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Estimation of ice formation in mortar saturated with sodium chloride solutions

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Abstract

Frost damage of concrete is usually caused by ice expansion, therefore, the ice formation of NaCl solutions is of significant importance for predicting the mechanical degradation of concrete under the combined frost action and NaCl attack. In this study, the ice formation in cementitious materials saturated with different concentrations of NaCl solution is theoretically investigated first. Then the ice formation in mortar is further studied experimentally by electrical measurements. To estimate the ice amount based on the electrical measurements, the relationship between temperature, saturation degree, solution concentration and the electrical conductivity of mortar specimen is clarified. With regard to ice formation and salt crystallization during freeze-thaw, the ice content estimation model is proposed for mortar specimens. In addition, electrical response of meso-scale mortar specimens saturated with NaCl solutions with freeze-thaw cycles (FTCs) is measured. The electrical test results are interpreted with the proposed model and the ice formation is estimated with FTCs. The results from electrical measurements are compared with the theoretical calculations, and acceptable agreement is observed.

Keywords: Ice content, sodium chloride, solution concentration, pore size distribution, electrical response, freeze-thaw cycles

1. Introduction

Frost damage of concrete is a serious and common durability problem to concern (Powers, 1945), especially for the concrete infrastructure related to transportation. In order to remove the ice on the surface of concrete during winter, deicing agents are usually sprayed on walkways, roadways and so on for the safety of vehicles and pedestrians. However, with the existing of deicing agent such as sodium chloride (NaCl), the frost damage of concrete can be accelerated (Litvan, 1976; Valenza and Scherer, 2007).

To predict the mechanical properties of the concrete damaged under the combined frost action and NaCl attack, the ice formation of different concentrations of NaCl solution is of significant importance. According to Glue-spall theory (Valenza and Scherer, 2007), the mechanical properties of ice on the surface of cementitious materials are essential for understanding of salt scaling. Since the thermal mismatch between the ice and cementitious materials can causes cracks of ice, and the cracks further propagate into cementitious materials cover, which results in scaling. The degree of damage depends on the volume fraction of ice during freezing temperatures, as a result, it varies with the solution concentration on the surface of cementitious materials (Valenza and Scherer, 2006; Sun and Scherer, 2010a). On the other hand, since ice can induce pore pressures such as the hydraulic pressure, crystallization pressure and cryosuction pressure, the ice formation inside of cementitious materials is the key point to understand internal frost damage (Coussy and Monteiro, 2008; Liu et al., 2011, 2014a,b; Powers and Willis, 1949; Scherer and Valenza, 2005; Zeng et al., 2014). From the study of Gong et al. (2015a,b), the total pore pressure in cementitious materials can be calculated with the ice content, and the damage caused by the

1 pore pressures can be predicted correspondingly. Therefore, the ice formation information on
2 the cementitious material's surface (outside) and pores (inside) is needed.

3 To clarify the mechanisms of concrete frost damage, many researchers concerned about
4 the ice formation in cementitious materials (Coussy and Monteiro, 2008; Chatterji, 1999; Dai
5 et al., 2012; Esmaeeli et al., 2017; Setzer, 2001; Scherer and Valenza, 2005; Zeng et al., 2013,
6 2015, 2016; Zuber et al., 2000). Based on chemical potential equilibrium, ice formation in
7 confined pores with solution was analyzed (Scherer and Valenza, 2005; Zeng et al., 2014;
8 Zuber and Marchand, 2004). However, most of the studies focused on the pure water case, or
9 only thermodynamic equilibrium equation was given for porous materials saturated with NaCl
10 solutions. These functions are difficult to be applied to engineering purpose.

11 In addition to the analytical study of ice formation, several techniques have been applied
12 to measure the ice content. For example, electrical measurement was proposed by Katsura et
13 al. (1996) and Cai and Liu (1998), which was further developed by McCarter et al., (2015)
14 and Wang et al., (2016a). Besides, dielectric capacity method was deployed by Fabbri and his
15 coworkers (2006, 2009, 2013). Thermoporometry (also called low temperature calorimetry)
16 was applied by Johannesson (2010) and Wu et al., (2014), based on ice content, this technique
17 was also used to determine the pore size and shape (Sun and Scherer, 2010). Since the ice
18 formation is related to pore size distribution, mercury intrusion porosimetry (MIP) was used
19 to estimate the ice formation (Fabbri and Fen-Chong, 2013; Zeng et al, 2014; Zuber and
20 Marchand, 2004)). Because the electrical measurement is easy and rapid to apply, it was
21 favored in this study.

22 Although using the electrical measurement to estimate ice content of specimen saturated
23 with deionized (DI) water has been successfully applied in our previous study (Wang et al.,
24 2016a), the case of NaCl solution is much more complicated. The pore solution concentration
25 may also be changed with temperature decreases due to the chemical reactions (Farnnam et al.,

2014), which may affect the electrical results significantly. Therefore, the ice content estimation model for specimens saturated with NaCl solutions needs further investigation.

The objective of this study is to estimate the ice amount in mortar specimen saturated with NaCl solutions. The ice formation estimation model based on electrical measurements was extended from DI water case to NaCl solutions. In addition to analytical studies, the experimentation was also conducted to verify the prediction model.

2 Estimation of ice formation in mortar saturated with NaCl solutions

2.1 Ice formation in bulk NaCl solutions

When the temperature drops to below the freezing point of salt solution, which depends on the solution concentration, water transforms to ice. After ice formation the concentration of the solution will increase since the solvent reduces. The increasing concentration further reduces the freezing point. Thus, the ice formation will occur gradually as the temperature decreases to the freezing point of the new solution, the amount of ice formation differs from that of DI water for the same temperature level. By collecting the data from Weast and Astle (1981), the relationship between the freezing point and solution concentration by weight has been regressed (see Fig. 1). The regressed relationship for the freezing point of a certain concentration of NaCl solution can be expressed as Eq. (1).

$$T_{c_0} = -0.0157N^2 - 0.5153N \quad (1)$$

where T_{c_0} is the freezing point (°C) while N is the concentration of NaCl solution by weight (%wt).

For a certain temperature, the concentration of solution just before it reaches the freezing point can be derived from Eq. (1).

$$N = -0.028T_{c_0}^2 - 1.6744T_{c_0} \quad (2)$$

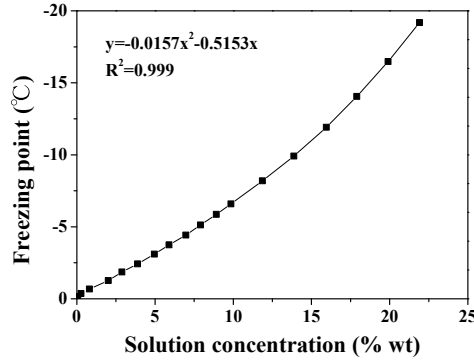


Fig. 1 Freezing point versus solution concentration by weight (Weast and Astle, 1981)

Based on solute mass conservation, the approach on how to calculate the volume fraction of ice with temperature change is derived as Eq. (3) (the derivation can be seen in Appendix) and the results of certain concentrations and comparison with existing test results from Perovich and Gow (1996) are shown in Fig. 2 (a) and (b). The volume fraction of ice decreases significantly with solution concentration and the estimated results agree reasonably with the exiting test results.

$$V_c = 1 - \frac{(0.028T_t^2 + 1.6744T_t + 100)}{(100 - N_0)(-0.028T_t^2 - 1.6744T_t) - 9N_0} \quad (3)$$

where V_c is the volume fraction of ice, T_t is the current temperature (°C) while N_0 is the initial concentration of NaCl solution by weight (%wt).

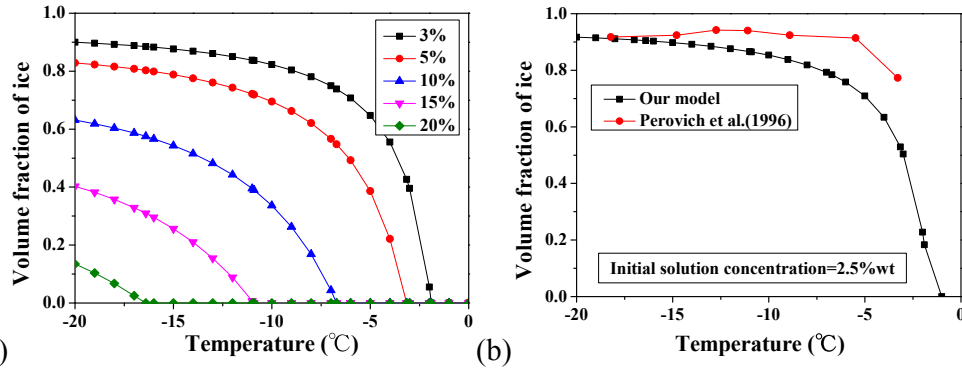


Fig. 2 Volume fraction of ice in solutions of NaCl versus temperature

2.2 Ice formation in cementitious materials saturated with NaCl solutions

2.2.1 Freezing point change with pore radius

Ice formation in cementitious materials is very different from bulk solution, because the freezing point would change due to chemical potential difference with different pore size. The smaller the pore size is, the lower the freezing point is (see Fig. 3). According to thermodynamics analysis (Scherer and Valenza, 2005), if there is no additional pressure and liquid/vapor menisci are flat, the ice formation in brine system could be described as

$$v_c \gamma_{CL} \kappa_{CL} = -(S_L - S_C)(T - T_m) + R_g T \ln(a) \quad (4)$$

where v_c is the molar volume of ice, γ_{CL} is the specific energy of crystal/liquid interface, κ_{CL} is the mean curvature of the solid surface, S_L and S_C are the entropy of liquid and ice, R_g is the gas constant, a is the water activity in the solution which depends on the solution concentration, T is the absolute temperature when the freezing occurs (K) and T_m is the freezing point of a large flat ice crystal (K) in pure water.

Then the freezing point in pore solution T_c (K) (cementitious materials) can be

$$T_c = \frac{(S_L - S_C)T_m}{S_L - S_C - R_g \ln(a)} - \frac{v_c \gamma_{CL} \kappa_{CL}}{S_L - S_C - R_g \ln(a)} \quad (5)$$

2

3 If the ice crystal is in macroscopic, κ_{CL} is about zero, the second term of Eq. (5) become
 4 zero. In Eq. (5), the unit of temperature is K since the derivation is based on thermodynamics.
 5 Considering the temperature unit, then the freezing point ($^{\circ}\text{C}$) of NaCl solution is

6

$$T_{c_0} = \frac{T_m(S_L - S_C)}{S_L - S_C - R_g \ln(a)} - T_m \quad (6)$$

8

9 For a spherical crystal in a pore radius is r_p , $\kappa_{CL} = 2/(r_p - \delta)$. δ is the thickness of the liquid
 10 film between crystal and the pore wall (about 0.9 nm) (Gong et al., 2015a). If the pore
 11 solution is pure water, the water activity is 1. So the freezing point of pore water T_p ($^{\circ}\text{C}$) is

12

$$T_p = T_m - \frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}} - T_m = -\frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}} \quad (7)$$

14

15 where r_p is the radius of pore, δ is the thickness of the liquid film between the crystal and the
 16 pore wall, and $\Delta S_{fv} = (S_L - S_C)/v_c$ is the molar entropy of fusion. For ice, $\gamma_{CL} \approx 0.04 \text{ J/m}^2$,
 17 $\Delta S_{fv} \approx 1.2 \times 10^6 \text{ (J/m}^3\text{/K)}$, for water $\delta \approx 0.9 \text{ nm}$ (Scherer and Valenza, 2005).

18

19 Combining Eq. (6) with the regressed Eq. (1), we have

20

$$T_{c_0} = \frac{T_m(S_L - S_C)}{S_L - S_C - R_g \ln(a)} - T_m = -0.0157N^2 - 0.5153N \quad (8)$$

$$S_L - S_C - R_g \ln(a) = \frac{T_m (S_L - S_C)}{T_m - 0.0157N^2 - 0.5153N} \quad (9)$$

2

3 Substituting of Eq. (9) into Eq. (5), and considering the pore curvature κ_{CL} in Eq. (5), κ_{CL}
 4 $= 2/(r_p - \delta)$, the freezing point of pore solution (K)(see Fig. 3) is

5

$$T_c = \frac{(T_m - 0.0157N^2 - 0.5153N)}{T_m} \left(T_m - \frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}} \right) \quad (10)$$

7

8 Then, by changing the unit, the freezing point of pore solution T_{cc} (°C) could be

9

$$T_{cc} = \frac{(T_m - 0.0157N^2 - 0.5153N)}{T_m} \left(T_m - \frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}} \right) - T_m \quad (11)$$

11

12 Substituting Eq. (6) into Eq. (11), we can obtain the following equation.

$$T_{c_0} = \frac{T_{cc} + T_m}{T_m - \frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}}} T_m - T_m \quad (12)$$

14

15 For a certain temperature and a certain size of pore, the concentration of solution just
 16 reaches the freezing point is obtained from Eq. (11) as follows;

$$N = -0.028 \left(\frac{T_{cc} + T_m}{T_m - \frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}}} T_m - T_m \right)^2 - 1.6744 \left(\frac{T_{cc} + T_m}{T_m - \frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}}} T_m - T_m \right) \quad (13)$$

18

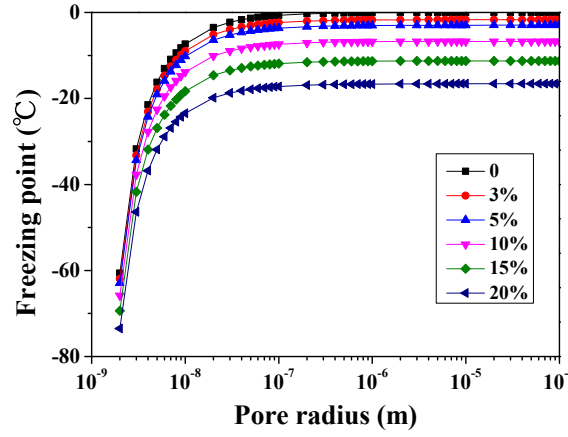


Fig. 3 Freezing point of solutions of NaCl versus pore radius (m)

2.2.2 Ice formation in cementitious materials with different NaCl solutions

For the initial concentration of solution with $N_0\%$, the ice would be formed once the temperature drops to its freezing point T_{cc} (°C), as shown in Eq. (14) (see Eq. (11)).

$$T_{cc} = \frac{(T_m - 0.0157N_0^2 - 0.5253N_0)}{T_m} \left(T_m - \frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}} \right) - T_m \quad (14)$$

Here we assume the mass ratio of ice is $m_c(r_p)$ in pore radius (r_p), so the mass of ice in cementitious materials is

$$m_c = \int_{r_p}^{+\infty} m_c(r_p) v(r_p) dr \quad (15)$$

where $v(r_p)$ is the relative volume of pore with radius r_p . The brine solution is $100 - m_c$, and water is $100 - N_0 - m_c$, the new concentration of solution in the pore would be

$$N_1 = \frac{100N_0}{100 - m_c(r_p)} \quad (16)$$

2

3 Current temperature should be freezing point of N_1 concentrated NaCl solution. As a result,

$$\frac{100N_0}{100 - m_c(r_p)} = -0.028 \left(\frac{T_m(T_t + T_m)}{T_m - \frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}}} - T_m \right)^2 - 1.6744 \left(\frac{T_m(T_t + T_m)}{T_m - \frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}}} - T_m \right) \quad (17)$$

5

6 So the mass of ice in the pore would be

7

$$m_c(r_p) = 100 - \frac{100N_0}{-0.028 \left(\frac{T_m(T_t + T_m)}{T_m - \frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}}} - T_m \right)^2 - 1.6744 \left(\frac{T_m(T_t + T_m)}{T_m - \frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}}} - T_m \right)} \quad (18)$$

9

10 As it is shown in Eq. (18), three parameters (initial solution concentration, temperature
 11 and pore size) are in need for calculating the ice content in a pore. To sum the ice content in
 12 all of the pores, we may get the ice content in bulk cement paste, mortar or concrete. For ice
 13 formation in cement paste, mortar and concrete, the difference is due to the pore size
 14 distribution and this can be calculated by an empirical model proposed by Gong et al. (2014).
 15 Based on the empirical pore size model, we could get the volume density of each size of pores
 16 and the ice formation for different size of pores can be calculated by Eq. (18). Combing the
 17 ice formation in each size of pores and pore size distribution with Eq. (15), the ice formation
 18 in cementitious materials can be obtained. As a result, the amount of ice formation for
 19 different concentration of NaCl solutions under different temperature is estimated (see Fig. 4).
 20 Compared with cement paste and mortar, there is more ice content in concrete at a certain

temperature for different solution concentrations. The reason may be attributed to the existence of interfacial transition zone (ITZ). Because of the ITZ, concrete and mortar have more meso-pores while cement paste has more micro-pores that is difficult for ice to form.

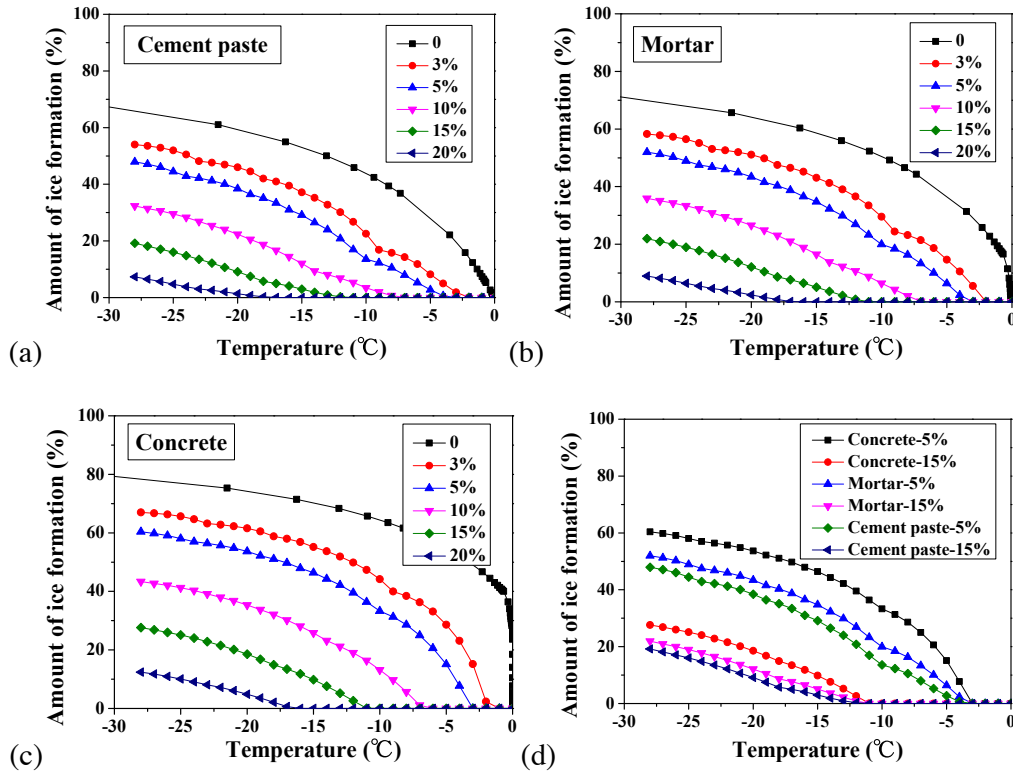


Fig. 4 Amount of ice content with different concentrations of NaCl solutions in (a) cement paste, (b) mortar, (c) concrete and (d) comparison of cement paste, mortar and concrete (W/C=0.5)

3 Theoretical model for ice content estimation in mortar saturated with NaCl solutions based on electrical measurements

3.1 Moisture content

The ice content estimation model was preliminarily developed in the study by Wang et al. (2016a), which can be applied to specimen saturated with DI water. However, for specimen saturated with NaCl solutions, the model is not applicable to estimate the ice content upon

freezing since the chemical reactions could occur. Therefore, the model not only needs to clarify the relationship between moisture content and temperature, but also to consider the pore solution concentration. Besides, to consider the effect of frost damage, the pore characteristics change with FTCs also needs to be included.

As described by Wang et al. (2016a), the moisture content can change the electrical conductivity of specimen significantly. The relationship can be presented as Archie's law (1949). The model was further derived to consider the pore solution concentration change. For cementitious materials, the electrical conductivity at full saturation is

$$\sigma_{ref,C,s,c_0} = F \cdot \sigma_{ref,p,s,c_0} \quad (19)$$

where σ_{ref,C,s,c_0} is the electrical conductivity of cementitious material specimen at full saturation with pore solution concentration equals to c_0 at reference temperature, σ_{ref,p,s,c_0} is the electrical conductivity of pore solution with concentration equals to c_0 in fully saturated specimen at reference temperature and F is the formation factor which accounts for the connectivity and porosity of specimen. For partially saturated cementitious materials (Weiss et al., 2012)

$$\sigma_{ref,C,p,c_2} = F \cdot \sigma_{ref,p,p,c_2} \cdot f(S) \quad (20)$$

$$f(S) = S^n \quad (21)$$

where σ_{ref,C,p,c_2} is the electrical conductivity of cementitious material specimen at partial saturation with pore solution concentration equals to c_2 at reference temperature, σ_{ref,p,p,c_2} is the electrical conductivity of pore solution with concentration equals to c_2 in partially

saturated specimen at reference temperature, $f(S)$ is the saturation function, S is the degree of saturation and n is the saturation coefficient.

If there are no ionic interactions in pore solution, the relationship of electrical conductivity of pore solution and degree of saturation can be

$$\sigma_{ref,p,p,c_2} = \frac{\sigma_{ref,p,s,c_0}}{S} \quad (22)$$

Combining the Eqs. (19)-(22), the variation of electrical conductivity of cementitious materials based on changing of degree of saturation can be calculated as following

$$\frac{\sigma_{ref,C,p,c_2}}{\sigma_{ref,C,s,c_0}} = \frac{\sigma_{ref,p,p,c_2} \cdot f(S)}{\sigma_{ref,p,s,c_0}} = \frac{S^n}{S} = S^{n-1} \quad (23)$$

3.2 Ions concentration

Since the electrical conductivity is sensitive to the pore solution concentration, the effect of concentration change due to saturation degree reduction (solvent change) and salt crystallization (solute change) should be clarified. According to Weiss et al. (2012), the electrical conductivity of pore solution is changing with the ionic strength as Eq. (24).

$$\sigma \propto \frac{I_M}{1 + G\sqrt{I_M}} \quad (24)$$

$$I_M = \frac{1}{2} \sum_{i=1}^N z_i^2 \cdot c_i \quad (25)$$

where I_M is ionic strength (for species with valence z and molar concentration c), parameter G and c are the known values (G = conductivity parameter [assumed to be approximately 0.4 (mol/L)^{-1/2} for a typical pore solution], c_i is designed solution concentration (mol/L)). In the phase transition process, for Eq. (25), valence would not be changed and only molar concentration would be affected. Besides, for sodium chloride solution, the ionic strength has the same value of molar concentration of solution.

The pore solution concentration could be changed due to reduction of solute content such as salt crystallization. As a result, the electrical conductivity change of pore solution will be

$$\frac{\sigma_{ref,p,p,c_1}}{\sigma_{ref,p,s,c_0}} = \frac{I_{M_1}}{1 + G\sqrt{I_{M_1}}} \cdot \frac{1 + G\sqrt{I_{M_0}}}{I_{M_0}} = \frac{c_1}{c_0} \cdot \frac{1 + G\sqrt{c_0}}{1 + G\sqrt{c_1}} \quad (26)$$

where I_{M_0} and I_{M_1} are the ionic strength of pore solution having concentration c_0 and c_1 respectively, namely $I_{M_1}/I_{M_0} = c_1/c_0$. c_0 and c_1 are the pore solution concentration before and after salt crystallization.

On the other hand, during drying or freezing, the increasing of solution concentration is due to the reducing of solvent. Since the solute does not change, so the solution concentration is corresponding to the saturation degree. Based on Eq. (26), the electrical conductivity of pore solution change due to drying or freezing can be simplified as (Weiss et al., 2012)

$$\frac{\sigma_{ref,p,p,c_2}}{\sigma_{ref,p,s,c_0}} = \frac{I_{M_2}}{I_{M_0}} \cdot \frac{1 + G\sqrt{I_{M_0}}}{1 + G\sqrt{I_{M_2}}} = \frac{1}{S} \cdot \frac{1 + G\sqrt{I_{M_0}}}{1 + G\sqrt{I_{M_0}/S}} \cong S^{\delta_0-1} \quad (27)$$

where δ_0 is the correction term which can account for ionic interactions (or ion concentration change) in pore solution, c_0 and c_2 are the pore solution concentration before and after drying

or freezing. Because of the drying or freezing, the solution concentration could be changed and it can be calculated based on the saturation degree due to solute mass conservation, $c_2=c_0/S$. So the ionic strength of pore solution ratio is $I_{M2}/I_{M0}=1/S$.

According to the data presented by Weiss et al. (2012), the relationship between the correction term and ionic strength can be regressed as below

$$\delta_0 = 0.0565 \ln(I_M) + 0.213 \quad (28)$$

In the case of NaCl solution, when $c=5\%$ wt, $\delta_0=0.207$ and when $c=15\%$ wt, $\delta_0=0.276$.

3.3 Temperature

As shown in the study by Wang, et al. (2016a), temperature effect to electrical conductivity was usually described by Arrhenius equation (Chrisp et al., 2001) as follows

$$\frac{\sigma_{T,C,s,c_0}}{\sigma_{ref,C,s,c_0}} = e^{-\left[\frac{E_{a,s}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]} \quad (29)$$

where σ_{T,C,s,c_0} is the electrical conductivity of cementitious material specimen at full saturation with pore solution concentration equals to c_0 at measured temperature $T(K)$, σ_{ref,C,s,c_0} is the electrical conductivity of cementitious material specimen at full saturation with pore solution concentration equals to c_0 at the reference temperature, $E_{a,s}$ is the activation energy for specimen fully saturated with solution (kJ/mol) and R_g is the universal gas constant (8.314 J/mol/K). Among them, the activation energy shows the sensitivity of electrical conductivity of specimen to temperature. It depends on saturation degree, pore characteristics and pore

solution concentration. However, from our experimental results, the activation energy has no big variation with FTCs. To simplify the derivation at this stage, the effect of damage and ion concentration change during FTCs to activation energy was neglected. So the activation energy at partial saturation can be (Wang et al., 2016a)

$$E_{a,p} = E_{a,s} - R_g T_{ref} \ln(S^{\delta_0-1+n}) \quad (30)$$

where $E_{a,s}$ and $E_{a,p}$ are the activation energy of fully and partially saturated specimen.

3.4 Combined effects of moisture, temperature and solution concentration

Firstly, the combined effect of ions concentration and saturation degree was studied. As described in the above section, both of the moisture content and solution concentration change affect the electrical conductivity of specimen. Usually, for drying or freezing process, while the saturation degree decreases, the solution concentration increases. To evaluate the moisture content exactly, the combined effects are necessary to be clarified. By considering Eqs. (19)-(21) and (27), the variation of bulk conductivity of cementitious materials can be written as Eq. (31).

$$\frac{\sigma_{ref,C,p,c_2}}{\sigma_{ref,C,s,c_0}} = \frac{F \cdot \sigma_{ref,p,p,c_2} \cdot f(S)}{F \cdot \sigma_{ref,p,s,c_0}} = \frac{\sigma_{ref,p,p,c_2}}{\sigma_{ref,p,s,c_0}} \cdot S^n = S^{\delta_0-1} \cdot S^n = S^{\delta_0-1+n} \quad (31)$$

From the derivation, the saturation estimation equation was obtained as Weiss, et al. (2012) presented. Based on Eq. (31), the saturation degree of cementitious materials can be obtained by using the electrical conductivity results. The detailed discussion of this equation was shown by Wang et al. (2016a).

Furthermore, from the existing test results, salt crystallization or calcium leaching is very likely to occur when temperature decreases. In this case, the electrical conductivity of specimen changes with the ions concentration and temperature. To analyze the amount of crystallized salt, the combined effects of concentration and temperature to electrical conductivity should be considered. With regard to Eqs. (26) and (29), the electrical conductivity variation due to combined effects of concentration and temperature can be written as Eq. (32)

$$\frac{\sigma_{T,C,s,c_1}}{\sigma_{ref,C,s,c_0}} = \frac{\sigma_{ref,C,s,c_1}}{\sigma_{ref,C,s,c_0}} \cdot e^{\left[\frac{E_{as}}{R_s} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]} = \frac{c_1}{c_0} \cdot \frac{1 + G\sqrt{c_0}}{1 + G\sqrt{c_1}} \cdot e^{\left[\frac{E_{as}}{R_s} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]} \quad (32)$$

By reversing Eq.(32), the pore solution concentration after salt crystallization can be

$$\frac{c_1}{1 + G\sqrt{c_0}} = \frac{\sigma_{T,C,s,c_1}}{\sigma_{ref,C,s,c_0}} \cdot \frac{c_0}{1 + G\sqrt{c_0}} \cdot e^{\left[\frac{E_{as}}{R_s} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]} \quad (33)$$

In order to simplify the derivation, here we may define the right term of Eq. (33), which is the known value, as follows;

$$a = \frac{\sigma_{T,C,s,c_1}}{\sigma_{ref,C,s,c_0}} \cdot \frac{c_0}{1 + G\sqrt{c_0}} \cdot e^{\left[\frac{E_{as}}{R_s} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]} \quad (34)$$

Then, by substituting Eq. (34) into Eq. (33), Eq. (33) can be rewrite as

$$c_1 = a + aG\sqrt{c_1} \quad (35)$$

Eq. (35) can be solved and the solution is as follows;

$$c_1 = \frac{2a + a^2G^2 + aG\sqrt{4a + a^2G^2}}{2} \quad (36)$$

$$\Delta c = c_0 - c_1 \quad (37)$$

where Δc is the concentration difference before and after salt crystallization.

If the salt crystallization is reversible, during the thawing process, the pore solution concentration changes from c_1 to c_0 . Based on Eq. (36), the tendency can also be observed.

During freezing or thawing, the degree of saturation changes with temperature, as well as solution concentration. With ice formation, the combined effects of temperature, saturation degree and solution concentration (with salt crystallization) are as below

$$\begin{aligned} \frac{\sigma_{T,C,p,c_2}}{\sigma_{ref,C,s,c_0}} &= \frac{\sigma_{T,C,p,c_2}}{\sigma_{ref,C,s,c_1}} \cdot \frac{\sigma_{ref,C,s,c_1}}{\sigma_{ref,C,s,c_0}} = \frac{\sigma_{ref,C,p,c_2}}{\sigma_{ref,C,s,c_1}} \cdot e^{\left[\frac{E_{a,p}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]} \cdot \frac{c_1}{c_0} \cdot \frac{1 + G\sqrt{c_0}}{1 + G\sqrt{c_1}} \\ &= \frac{c_1}{c_0} \cdot \frac{1 + G\sqrt{c_0}}{1 + G\sqrt{c_1}} \cdot S^{\delta_0 - 1 + n} \cdot e^{\left[\frac{E_{a,s} - R_g T_{ref} \ln(S^{\delta_0 - 1 + n})}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]} \end{aligned} \quad (38)$$

where

$$S^{\delta_0 - 1} \equiv \frac{c_2}{c_1} \cdot \frac{1 + G\sqrt{c_1}}{1 + G\sqrt{c_2}} \quad (39)$$

The Eq. (39) was derived from Eqs. (26) and (27). Since Eq. (26) equals to Eq. (27), comparing the final term of the two equations, the Eq. (39) can be obtained.

Then by solving Eq. (38), the saturation degree can be given as follows

$$S = (\delta_0 - 1 + n) \frac{T_{ref}}{T} \sqrt{\frac{\sigma_{T,C,p,c_2}}{\sigma_{ref,C,s,c_0}}} \cdot \frac{c_0}{c_1} \cdot \frac{1 + G\sqrt{c_1}}{1 + G\sqrt{c_0}} e^{\left[\frac{E_{as}}{R_s} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]} \quad (40)$$

Then relative ice content can be calculated as

$$I = S_0 - S \quad (41)$$

where S_0 is the initial saturation degree.

Considering Eq. (37), the amount of crystallized salt can be evaluated by

$$m_s = (c_0 - c_1) \cdot \phi_0 \cdot V_0 \quad (42)$$

where m_s is the mass of crystallized salt, ϕ_0 is the porosity of the sample and V_0 is the volume of the sample.

If there is no salt crystallization when ice starts to form, in the ice formation stage, the concentration variation is due to degree of saturation change. The solution concentration change can be calculated based on Eqs. (26) and (27), as below

$$\frac{c_2}{c_0} \cdot \frac{1 + G\sqrt{c_0}}{1 + G\sqrt{c_2}} = S^{\delta_0 - 1} \quad (43)$$

where c_0 and c_2 is the pore solution concentration before and after freezing.

The above equation can be rewritten as

$$\frac{c_2}{1+G\sqrt{c_2}} = \frac{c_0}{1+G\sqrt{c_0}} \cdot S^{\delta_0-1} \quad (44)$$

2

3

If we define

$$b = \frac{c_0}{1+G\sqrt{c_0}} \cdot S^{\delta_0-1} \quad (45)$$

5

6

Then Eq. (44) can be solved and the solution is

7

$$c_2 = \frac{2b + b^2 G^2 + bG\sqrt{4b + b^2 G^2}}{2} \quad (46)$$

9

10 Considering the case with salt crystallization, the solution concentration with freezing
 11 can also be calculated by Eq. (46). However, for calculating the parameter b in Eq. (45), c_0
 12 should be represented with c_1 .

13 According to the study of Farnam et al. (2014), upon freezing, the salt crystallization
 14 (formation of Friedel's salt and Kuzel's salt) would occur above the freezing point. The salt
 15 could be the reason for damage of specimen saturated with high concentration of NaCl
 16 solutions. In this case, the salt crystallization and ice formation processes are in separate
 17 stages. The amount of salt could be calculated with regard to combined effects of ions
 18 concentration and temperature, while the ice amount involved the combined effects of
 19 saturation degree, ions concentration and temperature. Therefore, the pore solution
 20 concentration change and relative ice content during FTC could be obtained as follows;

20

21 (a) When temperature is higher than freezing point $T > T_F$ (freezing)

22

$$c_1 = \frac{2a + a^2G^2 + aG\sqrt{4a + a^2G^2}}{2}; \quad a = \frac{\sigma_{T,C,s,c_1}}{\sigma_{ref,C,s,c_0}} \cdot \frac{c_0}{1 + G\sqrt{c_0}} \cdot e^{-\left[\frac{E_{a,s}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]} \quad (47)$$

2

3 (b) When the temperature is less than the freezing point but higher than the lowest
4 temperature $T_L < T < T_F$ (freezing)

5

$$c_2 = \frac{2b + b^2G^2 + bG\sqrt{4b + b^2G^2}}{2}; \quad b = \frac{c_1}{1 + G\sqrt{c_1}} \cdot S^{\delta_0 - 1} \quad (48)$$

7

8 (c) When the temperature is higher than the freezing point but less than the thawing point
9 $T_L < T < T_T$ (thawing)

10

$$c_2 = \frac{2b + b^2G^2 + bG\sqrt{4b + b^2G^2}}{2}; \quad b = \frac{c_1}{1 + G\sqrt{c_1}} \cdot S^{\delta_0 - 1} \quad (49)$$

12

13 (d) When the temperature is higher than the thawing point $T > T_T$ (thawing)

14

$$c_1 = \frac{2a + a^2G^2 + aG\sqrt{4a + a^2G^2}}{2}; \quad a = \frac{\sigma_{T,C,s,c_1}}{\sigma_{ref,C,s,c_0}} \cdot \frac{c_0}{1 + G\sqrt{c_0}} \cdot e^{-\left[\frac{E_{a,s}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]} \quad (50)$$

16

17

18

19

20

Considering the effect of the salt frost damage on the electrical property of cementitious materials (Wang et al., 2016a), with assumption that damage occurs linearly only in freezing process, the ice formation estimation model could be extended to the case of FTCs

$$S_{F,i} = (\delta_0 - 1 + n) \frac{T_{ref}}{T} \sqrt{\frac{\sigma_{T,C,p,c_{2,i}}}{\sigma_{ref,C,s,c_{0,i}} + \frac{T - T_{Fi}}{T_L - T_{Fi}} (\sigma_{ref,C,s,c_{0,i+1}} - \sigma_{ref,C,s,c_{0,i}})}} \cdot \frac{c_{0,i} (1 + G \sqrt{c_{1,i}})}{c_{1,i} (1 + G \sqrt{c_{0,i}})} \cdot e^{\left[\frac{E_{a,s,i}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]} \quad (51)$$

$$S_{T,i} = (\delta_0 - 1 + n) \frac{T_{ref}}{T} \sqrt{\frac{\sigma_{T,C,p,c_{2,i}}}{\sigma_{ref,C,s,c_{0,i+1}}}} \cdot \frac{c_{0,i} (1 + G \sqrt{c_{1,i}})}{c_{1,i} (1 + G \sqrt{c_{0,i}})} \cdot e^{\left[\frac{E_{a,s,i}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]} \quad (52)$$

where i is the number of cycles, $E_{a,s,i}$ is the activation energy of fully saturated specimen at i cycle of FTC, T_{Fi} is the freezing point of specimen at i cycle of FTC. For the electrical conductivity of specimen and solution concentration, only number of FTCs is different from previous definition. Eq. (51) is applicable to the ice formation estimation for the freezing process while Eq. (52) is for the thawing process.

The data from Farnam et al.'s study was applied for the calculation based on the above four-stages estimation model. The results of relative ice content and pore solution concentration were shown in Fig. 6 and 7 respectively. Note that the ice content of 5% NaCl case is even higher than DI water case, which may be the reason why the 5% NaCl case has the most severe damage. This may be explained by the solution absorption results in our previous study (Wang et al., 2016b), 5% NaCl solution saturated specimen could absorb higher water content than DI water case. As a result, during freezing, larger amount of water would form to ice. The much higher amount of salt crystallization is calculated for 23.3% NaCl concentration than the 15% concentration case. There is no crystallization in the case of 5% concentration.

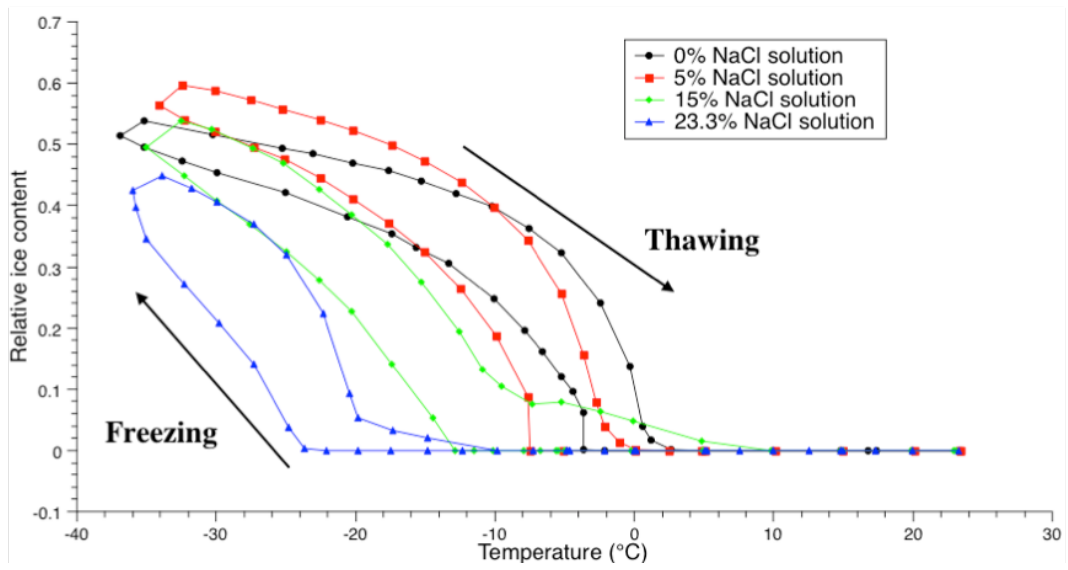


Fig. 6 Relative ice content of different concentrations of NaCl solution saturated mortar under freezing and thawing (calculated from the data of Farnam et al., 2015)

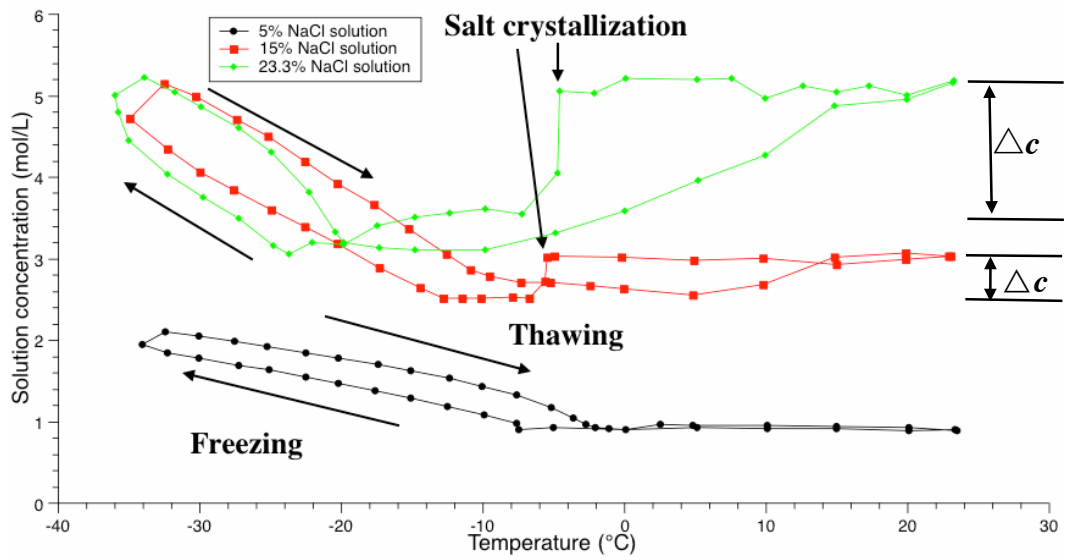


Fig. 7 Solution concentration change with temperature (calculated from the data of Farnam et al., 2015)

4 Test programs

4.1 Specimen preparation

Mortar specimens were used in this experimental program. Mix proportions with different water-to-cement ratios (W/C), excluding coarse aggregate, were based on ACI 211.1 (1991) design, as shown in Table 1. The materials include ordinary Portland cement. The physical properties and chemical compositions are presented in Table 2. The size of fine aggregate is 1.2 mm or lesser and its density is 2.67 g/cm³. To promote frost damage, no air-entraining agent was incorporated. After proper mixing, it was cast into 40×40×160 mm form and cured for 24 hours prior to removing the form. Once demolded, specimens were cured under water for 90 days at the temperature of 20 to 23 °C. Then the specimens were cut into size of 70×30×5 mm after curing. The meso-scale size was chosen because the pore solution concentration can be assumed to be uniform in the specimen. As a result, salt frost damage could be quantitatively understood.

The electrical test samples were prepared as shown in Fig. 8. Firstly, the electrodes were attached to mortar samples with conductive paste (see Fig. 8(a)). Once the conductive paste was cured, to solidify the interface bonding of electrodes and specimens, the epoxy resin was also deployed to cover the conductive paste and electrode. After one week curing of epoxy resin, the samples were placed into a vacuum desiccator for another week to obtain dried condition. After drying, they were sealed with a plastic bag to prevent moisture transfer and kept in a vacuumed chamber until testing. In order to obtain fully saturated specimens, firstly, the samples were vacuumed for 20 minutes to remove the air inside. Then the containers with solutions were also placed in the desiccator under vacuuming for 15 minutes to remove the air in the solution. After that, the samples were immersed into DI water, 5% and 15% NaCl solutions respectively and continuous vacuuming for one hour. Then the samples remained in

solution for 7 days at room temperature until they were taken out. To prevent moisture transfer, they were sealed with saran and tape after surface dried by towel paper (see Fig. 8(b)).

Table 1 Mix proportions and properties of mortar

Water/Cement Ratio (W/C)	Water kg/m ³	Cement kg/m ³	Fine aggregate kg/m ³	Bulk dry density (ρ_b) kg/m ³	Skeletal density (ρ_0) kg/m ³	Porosity
0.3	207	690	755	2173	2676	0.188
0.5	207	414	990	2137	2688	0.205
0.7	207	296	1090	2125	2703	0.214

Table 2 Physical properties and chemical compositions of cement (OPC)

Physical properties	Specific gravity		Specific surface (cm ² /g)		Compressive strength (MPa)			
	3.16		3350		3d	7d	28d	
					31.3±1.63	47.1±1.76	63.5±1.88	
Composition	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	K ₂ O	Na ₂ O
Content (%wt)	64.20	21.40	5.51	2.92	2.03	1.74	0.36	0.21

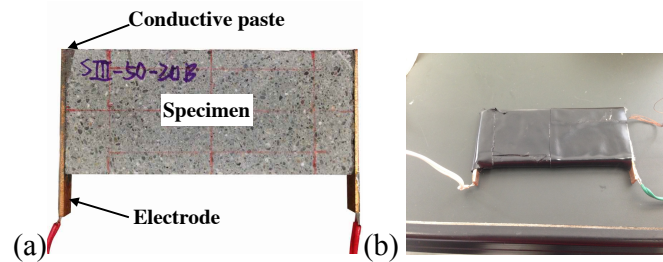


Fig. 8 Prepared specimen details 70 mm × 30 mm × 5 mm (a) dried specimen (b) sealed saturated specimen

4.2 Electrical and freeze-thaw cycles tests

In the electrical test, the electrical resistance of specimen was measured by alternating current (AC) two-point method with FTCs (Wang et al., 2016a). The frequency of the alternating current is 1 kHz and the test data was collected every 10 seconds by computer continuously. Before the test, the electrical resistance of conductive paste under FTCs was measured and the value was around 0.5 Ω , which can be neglected compared with electrical

resistivity of mortar samples. To consider the geometrical effect, the electrical resistivity of the specimen is

$$\rho = \frac{AR}{L} \quad (53)$$

where R is the resistance of the specimen, A is the cross-sectional area and L is the length of the specimen.

The prepared specimens were placed into an environmental chamber to undergo FTCs. The freeze-thaw temperature history of the chamber can be seen in Fig. 9. Since the specimens were sealed, the relative humidity inside the chamber has no effect on the frost damage process, therefore only the temperature was controlled and measured by a temperature sensor recorded by computer. The temperature started at 23°C for 100 minutes, then decreased by 0.25°C per minute until it reached the minimum temperature -28°C and remained constant for 100 minutes, and then increased by 0.25°C per minute until the maximum temperature 23°C. The freeze-thaw cycle was repeated 10 times.

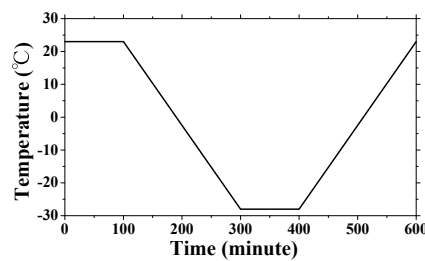
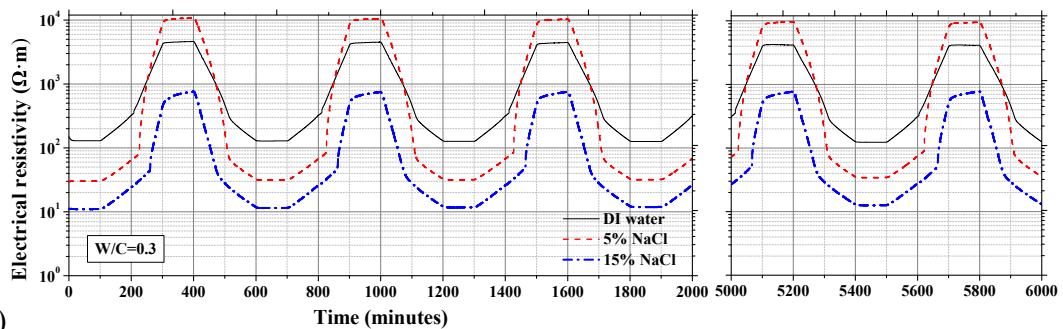


Fig. 9 Temperature history (one cycle)

5. Test results and discussions

5.1 Electrical resistivity of specimen under FTCs

During FTCs, the electrical resistivity of specimens was changing with temperature. As shown in Fig. 10, the measured electrical resistivity was presented as a function of time. Since the temperature was also changing with time, the relationship between electrical resistivity and temperature was further plotted with regard to FTCs (see Fig. 11). The freezing and thawing points can be seen from the slope change of the curves. Because once ice nucleates in meso and macro pores, the amount of movable ions would be reduced, as a result, the electrical resistivity of mortar increases dramatically. Clearly, there is a big difference among NaCl solution saturated specimens with different concentrations. As shown in Fig. 11, at reference temperature (23°C), the electrical resistivity reduces with increasing of NaCl concentration. However, the 5% NaCl case specimen reached the maximum electrical resistivity at the lowest temperature except for $W/C=0.7$ cases. The pore characteristics of hydrated products may be accounted as the reason. At the lowest temperature, water in pores partially forms ice, and the salt crystallization is also possible to occur to fill the pores. As a result, the amount of movable ions in 5% NaCl saturated samples with $W/C=0.3$ and 0.5 would be less than in DI water saturated samples as more pores are blocked by the ice and salt. However, for $W/C=0.7$ case, 5% NaCl saturated samples still have good connectivity under freezing because of more porous nature and can be more conductive than in DI water.



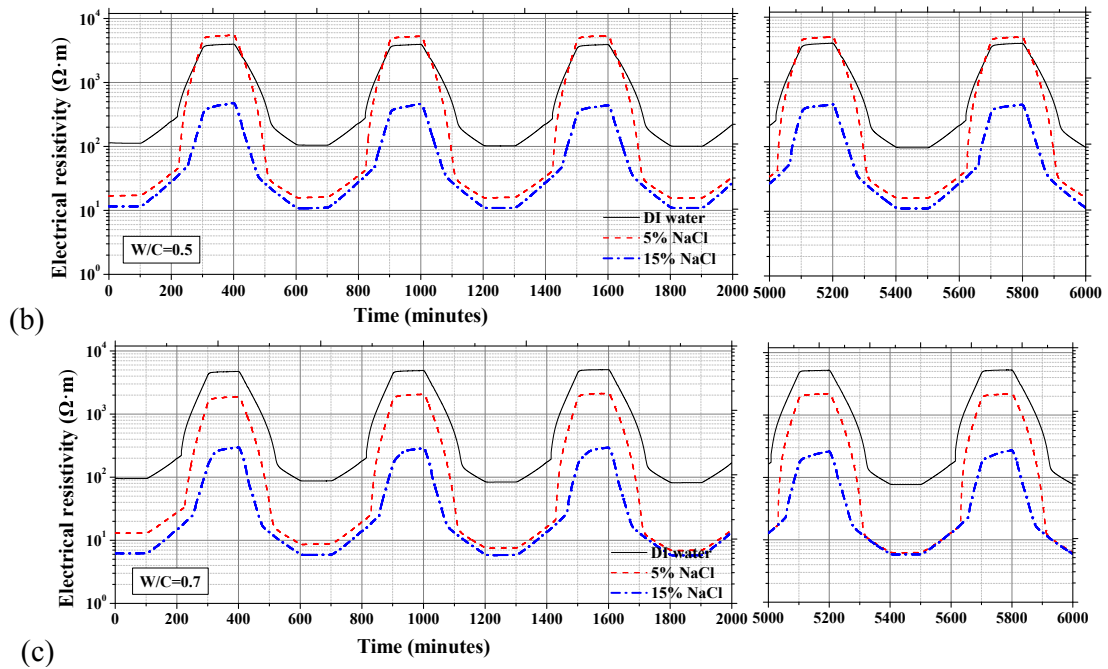


Fig. 10 Electrical resistivity changes under freeze-thaw cycles (a) W/C=0.3 (b) W/C=0.5
(c) W/C=0.7

In addition, for each W/C sample, the electrical resistivity decreases with W/C at reference temperature because of the greater amount of water in the samples. It is worthy to note that there were no additional phase changes (eg. formation of Friedel's salt and crystallization of NaCl) been observed during the freezing and thawing even for 15% NaCl saturated samples, which is different from Farnam et al. (2015)'s results (there was a sudden change of electrical resistivity-temperature curve slope at temperature higher than the freezing point). This implies that the additional phase change depends on the chemical composition of cement pastes (Baroghel-Bouny et al., 2012), for which further investigation is necessary. Besides, after the ice nucleation, the non-linear curve of electrical resistivity-temperature relationship indicates that the amount of ice formed increases non-linearly. From previous results (Wu et al., 2014), we understand that the samples contain 5% NaCl solution have more severe damage than the DI water case, but in theory the ice amount in 5% NaCl solution saturated sample is less than in DI water saturated sample. Since the range of electrical

resistivity in the case of 5% is highest in Fig. 11, it was believed that salt crystallization contributed to the electrical resistivity increase as well. However, no obvious change due to salt crystallization was observed. Therefore, it was assumed that the electrical resistivity increase was simply due to ice formation.

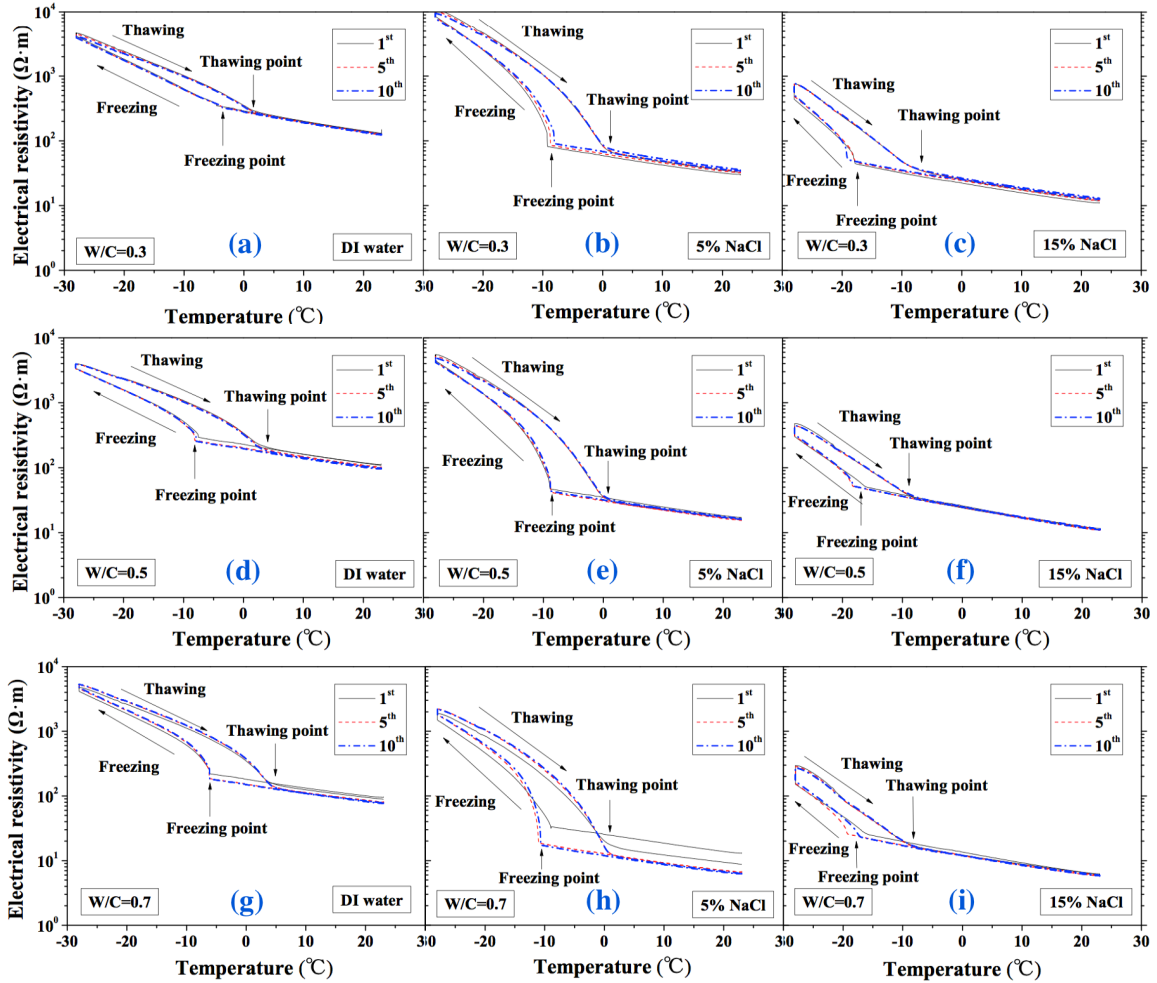


Fig. 11 Electrical resistivity changes with temperature

5.2 Estimation of ice content with consideration of frost damage

The experimental results were calculated based on the proposed model. Although from the thermodynamic properties of NaCl-water system, the eutectic point is around -21.3 °C, the NaCl·2H₂O would get crystallized when the temperature is below this point. The turning

1 point due to this salt crystallization, however, was not found in the electrical results of this
2 study. We may assume that the NaCl crystal was not precipitated at temperature higher than -
3 28 °C in this study, so only the ice formation needs to be considered. In this case, with regard
4 to the frost damage to the electrical property, the ice formation could be estimated based on
5 the model (Eqs. (51) and (52)), as shown in Fig. 12. Then the ice formation with FTCs was
6 further calculated and presented in Fig. 13. Similar to the results of Farnam et al. (2015), the
7 ice amount of 5% NaCl case reached the highest. But there was no significant change in the
8 ice content with FTCs. The experimental results of ice formation in mortar ($W/C=0.5$)
9 saturated with NaCl solutions were compared with the theoretical results. As shown in Fig. 14,
10 for 5% NaCl solution case, the experimental and theoretical results can basically reach an
11 agreement. However, for 15% NaCl case, the predicted results have an acceptable agreement
12 with our test results, but slightly lower than the results of Farnam et al. (2015)'s study. The
13 disagreement could be attributed to the actual pore size distribution difference. According to
14 Scherer and Valenza (2005), pore size distribution is very important for ice formation since it
15 relates not only to the freezing point but also disjoining pressure. In our theoretical
16 calculations, the pore size distribution information was taken from Gong's model, which was
17 used for the freezing point change calculation. However, the disjoining pressure was not
18 discussed in the ice content calculation. Although it plays a decisive role in frost action in the
19 case of unsealed or air-entrained specimens, the hydraulic pressure is mainly responsible for
20 the frost damage of sealed specimen (Liu et al., 2014b). In our study with sealed specimen, to
21 simplify the calculation, the effect of disjoining pressure was neglected because it is not
22 significant. Since Gong's pore size distribution model is empirical, which could be different
23 from the actual one. The theoretical result may not agree with our test results well. Besides,
24 for the ice content calculation based on the electrical test results, including those in the
25 previous study, the porosity was considered instead of the pore size distribution. Although in

the comparison both of our test samples and Farnam's are with the same $W/C=0.5$, the curing condition and aging are different. Thus the actual porosity and pore size distribution could be different. But it is worthy to note that the significance of this work is to develop a method which can estimate the ice content in mortar containing salt solutions, although the method needs further improvement for better accuracy. In addition, our calculations present a slow cooling process which is different from the discussion by Esmaeeli et al. (2017). This phenomenon is also related to the pore size distribution. When the volume fraction of larger pores is large, the freezing is rather rapid, as suggested by Esmaeeli et al.. However, if the fraction of larger pores is small, then the freezing process is pretty slow, as it was shown by thermoporometry in the work by Sun and Scherer (2010b). Our theoretical calculations couple the effects of pore size and solution concentration. The shape of the calculated ice formation curve is similar to Sun and Scherer's result. Therefore, discussion of the slow cooling process is reasonable.

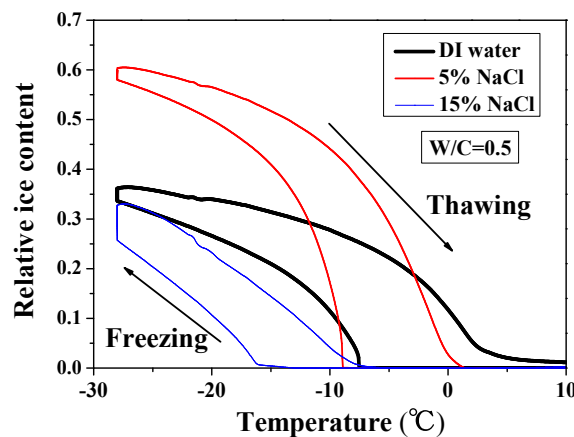


Fig. 12 Estimated relative ice content of specimen saturated with different NaCl solutions based on electrical measurement ($W/C=0.5$)

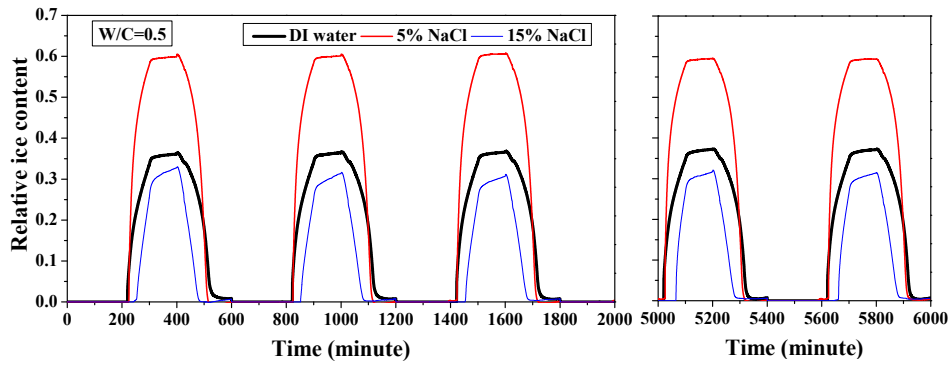


Fig. 13 Estimated relative ice content change with FTCs

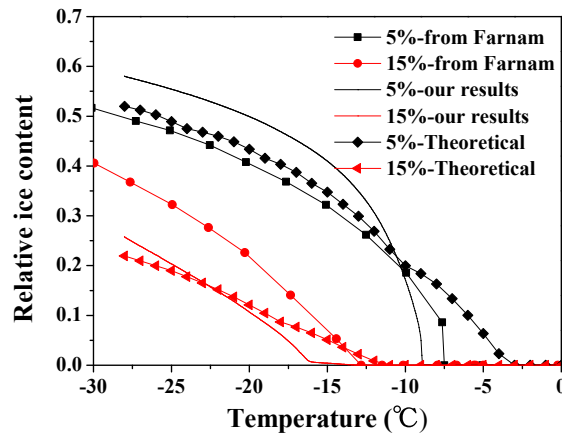


Fig. 14 Comparison the relative ice content from our theoretical calculations and experimental observations (during freezing process)

6 Conclusions

In this study, the ice formation in cementitious materials with different concentration of NaCl solutions was theoretically investigated. Beside, ice content in mortar specimens saturated with NaCl solution was estimated based on electrical measurements. Based on the results and discussion, the following conclusions could be reached.

(1) According to the solute mass conservation, ice content information for bulk NaCl solutions under freezing were calculated. From thermodynamic analysis, the effect of salt and pore size to freezing point was found in a product relationship. As a result, the freezing point

of solution in cementitious materials can be calculated. Then the ice formation of NaCl solutions in cementitious materials can be estimated as well.

(2) The ice content estimation model for DI water case was extended to the NaCl solution cases by clarifying the combined effects of moisture, temperature, ion concentration and electrical properties of pore solution. Based on the observed phenomena, four-stage ice content estimation model was proposed.

(3) To verify the model, the electrical response of mortar in meso-scale saturated with DI water, 5% and 15% NaCl solutions under FTCs was studied. The electrical results were used to estimate the ice content. Besides, the experimental data from Farnam's was applied to estimate the ice formation and salt crystallization based on the proposed model. Acceptable agreement was found when the calculated ice content from Farnam's results and our test results compared with the theoretical results.

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Appendix A. Derivation of Eq. (3)

If the initial concentration of solution is $N_0\%$, once the temperature drops to its freezing point, the ice would form and then the concentration would change

$$T_{c_0} = -0.0157N_0^2 - 0.5153N_0 \quad (\text{A.1})$$

Here we assume the mass ratio of ice is m_c , so the brine solution is $100-m_c$, and water is $100-N_0-m_c$, the new concentration of solution would be

$$N_1 = \frac{100N_0}{100-m_c} \quad (\text{A.2})$$

In addition, current temperature T_t ($^{\circ}\text{C}$) should be freezing point of N_1 concentrated NaCl solution. As a result, the new equilibrium can be

$$\frac{100N_0}{100-m_c} = -0.028T_t^2 - 1.6744T_t \quad (\text{A.3})$$

So the mass ratio of ice and the volume fraction of ice in solution of NaCl are determined as

$$m_c = 100 - \frac{100N_0}{-0.028T_t^2 - 1.6744T_t} \quad (\text{A.4})$$

$$V_c = \frac{m_c / \rho_c}{m_c / \rho_c + (100 - N_0 - m_c) / \rho_w} \cong \frac{1.09m_c}{0.09m_c + 100 - N_0} \quad (\text{A.5})$$

where V_c is the volume fraction of ice, ρ_c and ρ_w are the density of ice and water ($\rho_c=916.7$ kg/m³ and $\rho_w=999.8$ kg/m³ at 0 °C), respectively. By substituting of Eq. (A.4) into Eq. (A.5), there is Eq. (3).

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Notations

T_{c0}	—	Freezing point (°C)
N	—	Concentration of NaCl solution by weight (%wt)
V_c	—	Volume fraction of ice
ρ_c	—	The density of ice ($\rho_c=916.7 \text{ kg/m}^3$ at 0 °C)
ρ_w	—	The density of water ($\rho_w=999.8 \text{ kg/m}^3$ at 0 °C)
T_t	—	current temperature (°C)
T_{ref}	—	The reference temperature (K) (296K)
N_0	—	Concentration of NaCl solution by weight (%wt)
v_c	—	the molar volume of ice
γ_{CL}	—	the specific energy of crystal/liquid interface (J/m ²)
κ_{CL}	—	the mean curvature of the solid surface
S_L	—	the entropy of liquid
S_C	—	the entropy of ice
R_g	—	the gas constant (8.314 J/mol/K)

a	— the water activity in the solution which depends on the solution concentration
T	— the absolute temperature (K)
T_m	— the freezing point of a large flat ice crystal (K) in pure water
T_c	— the freezing point in pore solution (K)
δ	— the thickness of the liquid film between crystal and the pore wall (about 0.9 nm)
T_p	— the freezing point of pore water (°C)
r_p	— the radius of pore (m)
ΔS_{fv}	— the molar entropy of fusion (J/m ³ /K)
T_{cc}	— the freezing point of pore solution (°C)
$m_c(r_p)$	— the mass ratio of ice in pore radius (r_p)
$v(r_p)$	— the relative volume of pore with radius r_p
N_I	— the new concentration of solution in the pore after freezing (%wt)
$\sigma_{ref,C,s,c0}$	— the electrical conductivity of cementitious material specimen at full saturation with pore solution concentration equals to c_0 at reference temperature (S/m)
$\sigma_{ref,p,s,c0}$	— the electrical conductivity of pore solution with concentration equals to c_0 in fully saturated specimen at reference temperature (S/m)
F	— the formation factor which accounts for the connectivity and porosity of specimen
$\sigma_{ref,C,p,c2}$	— the electrical conductivity of cementitious material specimen at partial saturation with pore solution concentration equals to c_2 at reference temperature (S/m)
$\sigma_{ref,p,p,c2}$	— the electrical conductivity of pore solution with concentration equals to c_2 in partially saturated specimen at reference temperature (S/m)
$f(S)$	— the saturation function
S	— the degree of saturation
n	— the saturation coefficient

I_M	— ionic strength (mol/L)
z	— valence
c	— molar concentration (mol/L)
G	— conductivity parameter [assumed to be approximately $0.4 (\text{mol/L})^{-1/2}$ for a typical pore solution]
c_i	— designed solution concentration (mol/L)
I_{M0}	— the ionic strength of pore solution having concentration c_0 (mol/L)
I_{M1}	— the ionic strength of pore solution having concentration c_1 (mol/L)
c_0	— the initial pore solution concentration (before freezing, drying or salt crystallization) (mol/L)
c_1	— the pore solution concentration after salt crystallization (mol/L)
δ_0	— the correction term which can account for ionic interactions (or ion concentration change) in pore solution
c_2	— the pore solution concentration after drying or freezing (mol/L)
$\sigma_{T,C,s,c0}$	— the electrical conductivity of cementitious material specimen at full saturation with pore solution concentration equals to c_0 at measured temperature $T(\text{K})$ (S/m)
$\sigma_{ref,C,s,c0}$	— the electrical conductivity of cementitious material specimen at full saturation with pore solution concentration equals to c_0 at the reference temperature (S/m)
$E_{a,s}$	— the activation energy for specimen fully saturated with solution (kJ/mol)
$E_{a,p}$	— the activation energy for specimen partially saturated with solution (kJ/mol)
Δc	— the concentration difference before and after salt crystallization (mol/L)
m_s	— the mass of crystallized salt (kg)
ϕ_0	— the porosity of the sample
V_0	— the volume of the sample (m^3)

T_F	—	The freezing point (K)
T_L	—	The lowest temperature (K)
T_T	—	The thawing point (K)
$S_{F,i}$	—	The remaining water content during freezing at i FTCs
$S_{T,i}$	—	The remaining water content during thawing at i FTCs
i	—	the number of freeze thaw cycles
$E_{a,s,i}$	—	the activation energy of fully saturated specimen at i cycle of FTC (kJ/mol)
T_{Fi}	—	the freezing point of specimen at i cycle of FTC (K)
ρ	—	the resistivity of the specimen ($\Omega\cdot\text{m}$)
R	—	the resistance of the specimen (Ω)
A	—	the cross-sectional area (m^2)
L	—	the length of the specimen (m)