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**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, Gröbl 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 processes, 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  
59 during freezing, including the supercooling process, and demonstrated the decisive factors of the  
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  $46.4 \times 94.7$  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  $21.0 \times 94.7$  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  $21.0 \times 94.7$  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  
89 experiment. The air temperature in the test chamber was maintained at 293 K (20 °C) for 30 min to  
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**

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

100 *2.2.1. Constitutive equations*

101 Although most of the numerical simulations of the freeze-thaw processes of building materials have  
 102 been conducted using an isotropic model, it is considered that the anisotropy of the properties of fired  
 103 clay materials has considerable effects on its mechanical behavior. Therefore, in this study, we  
 104 developed a model that considered the anisotropy (transverse isotropy) of the elastic modulus and  
 105 water transfer. The constitutive equations of the saturated porous media are expressed as (Coussy,  
 106 2004):

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

$$108 \quad \varphi = \mathbf{b} : \boldsymbol{\varepsilon} + \frac{P}{N} - \alpha_\phi(T - T_r), \quad (2)$$

109 where  $\mathbf{b}$  is the Biot tangent tensor,  $\mathbf{D}$  is the material elastic stiffness tensor [Pa],  $N$  is the Biot tangent  
 110 modulus [Pa],  $p$  is the pressure [Pa],  $T$  is the temperature [K],  $T_r$  is the reference temperature [K],  $\boldsymbol{\alpha}$  is  
 111 the tensor of the thermal expansion coefficient of the skeleton [ $\text{K}^{-1}$ ],  $\alpha_\phi$  is the volumetric thermal  
 112 expansion coefficient related to the porosity [ $\text{K}^{-1}$ ],  $\boldsymbol{\varepsilon}$  is the strain tensor,  $\varphi$  is the increment of the  
 113 porosity, and  $\boldsymbol{\sigma}$  is the total stress tensor [Pa].

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

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

$$117 \quad \varphi_i = \mathbf{b}_i : \boldsymbol{\varepsilon} + \frac{P_i}{N_{ii}} + \frac{P_l}{N_{il}} - a_i(T - T_r) \quad \varphi_l = \mathbf{b}_l : \boldsymbol{\varepsilon} + \frac{P_i}{N_{li}} + \frac{P_l}{N_{ll}} - a_l(T - T_r), \quad (4)$$

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

123 
$$\mathbf{b}_j = \mathbf{b}S_j \quad j = i, l \quad (5)$$

124 The anisotropies of  $\mathbf{b}$  and  $\boldsymbol{\alpha}$  are ignored in this study. They are represented by values  $b$  and  $\alpha$ ,  
 125 respectively. Therefore, the final form of the constitutive equations used in this study are expressed as

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

127 
$$\varphi_i = b\varepsilon_v + \frac{P_i}{N_{ii}} + \frac{P_l}{N_{il}} - a_i(T - T_r) \quad \varphi_l = b\varepsilon_v + \frac{P_i}{N_{li}} + \frac{P_l}{N_{ll}} - a_l(T - T_r), \quad (7)$$

128 where  $b$  is the Biot coefficient,  $\mathbf{I}$  is the second-order unit tensor,  $\alpha$  is the thermal expansion coefficient  
 129  $[\text{K}^{-1}]$ , and  $\varepsilon_v$  is the volumetric strain.

130 The poroelastic parameters in Eqs. (6) and (7) to be determined are  $a_i$ ,  $a_l$ ,  $b$ ,  $N_{ii}$ ,  $N_{il}$ ,  $N_{li}$ , 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  
 132 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  
 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  $b$ ,  $N_{ii}$ ,  $N_{il}$ ,  $N_{li}$ , and  $N_{ll}$ . This assumption  
 135 leads to the relationship  $b = 1 - E_t/E_s$ , where  $E_s$  is the Young's modulus of the solid phase. Helmuth  
 136 and Turk (1966) derived the relationship  $E_t/E_s = (1 - \phi)^3$  for hardened cement paste, where  $\phi$  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 
$$\frac{1}{N_{ll}} \approx \frac{b - \phi_0}{E_s} S_l^2 \quad \frac{1}{N_{li}} = \frac{1}{N_{il}} \approx \frac{b - \phi_0}{E_s} S_l S_i \quad \frac{1}{N_{ii}} \approx \frac{b - \phi_0}{E_s} S_i^2 \quad (8)$$

140 where  $\phi_0$  is the porosity in a reference state.

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

145 
$$a_j = 3\alpha(b - \phi_0)S_j \quad j = i, l \quad (9)$$

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

- 148
  - The plastic deformation of the material was not considered.
  - 149 •  $\mathbf{b}_i$  and  $\mathbf{b}_l$  were set to be proportional to  $S_i$  and  $S_l$ , respectively, as shown in Eq. (5)
  - 150 (Coussy, 2005; Coussy & Monteiro, 2008).

- 151           • The anisotropy of  $b$  and  $\alpha$  was ignored.  
 152           • The simplified forms of the poroelastic parameters  $a_i$ ,  $a_l$ ,  $b$ ,  $N_{ii}$ ,  $N_{il}$ ,  $N_{li}$ , 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 ( $\mu_l = \mu_i$ , where  $\mu$  is the chemical potential) is expressed in Eq. (10) (Coussy & Monteiro, 2009).

$$159 \quad \frac{p_l}{\rho_l} - \frac{p_i}{\rho_i} = \frac{\Delta s}{\rho_i} (T - T_m), \quad (10)$$

160   where  $T_m$  is the melting point of bulk water [K],  $\Delta s$  is the melting entropy ( $\Delta s = 1.2$  [MPa/K]), and  $\rho$  is  
 161   the density [ $\text{kg/m}^3$ ]. The dependency of  $\rho_i$  and  $\rho_l$  on  $p$  and  $T$  is expressed in a linearized form (Coussy,  
 162   2005; Coussy & Monteiro, 2008).

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

164   where  $K$  is the bulk modulus and  $\rho^0$  is the density in the reference state.

165    $S_i$  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:

$$167 \quad S_i = \left[ \frac{1}{1 + (\beta(p_i - p_l))^n} \right]^m. \quad (12)$$

168   Models presented in (Koniorczyk, et al., 2015; Gawin, et al., 2019) consider the hysteresis during  
 169   freezing and thawing caused by the difference in the shape of the interface between liquid water and  
 170   ice. However, we focused on the freezing process, where the water is supercooled, in the calculation.  
 171   Accordingly, the equilibrium freezing and thawing processes in the calculation were not distinguished,  
 172   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 ( $\partial S_i / \partial t$ ) was derived  
 175   from the general kinetic equation.



176 
$$\frac{dS_i}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(S_i), \quad (13)$$

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  
 178 ( $=S_i^a(1 - S_i)^b$ , where  $a$  and  $b$  are constants),  $R$  is the gas constant ( $= 8.314$  [J/(K·mol)]), and  $t$  is time  
 179 [s]. The parameters in Eq. (13) were calibrated using the results of differential scanning calorimetry  
 180 as follows:  $A = 9.71 \times 10^{-9} s^{-1}$ ,  $E_a = -36694$  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 
$$\nabla \cdot \boldsymbol{\sigma} + \mathbf{F} = \mathbf{0}, \quad (14)$$

195 where  $\mathbf{F}$  is the body force vector [N/m<sup>3</sup>].  $\mathbf{F} = \mathbf{0}$  because we did not consider any sources of external  
 196 force.

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

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

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

200 where

201 
$$m_i = \rho_i (\phi_0 S_i + \varphi_i) \quad m_l = \rho_l (\phi_0 S_l + \varphi_l), \quad (17)$$

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

203 Here,  $c$  is the specific heat [ $\text{J}/(\text{kg}\cdot\text{K})$ ],  $H$  is the latent heat of solidification ( $= 334 \times 10^3$  [ $\text{J}/\text{kg}$ ]),  $\lambda$  is  
204 the tensor of thermal conductivity [ $\text{W}/(\text{m}\cdot\text{K})$ ], and  $\lambda'$  is the tensor of moisture permeability related to  
205 the liquid water pressure gradient [ $\text{kg}/(\text{m}\cdot\text{s}\cdot\text{Pa})$ ]. The subscript  $d$  represents the bulk material in the  
206 dry state.  $C$  is the volumetric specific heat of the wet material [ $\text{J}/(\text{m}^3\cdot\text{K})$ ], 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 [ $\text{kg}/\text{m}^3$ ].

#### 208 2.2.4. Calculation methods for freeze–thaw processes including supercooling

209 We began the calculation using the temperature above the freezing point to reproduce the temperature  
210 distribution in the specimen when freezing started. Therefore, the calculation included three states:  
211 unfrozen, non-equilibrium freezing, and equilibrium freezing. The calculation method accounting for  
212 these three states was similar to that in previous studies (Fukui, et al., 2020, 2021), in which we  
213 developed a hygrothermal model including supercooling processes. However, the conditions under  
214 which the state of water changes to another state were slightly different because we accounted for the  
215  $p_i$  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  
218 conditions, the start of freezing is delayed when the water is supercooled. We set the temperature  $T_f$   
219 [ $\text{K}$ ] 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]

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

230 During the heating period, the state of the water in the material changed directly from the  
231 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  
234 two-dimensionally on a cross-section with a size of  $40 \times 20$  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  $2 \times 2$  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  $\mathbf{u}$  [m] were  
 241 expressed using vectors of the nodal values  $\mathbf{T}_e$ ,  $\mathbf{p}_e$ , and  $\mathbf{u}_e$ , respectively, and the shape function  $\mathbf{N}$  and  
 242  $\mathbf{N}_u$ .

$$243 \quad T = \mathbf{N}\mathbf{T}_e \quad p_l = \mathbf{N}\mathbf{p}_e \quad \mathbf{u} = \mathbf{N}_u\mathbf{u}_e \quad (19)$$

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

$$245 \quad \begin{bmatrix} C_{TT} & C_{Tp} & C_{Tu} \\ C_{pT} & C_{pp} & C_{pu} \\ C_{uT} & C_{up} & C_{uu} \end{bmatrix} \frac{\partial}{\partial t} \begin{bmatrix} \mathbf{T}_e \\ \mathbf{p}_e \\ \mathbf{u}_e \end{bmatrix}, \quad (20)$$

$$= \begin{bmatrix} \mathbf{K}_{TT} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{K}_{uu} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} \end{bmatrix} \begin{bmatrix} \mathbf{T}_e \\ \mathbf{p}_e \\ \mathbf{u}_e \end{bmatrix} + \begin{bmatrix} \mathbf{f}_T \\ \mathbf{f}_p \\ \partial \mathbf{f}_u / \partial t \end{bmatrix}$$

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  $p_l$  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<sup>2</sup>·K)] to ensure that the calculation results of the temperature evolution is in agreement with the  
 262 measurement results.

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

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

264  $h$  is the heat transfer coefficient [ $\text{W}/(\text{m}^2 \cdot \text{K})$ ];  $\mathbf{J}$  and  $\mathbf{Q}$  are vectors of the moisture flow [ $\text{kg}/(\text{m}^2 \cdot \text{s})$ ] and heat  
 265 flow [ $\text{W}/\text{m}^2$ ], respectively;  $\mathbf{n}$  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

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

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

273 where  $E_{45}$  is the Young's modulus in the  $45^\circ$  direction from the height direction [Pa] and  $\nu_{tv}$  is the  
 274 Poisson's ratio corresponding to the loading in the normal direction.  $G_{tv}$  was obtained by assuming  
 275 that  $E_{45}$  was the average of  $E$  and  $E'$ . We adopted the value of a brick from (Kumaran, 1996) for  $c_d$ .

276 **Table 2.** Material properties with a constant value.

Property	Unit	Direction	Symbol	Value	Source
Dry density	kg/m <sup>3</sup>		$\rho_s$	1800	Measurement
Water content at vacuum saturation (regarded as porosity)	m <sup>3</sup> /m <sup>3</sup>		$\phi_0$	0.299	Measurement
Specific heat	J/(kg·K)		$c_d$	840	(Kumaran, 1996)
Young modulus	Pa	Height	$E_t$	$3 \times 10^9$	Measurement
		Normal to the height	$E_v$	$11 \times 10^9$	Measurement
Shear modulus	Pa		$G_{tv}$	$5 \times 10^9$	Equation (21)
Poisson's ratio		*1	$\nu_{tv}$	0.12	Measurement
			$\nu_{vt}$	0.44	
			$\nu_{vv}$	0.19	
Thermal expansion coefficient	K <sup>-1</sup>		$\alpha$	$2.91 \times 10^{-6}$	Measurement

277 \*1 A symbol  $\nu_{mn}$  represents the Poisson's ratio that corresponds to an expansion in direction  $n$  when a  
 278 contraction is applied in direction  $m$ .

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

281 
$$p_a - p_l = 2 \frac{\gamma_{al}}{r}, \quad (22)$$

282 
$$p_i - p_l = 2 \frac{\gamma_{il}}{r}, \quad (23)$$

283 where  $r$  is the pore radius [m], and  $\gamma_{al}$  and  $\gamma_{il}$  are the interfacial energies between the air and liquid  
 284 water ( $= 73 \times 10^{-3}$  J/m<sup>2</sup> at 20 °C) and between the ice and liquid water ( $= 33 \times 10^{-3}$  J/m<sup>2</sup> at 0 °C  
 285 (Ketcham & Hobbs, 1969)), respectively. The difference in  $p_a - p_l$  in Eq. (22) is the negative value of  
 286 the capillary pressure  $p_c$  [Pa]. Moreover,  $S_l$  of a frozen material can be obtained from the adsorption  
 287 isotherm of an unfrozen and unsaturated material using Eqs. (22) and (23).

288 
$$S_l = \left[ \frac{1}{1 + \left( \beta \frac{\gamma_{al}}{\gamma_{il}} (p_i - p_l) \right)^n} \right]^m \quad (24)$$

289 The adsorption isotherm of the employed material in the unfrozen state was derived in our previous  
 290 study (Fukui, et al., 2021) based on gas adsorption and pressure plate methods. The constants  $\beta$ ,  $n$ , and  
 291  $m$  in Eq. (12) were determined to be  $1.1 \times 10^{-6} \text{ Pa}^{-1}$ , 2.3, and 0.57, respectively. The hysteresis of  $S_l$   
 292 was not considered in the calculations.

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

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

299 Equation (26) was used to calculate the thermal conductivity during the freezing and thawing  
 300 processes.

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

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.

312 Finally, we present the equilibrium relationship derived from Eq. (24) and the moisture  
 313 permeability in Fig. 5. The liquid water content  $\psi_l$  [ $\text{m}^3/\text{m}^3$ ] and water chemical potential  $\mu$  [J/kg] for  
 314 free water in the previous study (Fukui, et al., 2021) were re-expressed using the saturation degree of  
 315 liquid water  $S_l (= \psi_l / \phi)$  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**

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

331 [insert Figure 6]

332 [insert Figure 7]

333 The results of the strain measurement show expansion due to freezing. The start of the expansion  
334 was delayed because of supercooling until the temperature reached  $-4.8$  °C, as shown by the dotted  
335 squares in Fig. 6 (a). The temperature rapidly increased to slightly less than 0 °C at the same time as  
336 the strain increased. The increase in strain was only a small value ( $0.0479 \times 10^{-3}$  in the y-axis direction).  
337 The strain in the y-axis direction then decreased and increased as the temperature decreased during  
338 the cooling period. Conversely, the strain measured in the x-axis direction continued to decrease after  
339 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  
346 reproduced although the trends of the calculated and measured temperature and strain evolutions are  
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  
358 coordinate shown in Fig. 4). The calculated temperature adequately reproduced the rapid rise observed  
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  
362 subsequent decrease in the calculated strain was much faster than the measured strain. The rapid  
363 increase in the calculated temperature and strain was 7–8 min later than that of the measured  
364 temperature and strain, which is probably because of imperfections in the material properties used in  
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.

376 The temperature of the specimen rapidly increased to approximately 0 °C during the experiment.  
377 A further increase in temperature was not observed, which indicated that the rapid ice formation  
378 stopped at that time. The temperature that was reached when the temperature stopped increasing was  
379 interpreted as the equilibrium temperature without supercooling effects (Grübl & Sotkin, 1980).  
380 Therefore, it is expected that the ice growth and resulting expansion were restricted by the equilibrium  
381 freezing temperature as the upper limit of the temperature rise accompanied by ice growth in the  
382 experiment.



383 Gröbl 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  
386 thawing ( $1.28 \times 10^{-3}$ ) was considerably larger than the rapid increase in the strain ( $0.0479 \times 10^{-3}$ ) in  
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  
390 than that in cement-based materials (Fukui, et al., 2020, 2021). As discussed by Gröbl and Sotkin  
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.

#### 397 **4.2. Mechanisms of the deformation with and without supercooling**

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

403 We conducted an additional calculation in which the water permeability was set to a 0.1 times  
404 larger value than that in the calculation described previously to examine the contribution of the water  
405 transfer to the strain and pressure evolution in the material. Figures 13 and 14 show the calculated  
406 liquid pressure and strain evolution, respectively. A much greater pressure takes place, and it takes  
407 longer to relax the pressure in the case of a small water permeability when the liquid pressure increases  
408 and then drops rapidly when using the original water permeability. Furthermore, Fig. 14 shows that  
409 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]

412 Therefore, the pressure developed owing to the rapid ice growth during the freezing of the  
413 supercooled water can be relaxed by the liquid water transfer, and it does not cause significant  
414 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  
436 with the freezing of the supercooled water was apparent. However, this increase in the strain was only  
437 small ( $0.0479 \times 10^{-3}$  in the thickness direction of the material). Conversely, after the rapid freezing of  
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.

445 Based on the comparison of the results of the strain measurement and calculated pressure and strain  
446 evolution, the reasons for the small impacts of supercooling on the deformation of the fired clay  
447 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  
456 pressure associated with the freezing of the supercooled water is relaxed by the water  
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.

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

## 468 **Appendix**

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

$$470 \quad \mathbf{C}_{TT} = \int_{\Omega} \frac{\partial}{\partial T} (CT - H_i m_i) \mathbf{N}^T \mathbf{N} d\Omega, \quad (\text{A.1})$$

$$471 \quad \mathbf{C}_{Tp} = \int_{\Omega} \frac{\partial}{\partial p_l} (CT - H m_i) \mathbf{N}^T \mathbf{N} d\Omega, \quad (\text{A.2})$$

$$472 \quad \mathbf{C}_{Tu} = \int_{\Omega} \frac{\partial}{\partial \varepsilon_v} (CT - H m_i) \mathbf{N}^T \mathbf{m}^T \mathbf{B} d\Omega, \quad (\text{A.3})$$

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

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

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

476 
$$\mathbf{C}_{uT} = - \int_{\Omega} \left[ \alpha \mathbf{B}^T \mathbf{D} + b \frac{\partial}{\partial T} (S_i p_i + S_l p_l) \mathbf{B}^T \right] \mathbf{m} \mathbf{N} d\Omega, \quad (\text{A.7})$$

477 
$$\mathbf{C}_{up} = - \int_{\Omega} b \frac{\partial}{\partial p_l} (S_i p_i + S_l p_l) \mathbf{B}^T \mathbf{m} \mathbf{N} d\Omega, \quad (\text{A.8})$$

478 
$$\mathbf{C}_{uu} = \int_{\Omega} \mathbf{B}^T \mathbf{D} \mathbf{B} d\Omega, \quad (\text{A.9})$$

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

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

481 where  $\Omega$  and  $\Gamma$  are the domain of an element and its boundary, respectively, and

482 
$$\mathbf{m} = [1 \quad 1 \quad 0]^T, \quad (\text{A.12})$$

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

484 During the unfrozen and equilibrium freezing states

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

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

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

488 where  $\mathbf{t}$  is the external force vector [N/m<sup>2</sup>]. During the non-equilibrium freezing state,  $\partial S_i / \partial t$  was

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

$$490 \quad \mathbf{f}_T = -\int_{\Gamma} (Q - \alpha T_{out}) \mathbf{N}^T d\Gamma - \int_{\Omega} \frac{\partial}{\partial S_i} (CT - Hm_i) \frac{\partial S_i}{\partial t} \mathbf{N}^T \mathbf{N} d\Omega \quad (\text{A.18})$$

$$491 \quad \mathbf{f}_p = -\int_{\Gamma} J \mathbf{N}^T d\Gamma - \int_{\Omega} \frac{\partial}{\partial S_i} (m_i + m_i) \frac{\partial S_i}{\partial t} \mathbf{N}^T d\Omega \quad (\text{A.19})$$

$$492 \quad \frac{\partial \mathbf{f}_u}{\partial t} = \frac{\partial}{\partial t} \int_{\Gamma} \mathbf{N}^T t d\Gamma + \int_{\Omega} b \frac{\partial}{\partial S_i} (S_i p_i + S_i p_l) \frac{\partial S_i}{\partial t} \mathbf{B}^T \mathbf{m}^T d\Omega \quad (\text{A.20})$$

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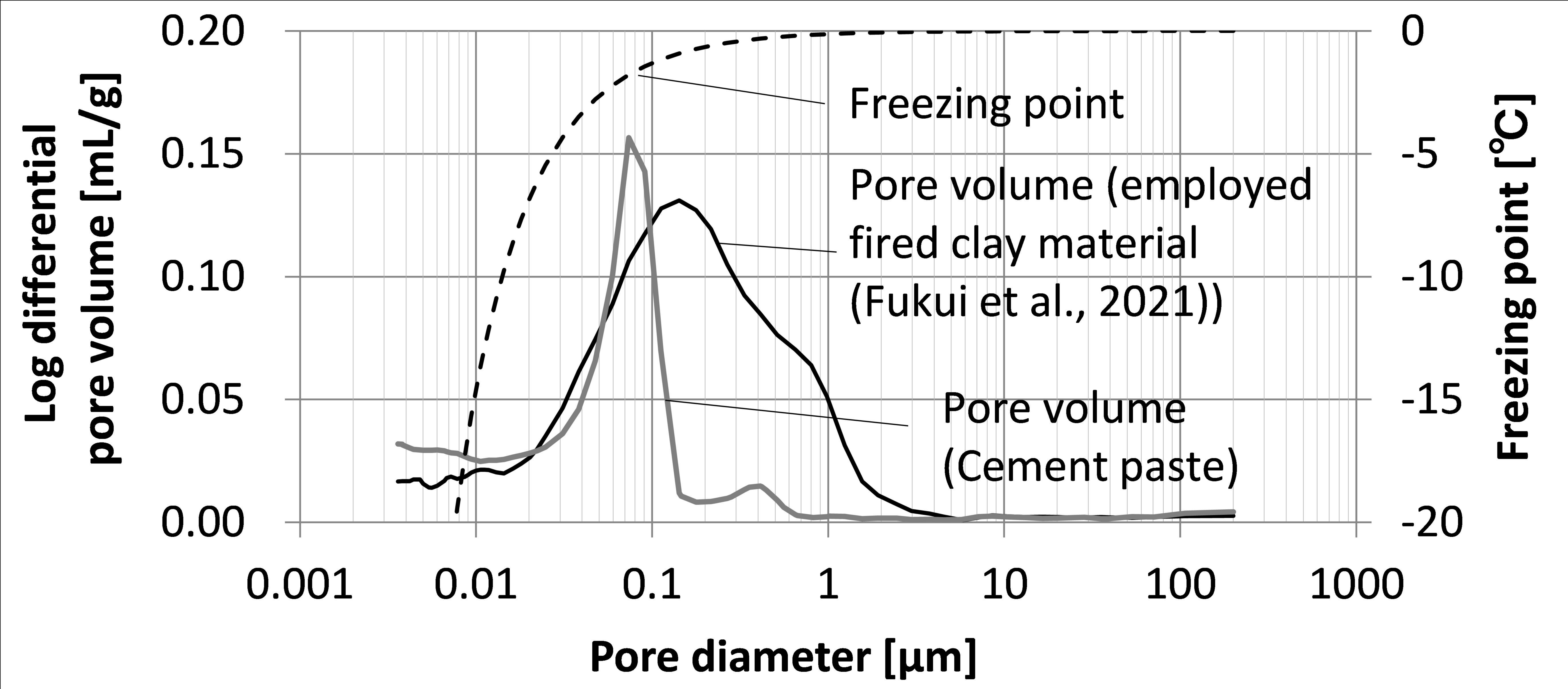
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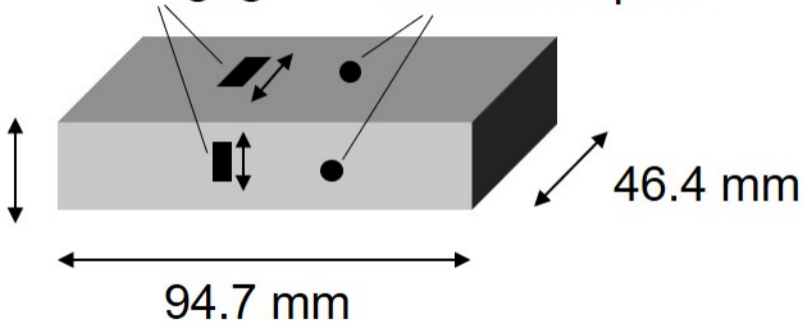


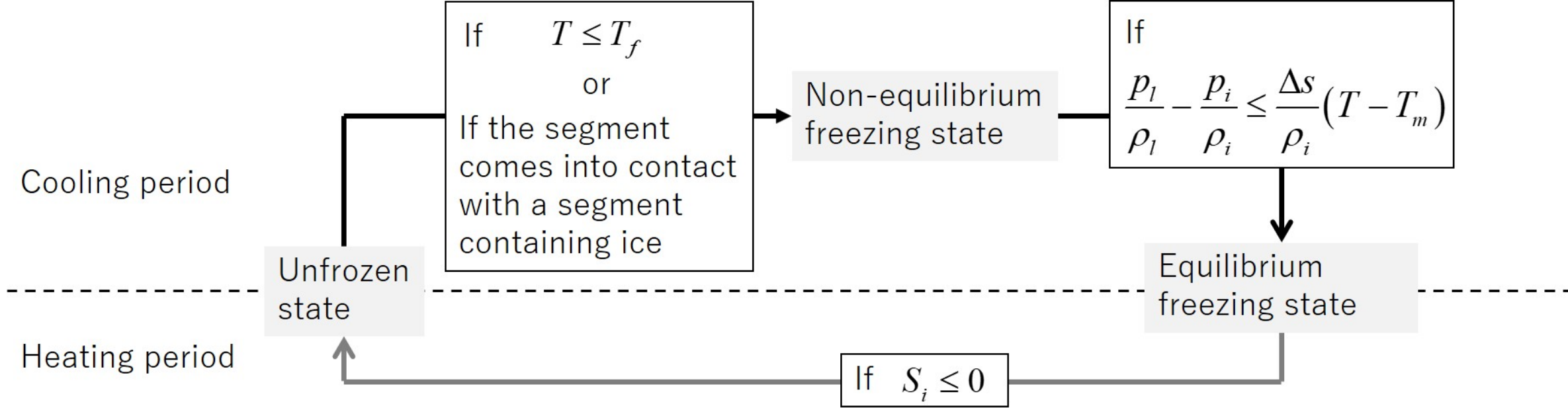




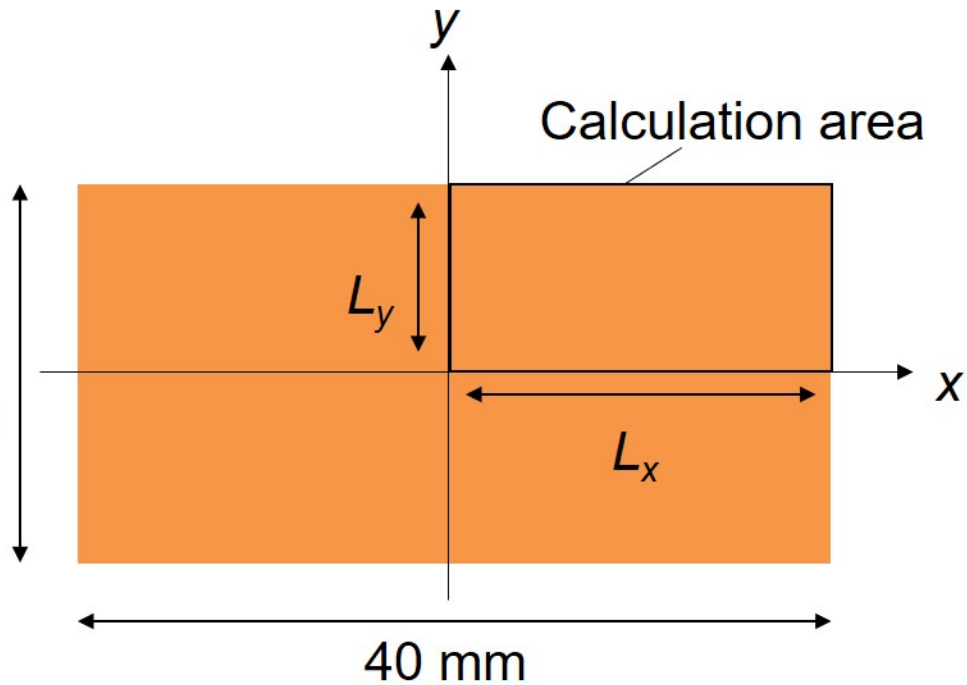
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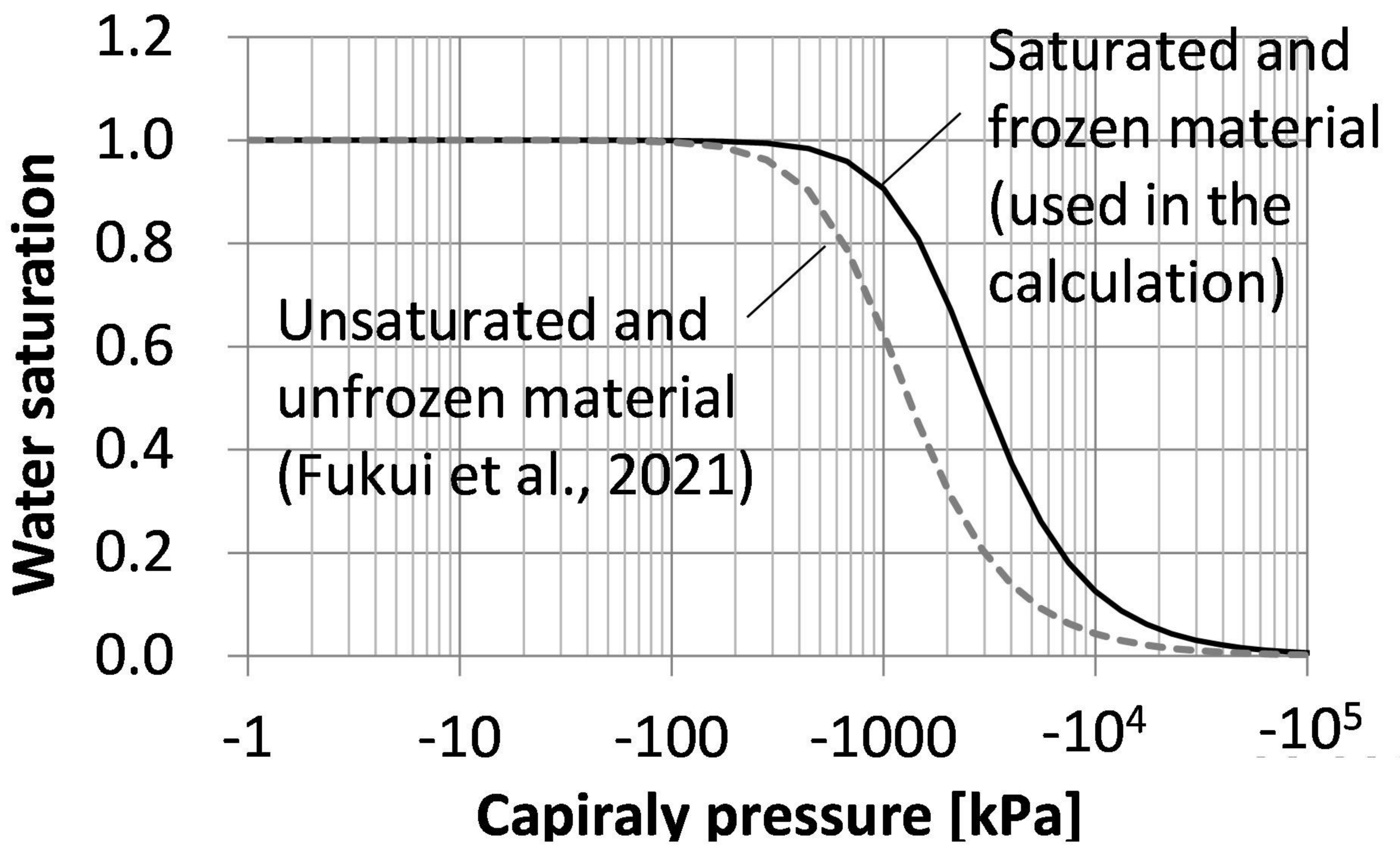
Strain gages      Thermocouples



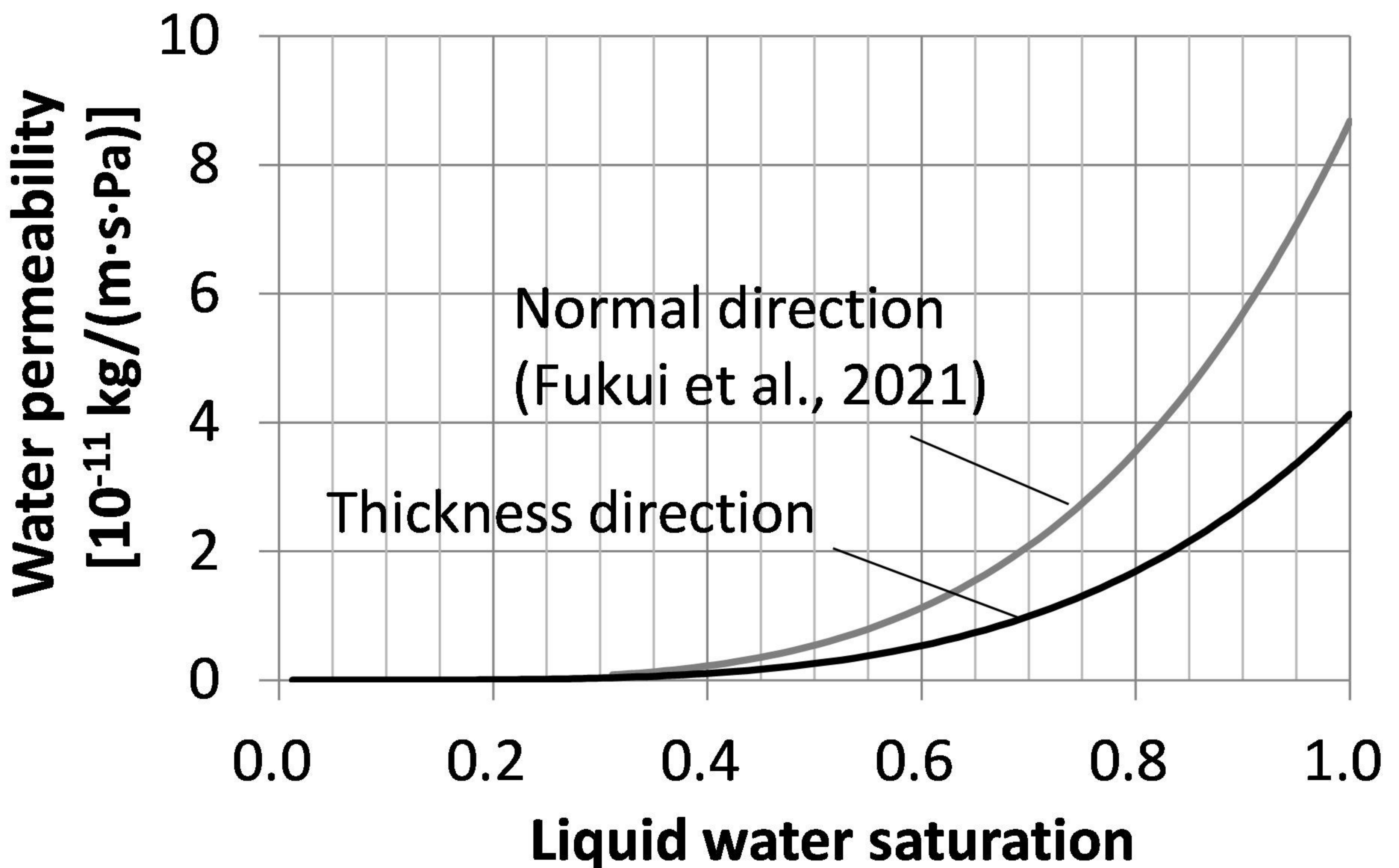


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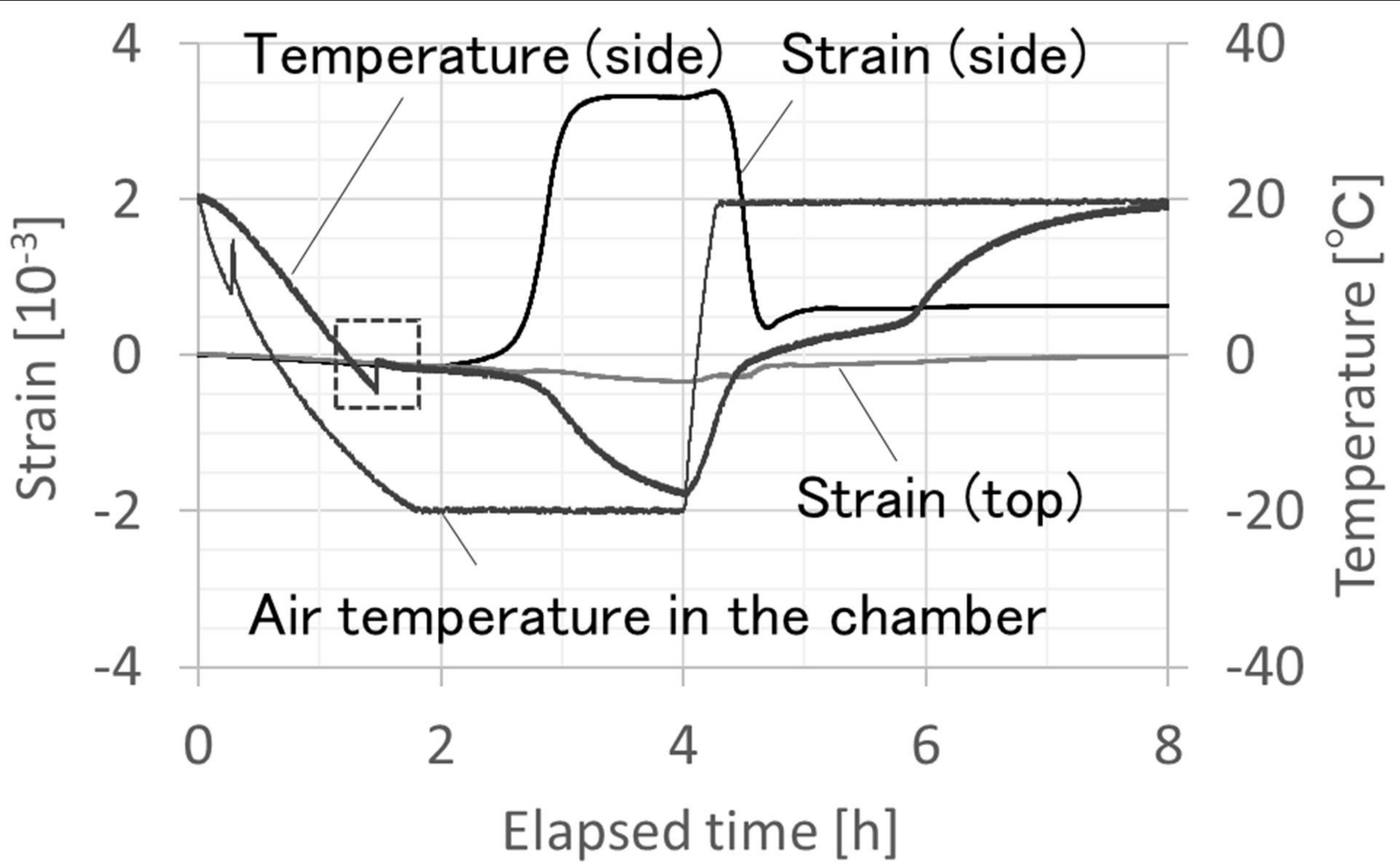




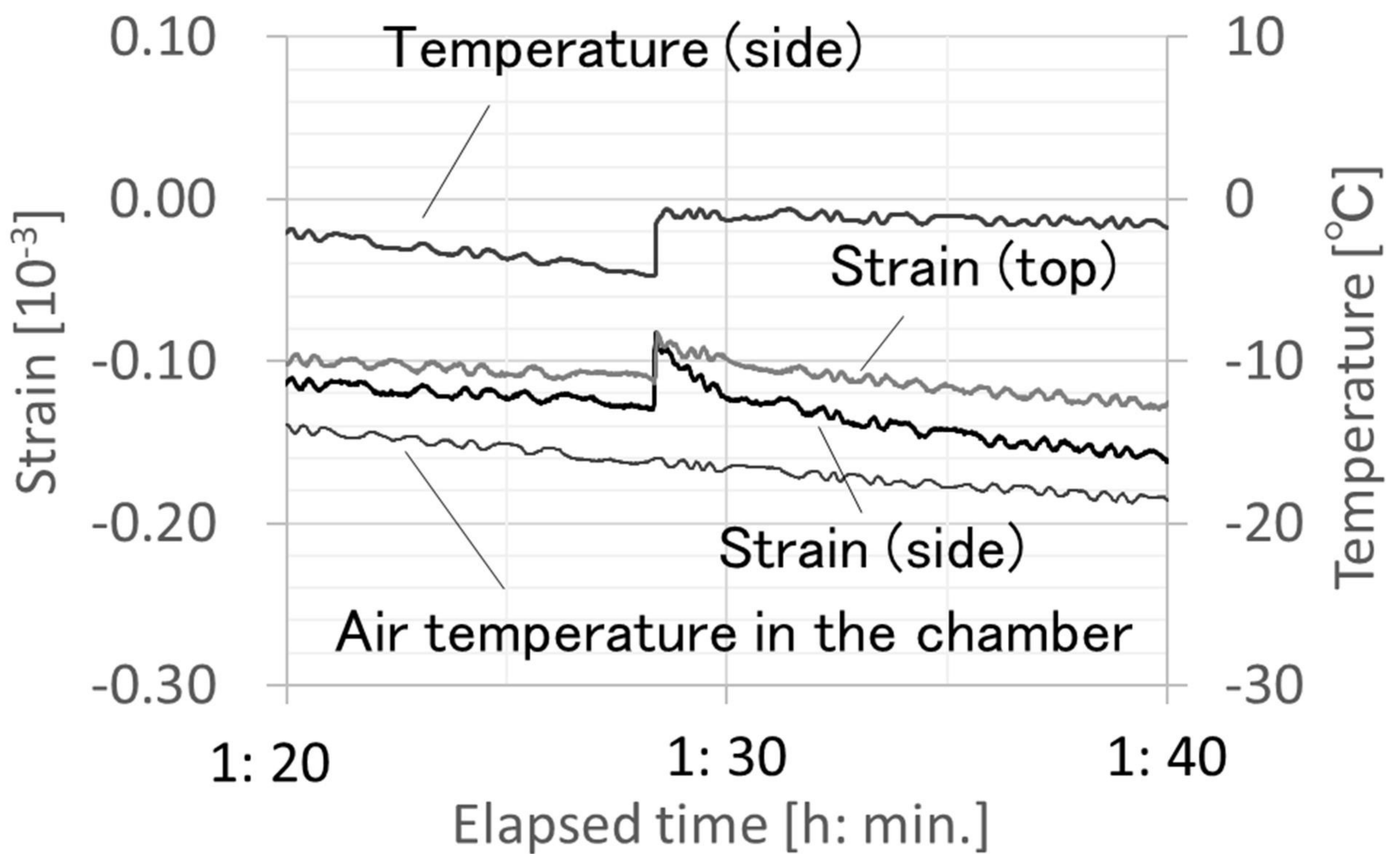
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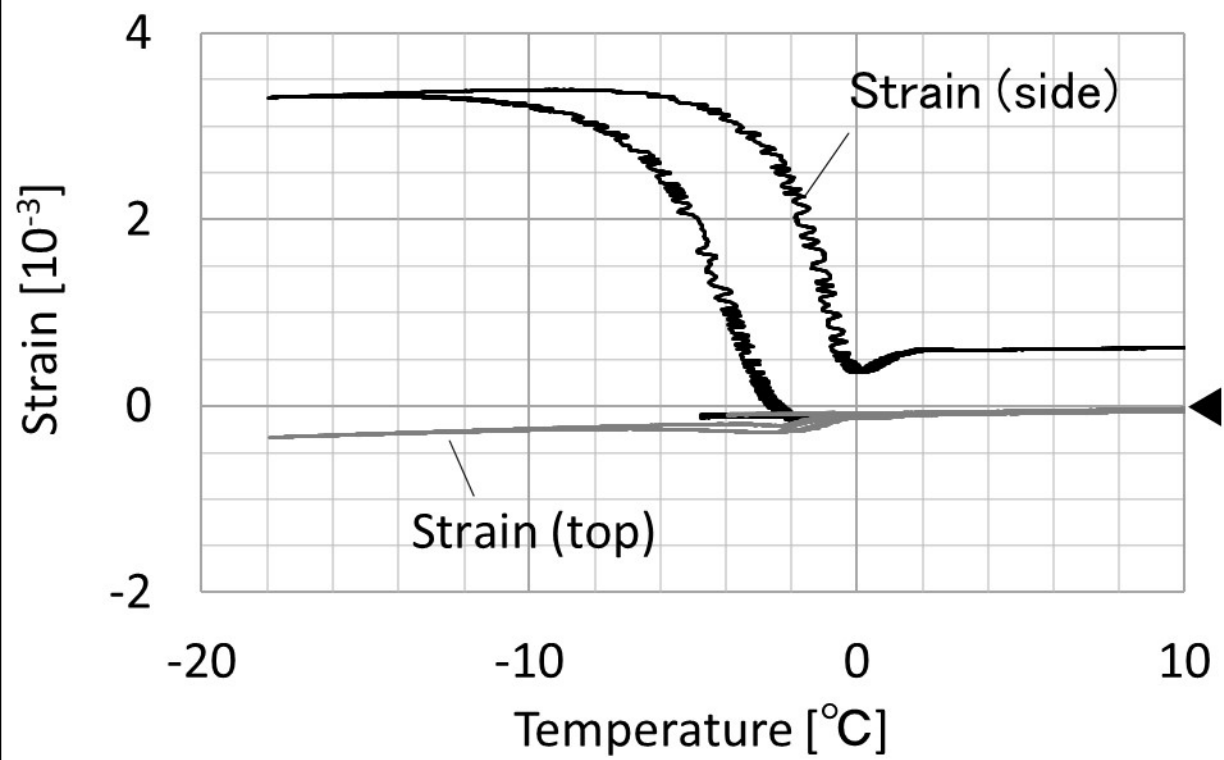
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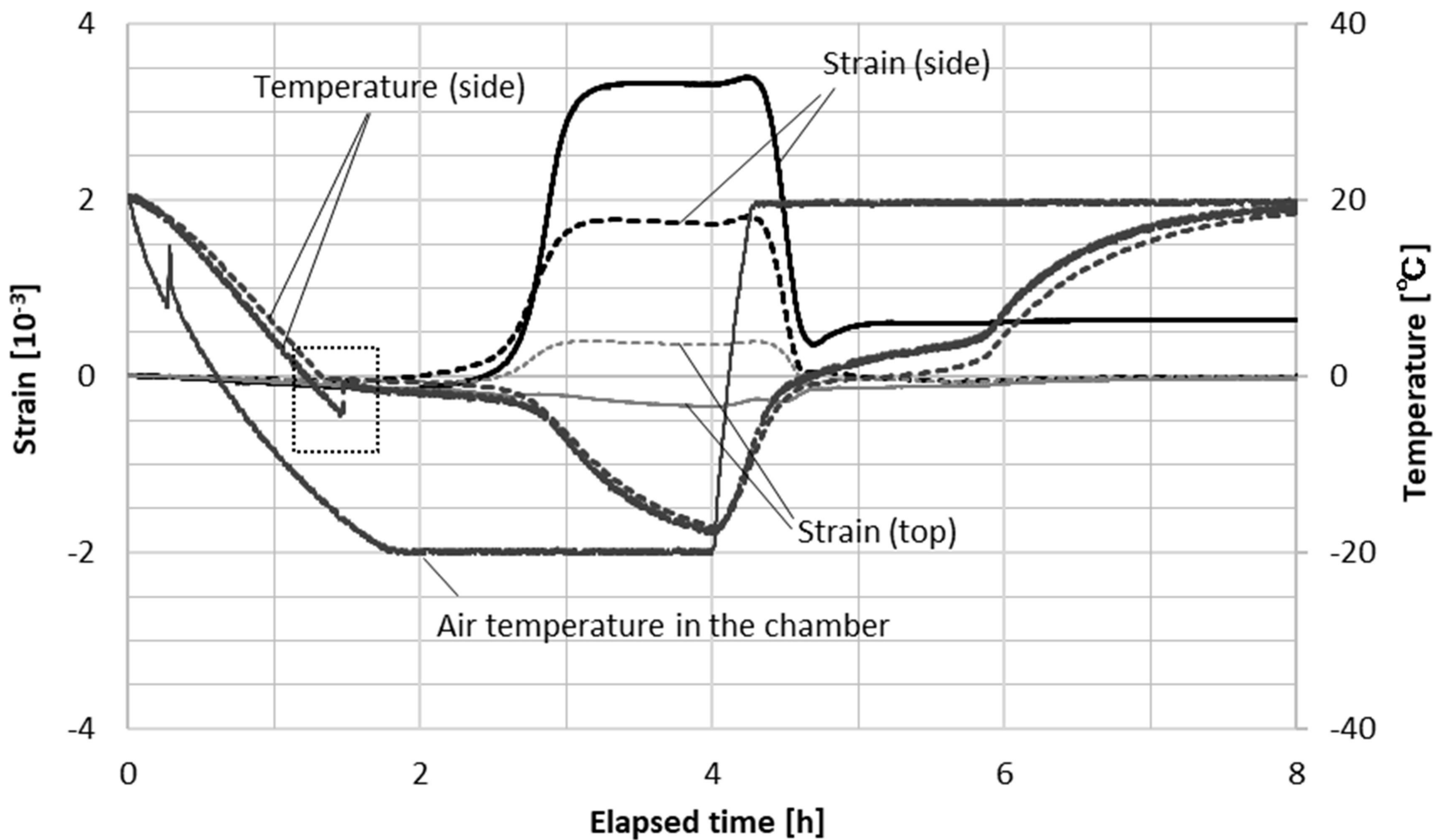
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(b)

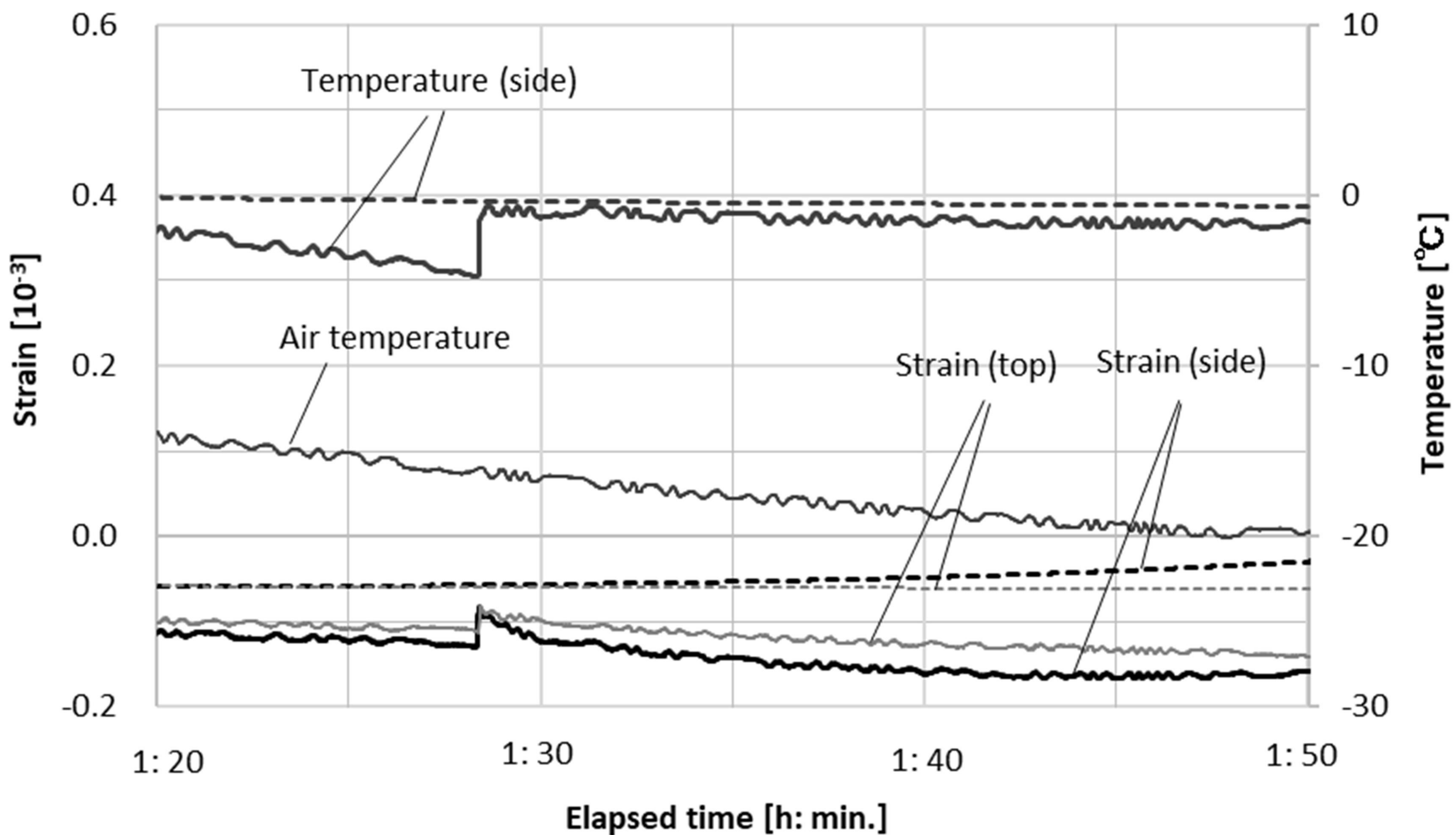


Solid lines: experiment; Dotted lines: calculation



(a)

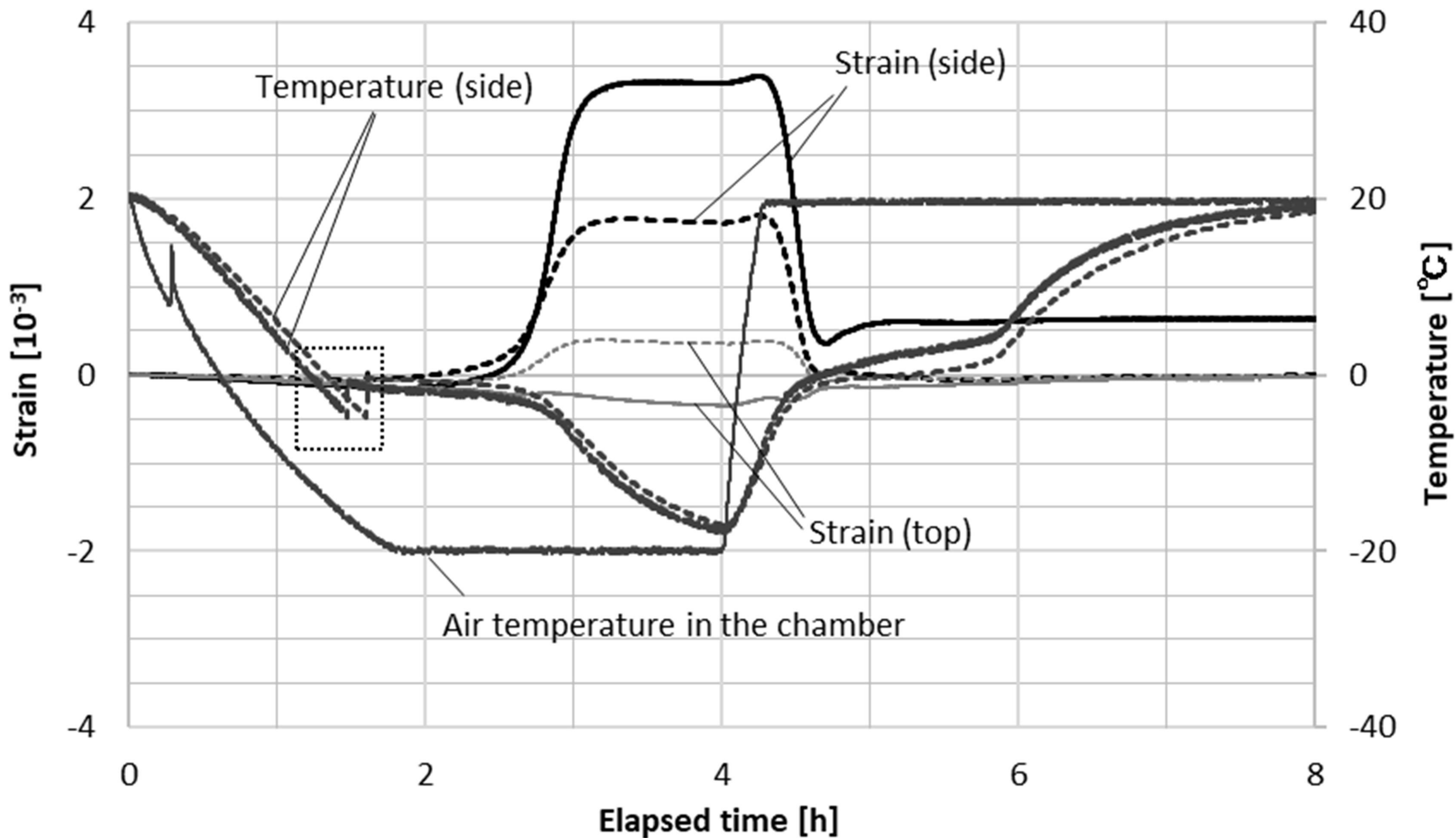
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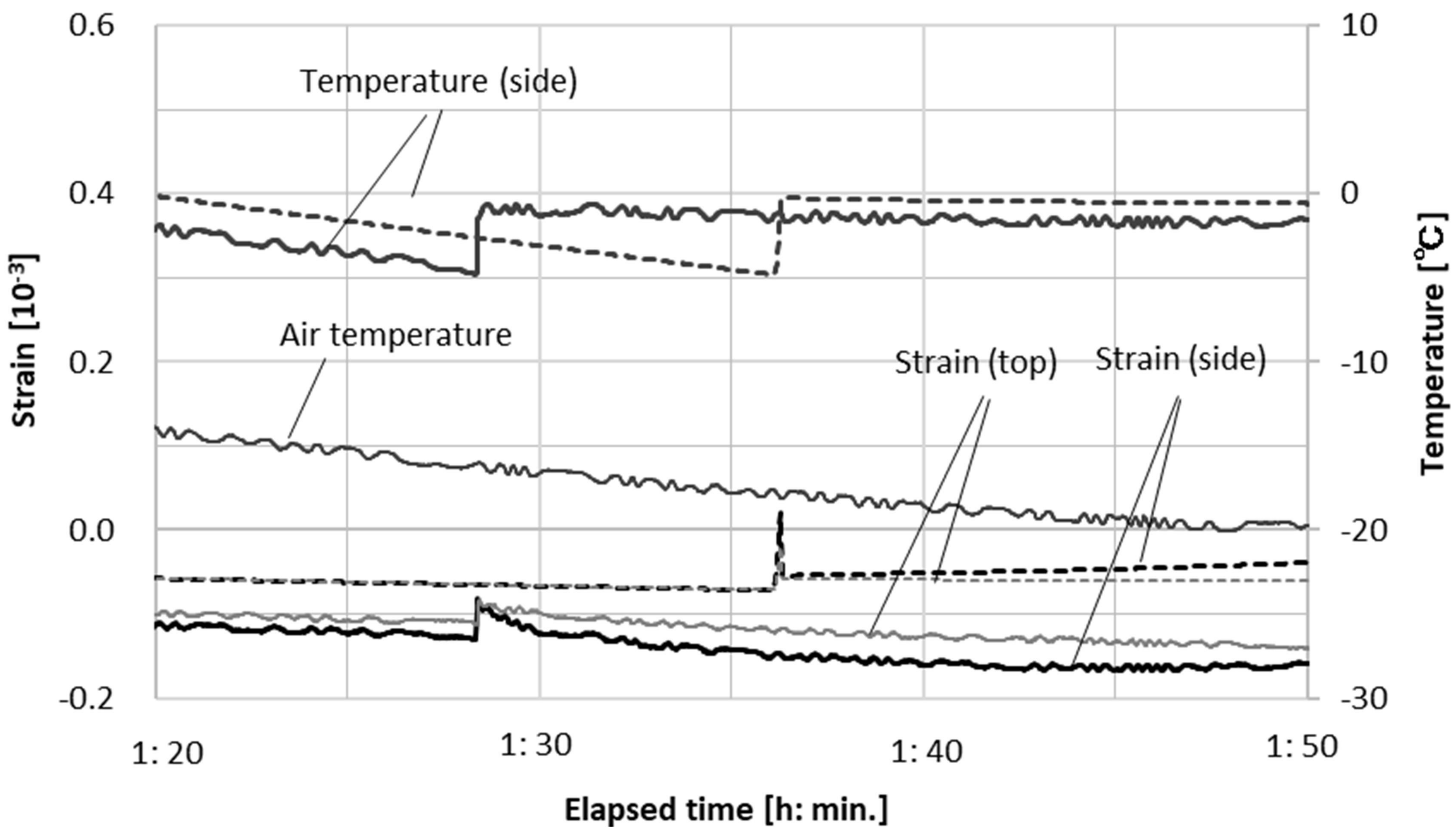


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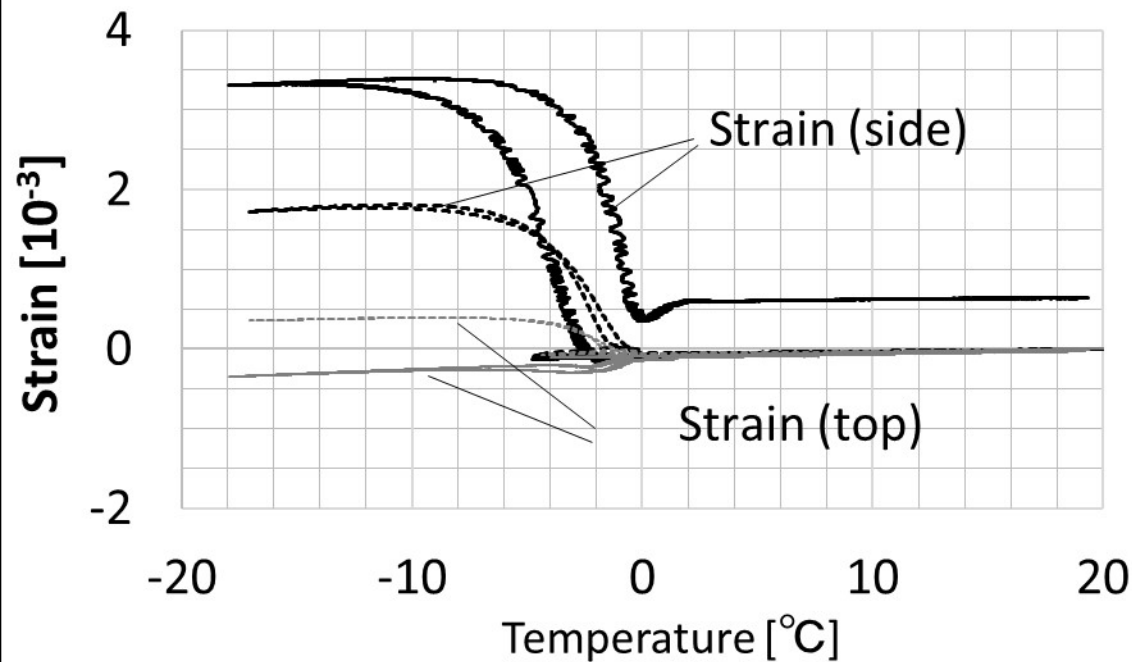
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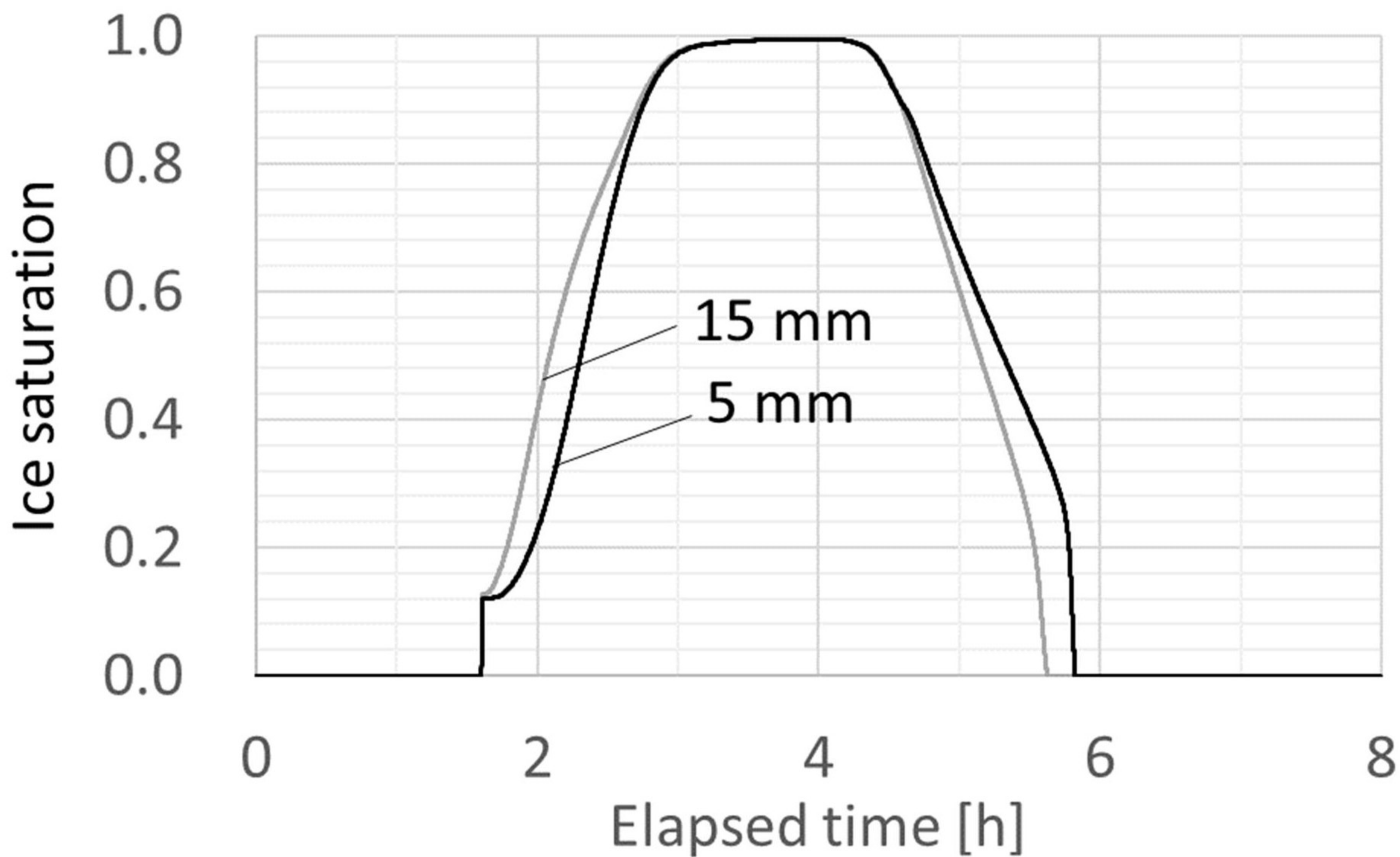
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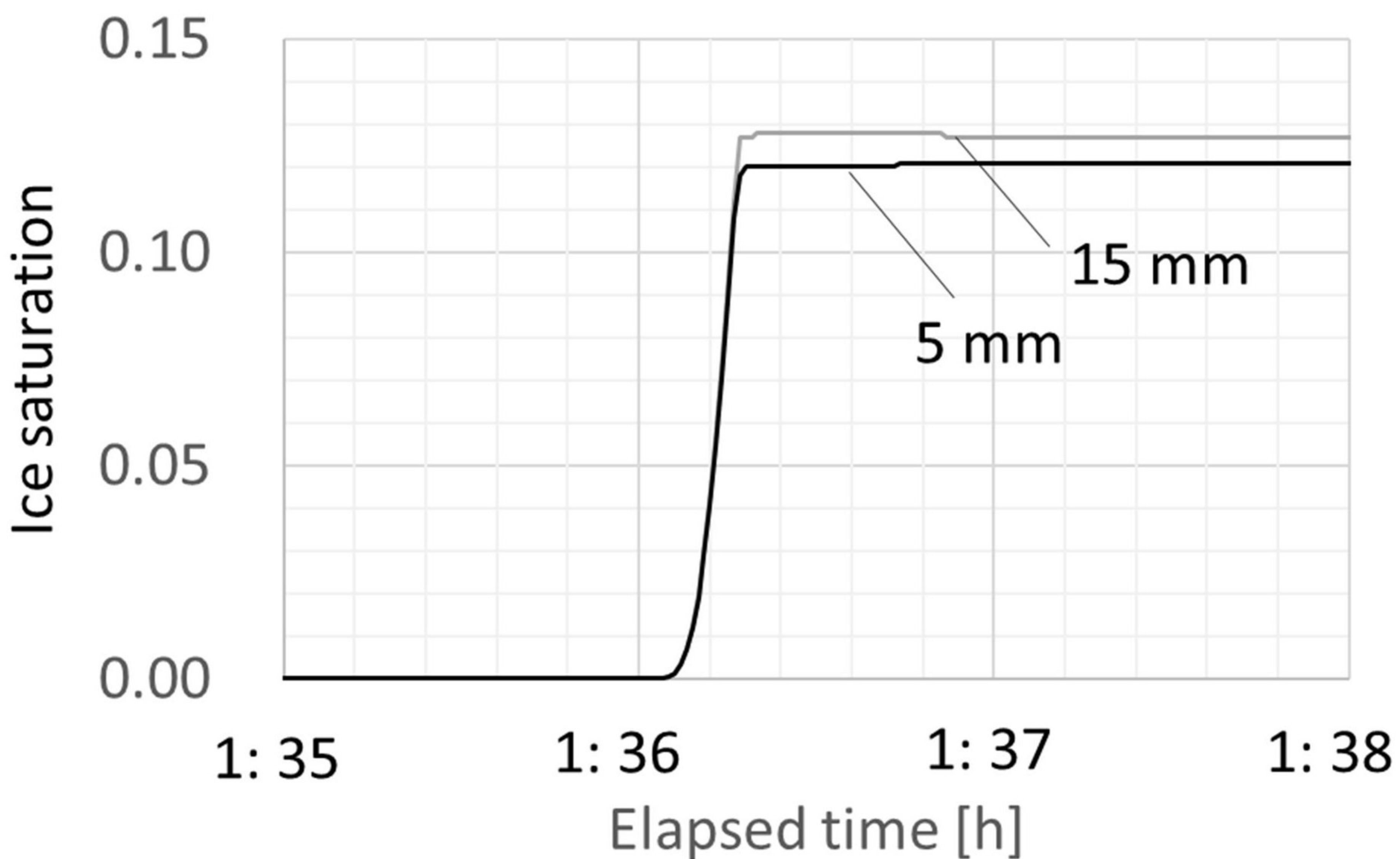
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Solid lines: experiment; Dotted lines: calculation



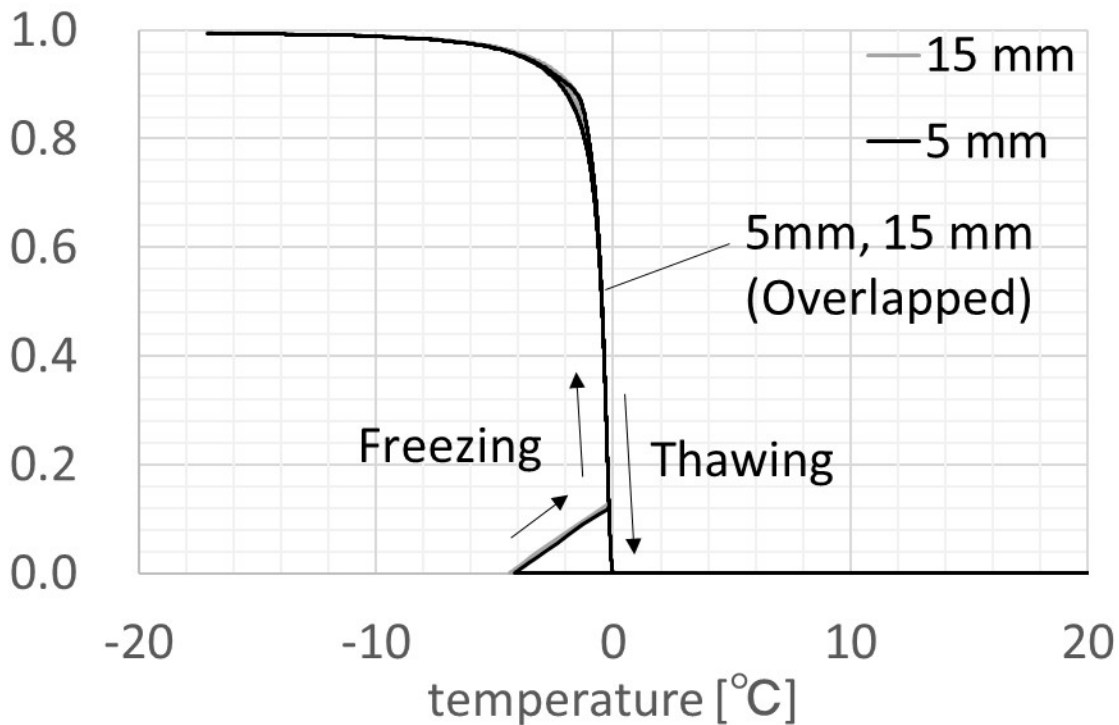


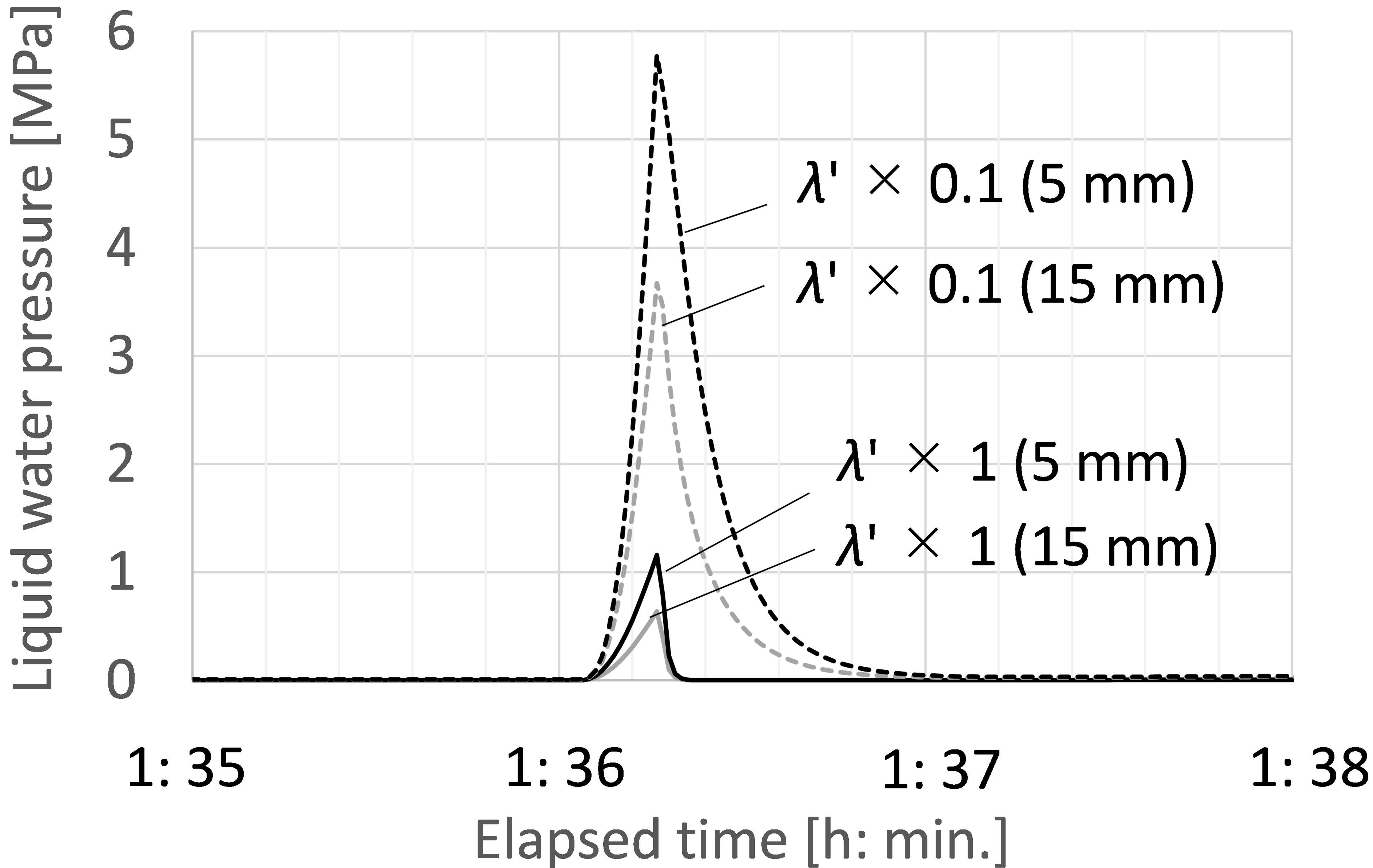
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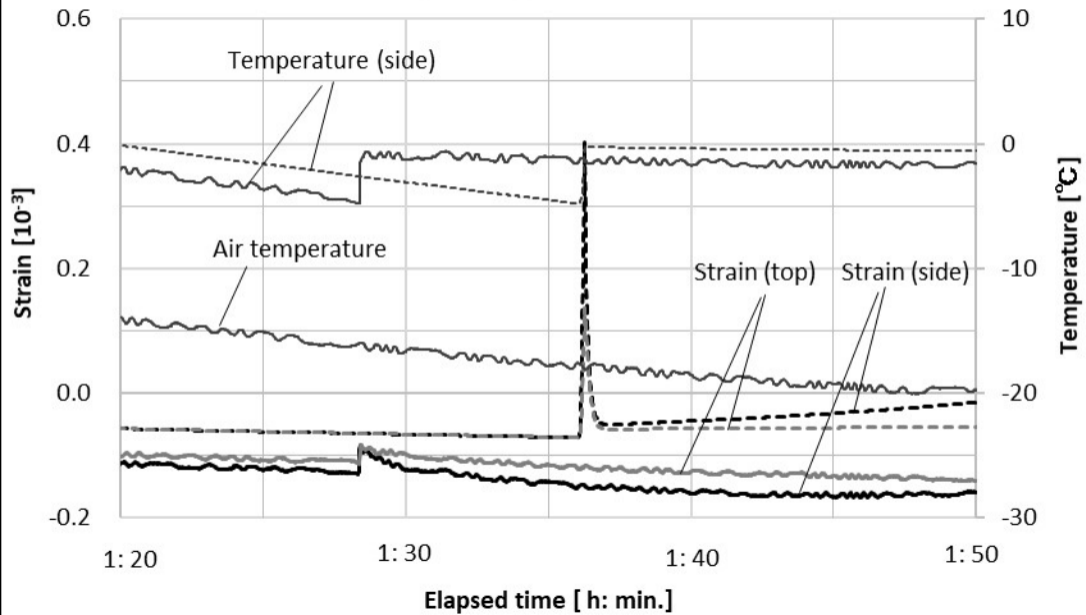
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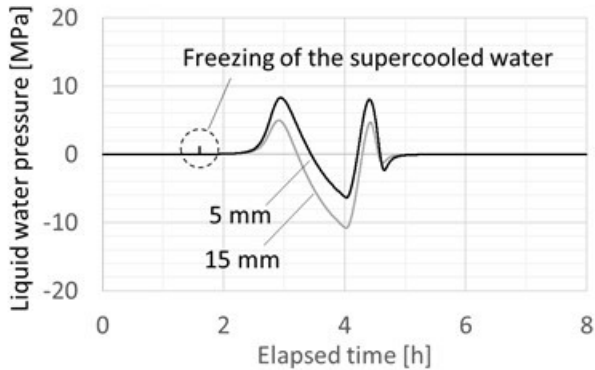
Ice saturation



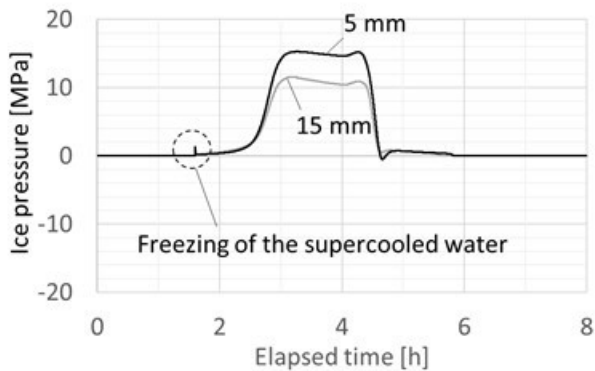


Solid lines: experiment; Dotted lines: calculation





(a)



(b)