteresis of S_l was not considered in the calculations.

Data on the thermal conductivity and moisture permeability of the material were available in our previous study (Fukui, et al., 2021). For simplicity, we ignored the anisotropy of λ . Therefore, the thermal conductivity of the material was represented by one value λ . The following linear relationship was derived from the measurement of the thermal conductivity of the air-dried and wet materials using the transient hot wire method (Fukui, et al., 2021):

298 $\lambda = 1.26S_l + 0.55$. (25)

Equation (26) was used to calculate the thermal conductivity during the freezing and thawingprocesses.

301
$$\lambda = 1.26 \left(S_l + \frac{\lambda_i}{\lambda_l} S_i \right) + 0.55$$
(26)

302 In this calculation, we considered the anisotropy of the water permeability, Young's modulus, and 303 Poisson's ratio. We obtained the moisture permeability in the direction normal to the height direction 304 using the Boltzmann transformation and gamma-ray attenuation method (Fukui, et al., 2021). However, 305 the gamma-ray attenuation method is not suitable for measurements in the height direction because 306 the material was too thin (only approximately 20 mm). Therefore, we conducted mass measurements 307 during water absorption to compare the water absorption coefficient and average moisture diffusivity, 308 which was proportional to the square of the water absorption coefficient (Kumaran, 1999), in the 309 parallel and normal directions. Based on the results, the average moisture diffusivity was 2.1 times 310 smaller in the height direction than in the normal direction. Then, we assumed that the water 311 permeability in the height direction was 2.1 times smaller in the entire saturation range.

Finally, we present the equilibrium relationship derived from Eq. (24) and the moisture permeability in Fig. 5. The liquid water content ψ_l [m³/m³] and water chemical potential μ [J/kg] for free water in the previous study (Fukui, et al., 2021) were re-expressed using the saturation degree of liquid water S_l (= ψ_l / ϕ) and water pressure (= $\mu \rho_l$), respectively, to calculate these properties.

316 [insert Figure 5]

317 In this subsection, the full set of material properties used to conduct the numerical analysis is shown.

318 Therefore, the heat transfer coefficient between the specimen surfaces and air in the test chamber was

319 the only calibrated parameter. In the next section, we verify the numerical model by comparing the

320 calculated and measured strains of the freeze-thaw experiment. Then, we investigate the supercooling

321 effects on the deformation of the fired clay material.

322 **3 Results**

323 **3.1. Freeze-thaw experiment**

Figures 6 and 7 present the results of the strain measurements during the first freeze-thaw cycle. The strain evolution during subsequent cycles is not exhibited in the figures because it did not change drastically, except for the development of the plastic strain. From the figures, the strain measured both on the side (in the y-axis direction) and top surface (in the x-axis direction) are shown, but the temperature on the top surface is omitted in Fig. 6 because it was almost the same as that on the side surface. Moreover, we presented the strain referring to the values at a temperature of 20 °C during the cooling process, as indicated by the triangle.

331 [insert Figure 6]

332 [insert Figure 7]

The results of the strain measurement show expansion due to freezing. The start of the expansion was delayed because of supercooling until the temperature reached -4.8 °C, as shown by the dotted squares in Fig. 6 (a). The temperature rapidly increased to slightly less than 0 °C at the same time as the strain increased. The increase in strain was only a small value (0.0479×10^{-3} in the y-axis direction). The strain in the y-axis direction then decreased and increased as the temperature decreased during the cooling period. Conversely, the strain measured in the x-axis direction continued to decrease after expansion, which indicates the strong anisotropy of the deformation.

340 **3.2.** Coupled hygrothermal and mechanical simulation

341 Figure 8 shows the comparison of the calculation results, which do not include the supercooling 342 process with the measurement results. In this calculation, the non-equilibrium freezing state in Fig. 3 343 was omitted during the cooling process, and the state of water directly changed from unfrozen to 344 equilibrium freezing. Therefore, Eq. (10) was used throughout the freezing process. The rapid 345 temperature rise and expansion associated with the freezing of the supercooled water could not be reproduced although the trends of the calculated and measured temperature and strain evolutions are 346 347 generally in agreement, except for the strain evolutions on the top surface (in the x-axis direction). 348 This difference on the top surface may be attributed to the anisotropy of the Biot coefficient; however, 349 the deformation of the top surface is small and its influence on the deformation of the side surface is 350 considered insignificant. The difference in the magnitude of the measured and calculated strain 351 evolution on the side surface may be due to inaccuracies in the material properties used in the 352 calculation, such as the water permeability and adsorption isotherm.

353 [insert Figure 8]

354 Figures 9 and 10 show the calculated temperature and strain using a model that includes 355 supercooling. In addition, the calculated ice saturation evolution using the model including the 356 supercooling process are presented in Figs. 11 and 12. The ice saturation at two different distances 357 from the center of the specimen along the x-axis is shown ((x, y) = (0.005, 0) and (0.015, 0) in the coordinate shown in Fig. 4). The calculated temperature adequately reproduced the rapid rise observed 358 359 in the experiment while the calculation results did not significantly change except for those when the 360 supercooled water started freezing (at an elapsed time of approximately 1 h and 30 min). During the 361 increase of the temperature, the calculated strain also rapidly increased as the measured strain although subsequent decrease in the calculated strain was much faster than the measured strain. The rapid 362 363 increase in the calculated temperature and strain was 7-8 min later than that of the measured temperature and strain, which is probably because of imperfections in the material properties used in 364 365 the calculation, such as the thermal conductivity, adsorption isotherm, and estimation of the heat 366 transfer coefficient between the surfaces of the specimen and air in the test chamber.

- 367 [insert Figure 9]
- 368 [insert Figure 10]
- 369 [insert Figure 11]
- 370 [insert Figure 12]

371 4 Discussion

372 4.1. Effects of supercooling on the deformation of a fired clay material

373 During the experiment, the increase in strain during the rapid temperature increase was much smaller 374 than that associated with the subsequent temperature decrease in the y-axis direction. Based on these 375 results, the effects of supercooling on the deformation of the fired clay material were small.

The temperature of the specimen rapidly increased to approximately 0 °C during the experiment. A further increase in temperature was not observed, which indicated that the rapid ice formation stopped at that time. The temperature that was reached when the temperature stopped increasing was interpreted as the equilibrium temperature without supercooling effects (Grübl & Sotkin, 1980). Therefore, it is expected that the ice growth and resulting expansion were restricted by the equilibrium freezing temperature as the upper limit of the temperature rise accompanied by ice growth in the experiment. 383 Grübl and Sotkin (1980), who conducted freeze-thaw experiments using cement-based materials, 384 showed that the remaining expansion after thawing had a good correlation with the rapid expansion 385 associated with non-equilibrium freezing. However, in our experiment, the residual strain after thawing (1.28×10^{-3}) was considerably larger than the rapid increase in the strain (0.0479×10^{-3}) in 386 387 the y-axis direction. Therefore, it is considered that the supercooling effects on the damage were also 388 small in the fired clay material, and the subsequent expansion associated with the temperature decrease 389 caused the residual strain instead. The supercooled water in the fired clay material freezes much faster than that in cement-based materials (Fukui, et al., 2020, 2021). As discussed by Grübl and Sotkin 390 391 (1980), the ice rapidly growing from the supercooled water can restrict the water movement in a 392 material and cause development of the hydraulic pressure resulting in instantaneous and residual 393 expansion. Therefore, it is possible that greater pressure occurs in the fired clay material because of 394 the more rapid volume change of the water than that in cement-based materials. The reasons for the 395 small expansion of the fired clay material caused by the freezing of supercooled water are discussed 396 in the following subsection.

4.2. Mechanisms of the deformation with and without supercooling

The varieties of ice saturation in the material were relatively small, and 11%–14 % of water solidified during the non-equilibrium freezing, as shown in Figs. 11 and 12. This amount of freezing water can cause significant liquid pressure if the material is sealed (Coussy & Monteiro, 2009). Therefore, it is expected that the pressure developed by freezing was relaxed because of the transfer of liquid water toward the surfaces of the material.

We conducted an additional calculation in which the water permeability was set to a 0.1 times larger value than that in the calculation described previously to examine the contribution of the water transfer to the strain and pressure evolution in the material. Figures 13 and 14 show the calculated liquid pressure and strain evolution, respectively. A much greater pressure takes place, and it takes longer to relax the pressure in the case of a small water permeability when the liquid pressure increases and then drops rapidly when using the original water permeability. Furthermore, Fig. 14 shows that the increase in strain is much greater than that in the original calculation shown in Fig. 9.

410 [insert Figure 13]

411 [insert Figure 14]

Therefore, the pressure developed owing to the rapid ice growth during the freezing of the supercooled water can be relaxed by the liquid water transfer, and it does not cause significant deformation if the material has sufficient water permeability. It is also probable that the difference in 415 the water permeability can cause a difference in the magnitude of the supercooling effects among the 416 materials.

417 Finally, Fig. 15 shows the calculated evolution of the liquid water and ice pressure during the entire 418 freezing and thawing processes using the model including the supercooling process and original water 419 permeability. In contrast to the pressure evolution during the non-equilibrium freezing shown in Fig. 420 13, the pressure develops significantly during equilibrium freezing as the temperature decreases and 421 ice saturation increases. The water permeability of the material decreases, accompanied by a decrease 422 in the liquid water saturation, preventing water from escaping toward the surface of the material. In 423 addition, the ice pressure is even higher than that of liquid water because of the relationship expressed 424 in Eq. (10). Therefore, the pressure evolution caused by the small water permeability after the 425 considerable amount of water solidified, and the ice pressure increases because of the chemical 426 potential equilibrium causing deformation in the fired clay material, rather than rapid ice growth 427 during non-equilibrium freezing.

428 [insert Figure 15]

429 5 Conclusion

430 In this study, we investigated the effects of supercooling on the deformation of a fired clay material 431 using strain measurements and coupled hygrothermal and mechanical simulations based on the 432 poromechanical approach. During the experiment, the specimen was maintained to be saturated by 433 preventing evaporation using a plastic wrap with negligible thermal resistance. The wrap loosely 434 covered the specimen surfaces to avoid constraining the deformation, allowing liquid water seepage. 435 During the measurement, the temperature rapidly increased, and an increase in the strain associated with the freezing of the supercooled water was apparent. However, this increase in the strain was only 436 small (0.0479×10^{-3} in the thickness direction of the material). Conversely, after the rapid freezing of 437 438 the supercooled water stopped, the strain in the thickness direction of the material increased 439 significantly as the temperature decreased. From these results, we concluded that the effects of 440 supercooling on deformation are small on the fired clay material compared to cement-based materials 441 reported in literature (Grübl & Sotkin, 1980). In addition, the supercooling effects on the damage were 442 small and the subsequent expansion associated with the temperature decrease caused the residual strain 443 because the residual strain after thawing was considerably larger than the rapid increase in the strain 444 associated with the freezing of the supercooled water.

Based on the comparison of the results of the strain measurement and calculated pressure and strain evolution, the reasons for the small impacts of supercooling on the deformation of the fired clay material are as follows:

448 The temperature of a material with a relatively large volume (i.e., specimen for the 449 strain measurement) rapidly increases after the supercooled water starts freezing 450 because the released latent heat cannot easily escape from the surfaces of the material. 451 This rapid temperature increase is then restricted by the equilibrium freezing 452 temperature, resulting in the restriction of the growth of ice and the resulting pressure. 453 Based on the comparison of the calculation results with different moisture 454 permeabilities, the small impact of supercooling on deformation can be due to the 455 sufficiently large moisture permeability of the fired clay material. The increased pressure associated with the freezing of the supercooled water is relaxed by the water 456 457 transfer toward the surfaces of the material, even though the supercooled water in the 458 fired clay material freezes much faster than that in cement-based materials (shown in 459 our previous study (Fukui, et al., 2021)). It is also shown that the effect of supercooling 460 can be more significant if a material has a low moisture permeability.

Further studies need to be conducted to reveal the impacts of supercooling on the deformation and damage of materials with various material properties, especially of those with low water permeability (e.g., cement-based materials). The freezing rates and degree of the freezing point depression also affects the significance of the supercooling, and their combined effects should be discussed. The strain measurements and numerical simulations were conducted under single temperature and moisture conditions. However, studies under conditions closer to the outdoor environment should be conducted to evaluate the effects of supercooling on real building components.

468 Appendix

469 The components in Eq. (20) are defined as follows:

470
$$\mathbf{C}_{\mathrm{TT}} = \int_{\Omega} \frac{\partial}{\partial T} (CT - H_{ii} m_i) \mathbf{N}^T \mathbf{N} d\Omega, \qquad (A.1)$$

471
$$\mathbf{C}_{\mathbf{T}\mathbf{p}} = \int_{\Omega} \frac{\partial}{\partial p_i} (CT - Hm_i) \mathbf{N}^T \mathbf{N} d\Omega, \qquad (A.2)$$

472
$$\mathbf{C}_{\mathrm{Tu}} = \int_{\Omega} \frac{\partial}{\partial \varepsilon_{\nu}} (CT - Hm_i) \mathbf{N}^T \mathbf{m}^T \mathbf{B} d\Omega , \qquad (A.3)$$

473
$$\mathbf{C}_{\mathbf{pT}} = \int_{\Omega} \frac{\partial}{\partial T} (m_i + m_l) \mathbf{N}^T \mathbf{N} d\Omega, \qquad (A.4)$$

474
$$\mathbf{C}_{\mathbf{pp}} = \int_{\Omega} \frac{\partial}{\partial p_l} (m_l + m_l) \mathbf{N}^T \mathbf{N} d\Omega, \qquad (A.5)$$

475
$$\mathbf{C}_{\mathbf{pu}} = \int_{\Omega} \frac{\partial}{\partial \mathcal{E}_{\nu}} (m_i + m_l) \mathbf{N}^T \mathbf{m}^T \mathbf{B} d\Omega, \qquad (A.6)$$

476
$$\mathbf{C}_{\mathbf{uT}} = -\int_{\Omega} \left[\alpha \mathbf{B}^{\mathrm{T}} \mathbf{D} + b \frac{\partial}{\partial T} (S_{i} p_{i} + S_{l} p_{l}) \mathbf{B}^{\mathrm{T}} \right] \mathbf{m} \mathbf{N} d\Omega, \qquad (A.7)$$

$$\mathbf{C}_{\mathbf{up}} = -\int_{\Omega} b \frac{\partial}{\partial p_l} \left(S_l p_l + S_l p_l \right) \mathbf{B}^{\mathrm{T}} \mathbf{m} \mathbf{N} d\Omega$$
(A.8)

478
$$\mathbf{C}_{\mathbf{u}\mathbf{u}} = \int_{\Omega} \mathbf{B}^{\mathrm{T}} \mathbf{D} \mathbf{B} d\Omega, \qquad (A.9)$$

479
$$\mathbf{K}_{\mathrm{TT}} = \int_{\Omega} \nabla \mathbf{N}^{T} \lambda \nabla \mathbf{N} d\Omega + \int_{\Gamma} h \mathbf{N}^{T} d\Gamma , \qquad (A.10)$$

480
$$\mathbf{K}_{pp} = \int_{\Omega} \nabla \mathbf{N}^{T} \boldsymbol{\lambda}' \nabla \mathbf{N} d\Omega, \qquad (A.11)$$

481 where Ω and Γ are the domain of an element and its boundary, respectively, and

$$\mathbf{m} = \begin{bmatrix} 1 & 1 & 0 \end{bmatrix}^T, \tag{A.12}$$

483
$$\mathbf{B} = \begin{bmatrix} \frac{\partial N_1}{\partial x_1} & 0 & \frac{\partial N_2}{\partial x_1} & 0 & \frac{\partial N_3}{\partial x_1} & 0 & \frac{\partial N_4}{\partial x_1} & 0 \\ 0 & \frac{\partial N_1}{\partial x_2} & 0 & \frac{\partial N_2}{\partial x_2} & 0 & \frac{\partial N_3}{\partial x_2} & 0 & \frac{\partial N_4}{\partial x_2} \\ \frac{\partial N_1}{\partial x_2} & \frac{\partial N_1}{\partial x_1} & \frac{\partial N_2}{\partial x_2} & \frac{\partial N_2}{\partial x_1} & \frac{\partial N_3}{\partial x_2} & \frac{\partial N_4}{\partial x_1} & \frac{\partial N_4}{\partial x_2} \end{bmatrix}.$$
(A.13)

484 During the unfrozen and equilibrium freezing states

485
$$\mathbf{f}_{\mathbf{T}} = -\int_{\Gamma} (Q - hT_{out}) \mathbf{N}^{T} d\Gamma, \qquad (A.15)$$

486
$$\mathbf{f}_{\mathbf{p}} = -\int_{\Gamma} J \mathbf{N}^{T} d\Gamma , \qquad (A.16)$$

487
$$\frac{\partial \mathbf{f}_{\mathbf{u}}}{\partial t} = \frac{\partial}{\partial t} \int_{\Gamma} \mathbf{N}_{\mathbf{u}}^{T} \mathbf{t} d\Gamma , \qquad (A.17)$$

488 where **t** is the external force vector [N/m²]. During the non-equilibrium freezing state, $\partial S_i/\partial t$ was

directly given by Eq. (13). In this case, Eqs. (A.15) to (A.17) were altered by Eqs. (A.18) to (A.20).

490
$$\mathbf{f}_{\mathrm{T}} = -\int_{\Gamma} (Q - \alpha T_{out}) \mathbf{N}^{T} d\Gamma - \int_{\Omega} \frac{\partial}{\partial S_{i}} (CT - Hm_{i}) \frac{\partial S_{i}}{\partial t} \mathbf{N}^{T} \mathbf{N} d\Omega$$
(A.18)

491
$$\mathbf{f}_{\mathbf{p}} = -\int_{\Gamma} J \mathbf{N}^{T} d\Gamma - \int_{\Omega} \frac{\partial}{\partial S_{i}} (m_{i} + m_{i}) \frac{\partial S_{i}}{\partial t} \mathbf{N}^{T} d\Omega$$
(A.19)

492
$$\frac{\partial \mathbf{f}_{\mathbf{u}}}{\partial t} = \frac{\partial}{\partial t} \int_{\Gamma} \mathbf{N}^{T} \mathbf{t} d\Gamma + \int_{\Omega} b \frac{\partial}{\partial S_{i}} (S_{i} p_{i} + S_{i} p_{i}) \frac{\partial S_{i}}{\partial t} \mathbf{B}^{T} \mathbf{m}^{T} d\Omega$$
(A.20)

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0 20	
0.15	
0.10	
0.05	
0.00	
0.001	
	0.20 0.15 0.10 0.05 0.00 0.001









Water saturation



Nater permeability [10⁻¹¹ kg/(m·s·Pa)]



(a)







(a)







Solid lines: experiment; Dotted lines: calculation



Solid lines: experiment; Dotted lines: calculation



Elapsed time [h: min.]

(b)

Solid lines: experiment; Dotted lines: calculation



(a)

Solid lines: experiment; Dotted lines: calculation



Elapsed time [h: min.]

(b)

Solid lines: experiment; Dotted lines: calculation





lce saturation





0.15







$\lambda' \times 0.1 (5 \text{ mm})$ $> \lambda' \times 0.1 (15 mm)$ Vate $\lambda' \times 1(5 \text{ mm})$ $\lambda' \times 1$ (15 mm) igue. 1:35 1:36 1:37

Elapsed time [h: min.]



Solid lines: experiment; Dotted lines: calculation



Elapsed time [h: min.]



(a)



(b)