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frost damage of mortar under effects of sodium chloride

塩化ナトリウムが存在する場合の凍害に関する準微視的な実験と
解析

Yi WANG

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解析

By

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A thesis submitted in partial fulfillment of the requirements for the
Degree of Doctor of Philosophy in Engineering

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ABSTRACT

Concrete is fragile to freeze-thaw cycles (FTCs) in cold and wet regions, especially with the presence of de-icing agents (eg. sodium chloride). While surface scaling spoils the appearance, more importantly, the internal frost damage threatens to the safety of concrete structures. Although it is well known that the sodium chloride (NaCl) can accelerate the frost damage, the internal damage mechanisms due to the combined effects of FTCs and NaCl attack still have not reached an agreement. On one hand, chloride ions may have reactions with hydrated products to form new salts (eg. Friedel's salt). The salts fill the mortar voids and the degree of frost damage is reduced because of lesser water content and porosity. On the other hand, the expansion due to salt crystallization induces internal pressures, subsequently, resulting in micro cracks of mortar. The calcium leaching could be accelerated due to the existing of NaCl, which deteriorates the mechanical performance and increases the porosity. Besides, with the salt presence, the freezing point of concrete is decreased, the ice content reduction eases the pressures in pores, but the sudden ice formation may be enough to cause serious damage. Therefore, the amounts of ice and crystallized salt with freezing temperatures are essential to understanding the salt frost damage mechanism. If the phase changes are known, it is possible to model the combined effects. In order to predict and evaluate the mechanical performance of concrete suffered from the combined effects, this study conducted the following steps: (1) estimation of ice content in mortar saturated with deionized (DI) water during FTC based on electrical measurements, which includes the combined effects of moisture and temperature to the electrical properties of mortar; (2) estimation of ice amount in mortar saturated with NaCl solutions during FTCs based on electrical measurements, which includes the combined effects of moisture, temperature, microstructure, pore solution concentration to the electrical properties of mortar. (3) moisture transport property change due to NaCl attack; (4) mechanical property and chemical components change before and after FTCs; (5) mechanical property prediction model for the combined effects.

Since NaCl concentrations are not uniform along with the depth, the pressures in pores could be very different. In order to understand the role of NaCl in frost damage quantitatively, the solution concentration in pores is better to be uniform. Therefore, the mortar specimen in meso-scale was deployed in this study. In this case, the mechanical behavior of each layer could be obtained, which could be applied for a specific position of bulk specimen.

Electrical measurement is a useful technique, which was widely used to study the durability problems of cementitious materials. Because electrical conductivity of mortar is determined by the moisture content, temperature, microstructural characteristics and pore solution compositions, they were coupled to estimate the ice content in mortar saturated with NaCl solutions during FTCs. Firstly, by introducing the relationship between activation energy for conductance and saturation degree, the combined effects of moisture and temperature to electrical conductivity of specimen was clarified. Sequentially, an ice content estimation model was proposed, test results of bulk cylinder specimens saturated with DI water were applied to verify the model. After that, the electrical response of meso-scale specimen saturated with NaCl solutions during FTCs was investigated. A damage index was developed to evaluate the frost damage degree based on the electrical resistivity at reference temperature and activation energy, the effect of microstructural change was clarified as well. Then

the ice content estimation model was extended to the cases of NaCl solutions. Besides, since the pore solution concentration was considered in the model, the crystallized salt with FTCs can also be calculated. In addition, the results from experimentation were compared with theoretical analysis, which shows acceptable agreement.

After NaCl attack, the pore characteristics will be altered due to the calcium leaching and salt crystallization. To understand the salt effect to meso-scale specimens, the absorption of NaCl solutions and reabsorption of DI water tests were conducted. As found, when exposed to low concentration NaCl solution, the diffusivity of mortar would increase due to faster calcium leaching. However, for high concentration NaCl solution, it would be reduced since pores filled by crystallized salt have dominant effect in this case.

In addition, after immersed in NaCl solutions for 7 days, the meso-scale specimens were sealed and exposed to FTCs. Afterwards, three-point bending test and TG/DTA test were applied to evaluate the mechanical performance and chemical components alterations. According to the mechanical and chemical test results, before FTCs, the flexural strength and elastic modulus fluctuated with the NaCl concentration, which was mainly due to Portlandite leaching during the immersing process. After FTCs exposure, for specimens with higher water-to-cement ratio (w/c), the frost damage was severer and the damage developed gradually with increase of FTCs. For specimens saturated with deionized water and intermediate concentration solution (5%wt NaCl), the flexural strength and elastic modulus dropped to less than 60% after 30 FTCs, while there was almost no damage for specimens with $w/c=0.3$ (high strength and stiffness). For specimens exposed to high concentration solution (20%wt NaCl), over than 20% mechanical reduction after 30 FTCs was observed in the case of $w/c=0.7$. The salt can contribute to the frost damage, but the chemical results imply that the formation of Friedel's salt is less likely to cause destructive crystallization pressure. Finally, the mechanical performance of specimen exposed to FTCs and NaCl solution was predicted based on the ice amount, which has acceptable agreement with the experimental results.

Keywords: meso-scale, ice formation, salt crystallization, NaCl solution, mortar, combined effect, mechanical deterioration

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Chapter 1

INTRODUCTION

1.1 BACKGROUND

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 to 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).

The damage phenomenon contains two aspects. On one hand, the concrete surface could be scalling, removing the small flakes or chips of binder, spoiling the aesthetic appearance. The scaling mechanism is rather complex. It may be the combination effects of glue-spalling, thermal shock, osmotic pressure and precipitation of NaCl. Among them, the glue-spalling was considered as the dominant effect since it can account for the majority of the observed phenomenon. According to the mechanism, the scaling damage is determined by the mechanical properties of ice on the concrete surface and the mechanical properties of concrete surface (Sun and Scherer, 2010). The mechanical properties of ice depend on the volume fraction of ice (Valenza and Scherer, 2006). For different concentrations of salt solution, the ice formation is different since the existing of salt decreases the freezing point (Scherer and Valenza, 2005). Besides, the mechanical properties of concrete surface could be deteriorated by the combined effects of salt attack and freeze-thaw cycles. Because the frost resistance of concrete could be highly improved if the binder added is high strength or contains air-entraining agent (Sun and Scherer, 2010). Thus, the ice formation in surface and inside of concrete is essential for understanding the salt frost damage mechanism.

On the other hand, the mechanical properties of internal concrete could be reduced due to the combined effects of salt attack and freeze-thaw cycles (Wu *et al.*, 2014). The decreasing of strength and stiffness may threat to the safety of concrete structures, but less attention was paid to this problem. Compared with classic frost damage of concrete simply due to the ice formation, the salt frost damage could be due to the combination of ice formation, crystallization of Friedel's salt and precipitation and growth of salt crystal. For the ice formation, it may induce the hydraulic pressure, crystallization pressure and cryosuction pressure. The micro cracks and then cracks could occur and propagate when the overall pore pressure exceeds the tensile strength of concrete. The frost damage can be predicted based on the total pore pressure (Gong *et al.*, 2015). According to Farnam *et al.* (2014), the most severe frost damage occurred at the case of 15%wt NaCl solution saturated mortar sample and the reason could be the formation of Friedel's salt. However, from deformation measurements of Zeng *et al.* (2014), it seems there was no significant frost damage for cement paste saturated with 15%wt NaCl solution. In addition, the precipitation of NaCl crystal was also reported can cause destructive damage when the sample is in a supersaturated condition (Winkler and Singer, 1972; Thaulow and Sahu, 2004). Thus, the salt frost damage mechanism still needs further investigation. The information of ice formation and salt crystallization inside of concrete is essential for predicting the mechanical deterioration.

Another, the pore solution concentration in bulk concrete is not uniform, since the diffusion of NaCl is time dependent (Wang and Ueda, 2013). As a result, the damage degree due to salt frost action would vary with layer of concrete, determining by the pore solution concentration. To predict the damage of concrete with high accuracy, meso-scale is needed

because the pore concentration of sample can be ensured the same in this case. The relationship of each factor affecting the salt frost deterioration of concrete can be viewed on the Fig.1.1.

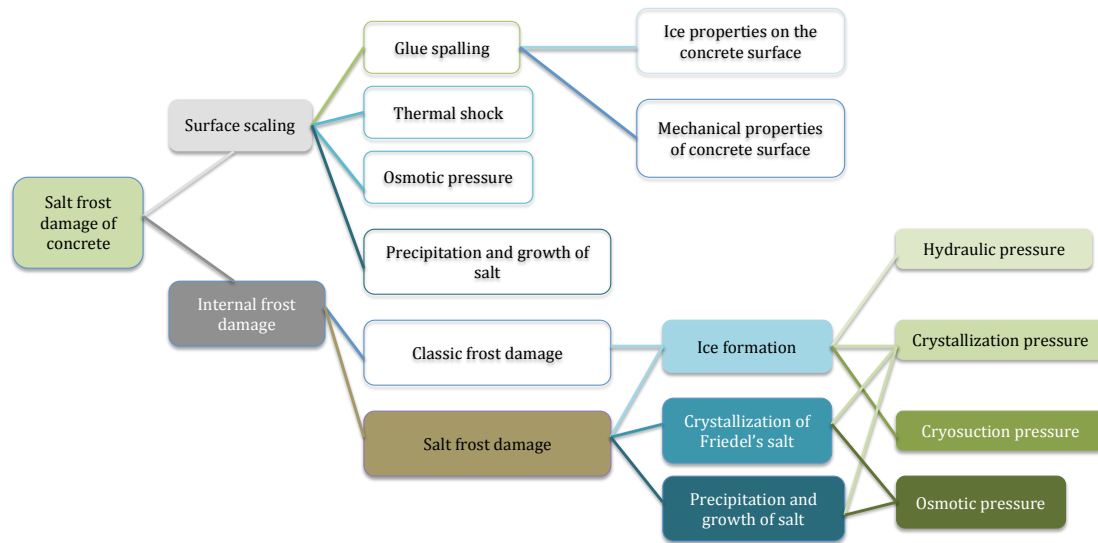


Fig.1.1 Factors affecting the salt frost damage of concrete (Valenza and Scherer, 2007)

1.2 OBJECTIVES AND SIGNIFICANCE

The main objectives of this study were to evaluate and predict the mechanical behavior of mortar suffered from FTCs and NaCl attack in sealed condition. The research flow is shown in Fig.1.2 and objectives are listed specifically as follows:

- 1) To estimate the ice formation in mortar saturated with DI water/NaCl solutions with FTCs based on electrical measurements.
- 2) To evaluate the damage degree of mortar suffered from the combined FTCs and NaCl attack based on electrical measurements.
- 3) To investigate the pore characteristics change due to salt crystallization and its effect on transport properties of mortar.
- 4) To understand the mechanical performance of mortar suffered from the combined FTCs and NaCl attack and to clarify the mechanical deterioration mechanism due to the combined effects.
- 5) To predict the mechanical behavior of mortar specimens suffered from the combined FTCs and NaCl attack.

The significance of this study is also described in this section. According to the experimental and analytical studies, the mechanical properties of concrete structures in cold regions can be predicted more accurately with the FTCs and the content of sprayed salt from a meso-scale point of view. In this case, the life cycle of concrete structures could be evaluated. Another, with regard to the clarified damage mechanism, effective measures to reduce the salt frost damage could be developed as well. Besides, electrical measurements could be applied as an effective non-destructive technique to evaluate the quality of concrete. The damage degree of concrete can be known from the electrical properties change, after that, related rehabilitation method can be proposed correspondingly to prolong the life cycle of concrete structures.

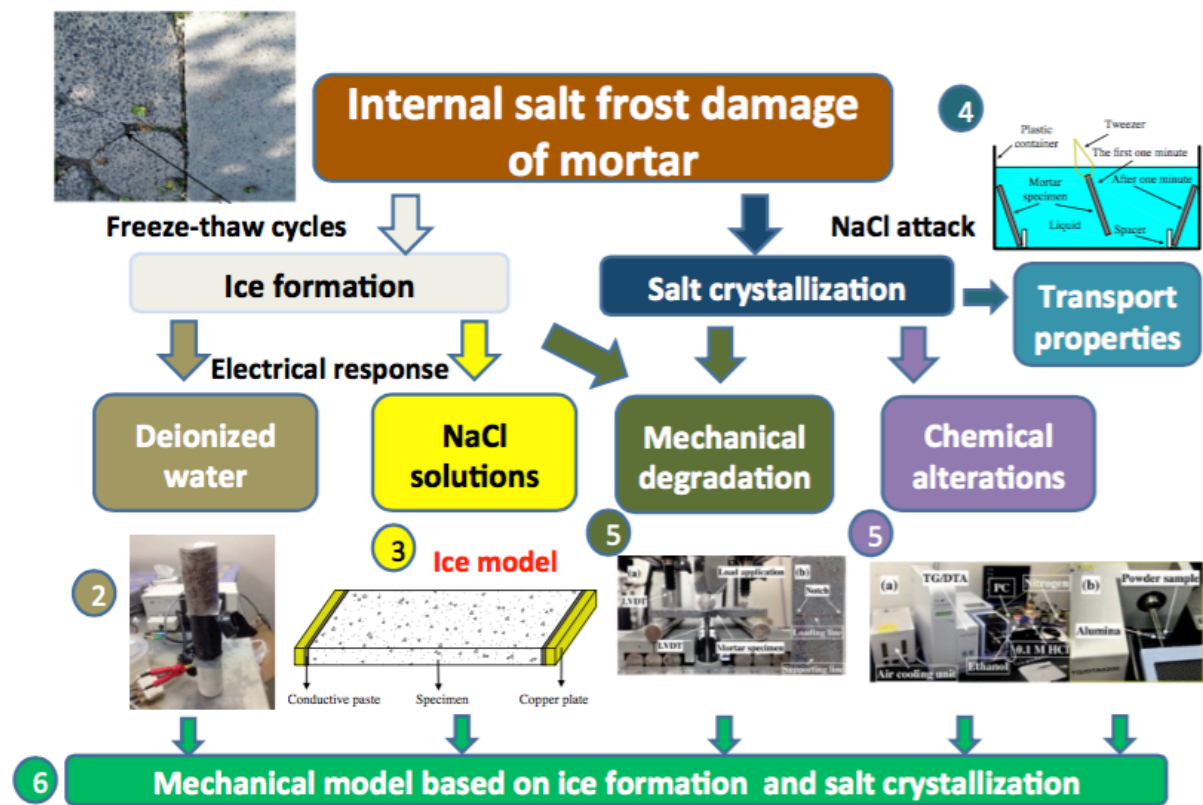


Fig.1.2 Research flow of dissertation (the number is the order of Chapters)

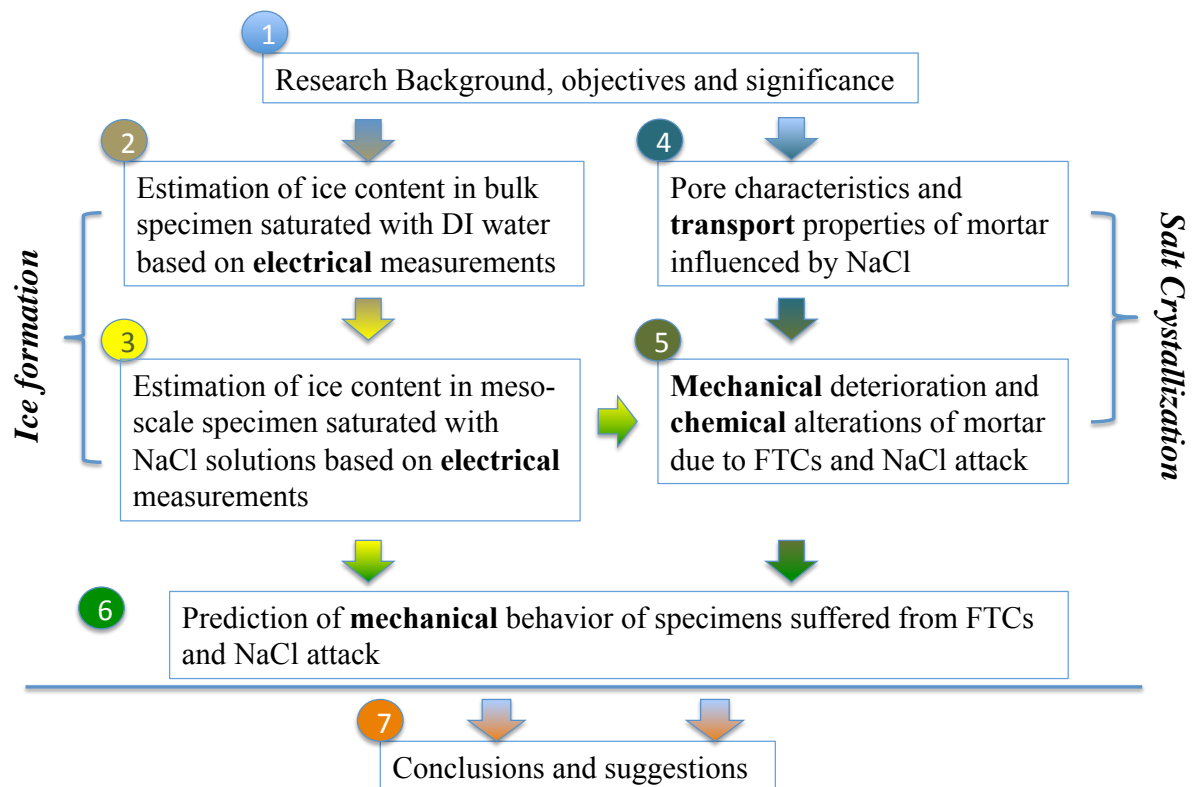


Fig.1.3 Organization of dissertation (the number is the order of Chapters).

1.3 OUTLINE OF THE DISSERTATION

This dissertation contains seven chapters. The organization is shown Fig.1.3.

Chapter 1 describes the background, objectives and significance of the present research. The organization of this dissertation is also briefly described.

Chapter 2 shows the proposed model to estimate the ice content by applying electrical measurements and clarifies the combined effects of temperature and moisture content for electrical conductivity of mortar. The ice content of mortar is estimated with the model by conducting the electrical test. To confirm the reliability of the model, the results are compared with theoretical results from thermodynamic analysis and the existing calorimetric test results.

Chapter 3 clarifies the relationship between temperature, saturation degree and solution concentration to electrical conductivity of mortar specimen. A model to estimate the ice content by applying electrical measurements is proposed for specimens with ice formation and salt crystallization. In addition, the ice formation within cementitious materials with different concentrations of NaCl solutions is theoretically investigated. Electrical response of meso-scale mortar specimens saturated with NaCl solutions with FTCs is experimentally studied. The variations of electrical resistivity at reference temperature and activation energy with FTCs are investigated specifically. The electrical resistivity at lowest temperature and freezing/thawing point change with FTCs are also discussed. The electrical results are interpreted with the proposed model. The results from electrical measurements are compared with the theoretical calculations.

Chapter 4 presents change in moisture uptake behaviors due to NaCl contamination. By obtaining the absorption curves of specimen immersing into NaCl solutions and re-dried specimen immersing into DI water, the salt contamination effect to meso-scale specimen is understood. Based on the test results, two-stage solution diffusion model is developed, which can describe the solution absorption process efficiently.

Chapter 5 describes the mechanical properties of mortar specimen in meso-scale and corresponding chemical analysis results under FTCs. The damage mechanism due to NaCl attack and FTCs is clarified. Empirical equations to predict the mechanical performance of the specimens exposed to the combined effects are proposed. To quantitatively evaluate the salt frost damage of mortar based on electrical response, theoretical model for damage index is also developed.

Chapter 6 proposes a theoretical model to predict the mechanical performance of mortar under the combined effects. During freezing, the ice content is used as the parameter to calculate the pore pressures which can cause the damage of specimen. Then the predicted results are compared with our experimental data.

Chapter 7 shows the conclusions of the finished work. The significant findings in this study are highlighted as well. Some suggestions for future study are also presented in this chapter.

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Chapter 2

ESTIMATION OF ICE CONTENT IN MORTAR BASED ON ELECTRICAL MEASUREMENTS UNDER FREEZE-THAW CYCLE

2.1 INTRODUCTION

Frost damage to concrete is of great concern in cold regions, especially for concrete infrastructure related to transportation (Valenza and Scherer, 2007). Many models have been proposed to explain the mechanism of frost damage such as hydraulic pressure (Powers, 1945), crystallization pressure (Scherer and Valenza, 2005) and cryosuction pressure (Sun and Scherer, 2010a). A comprehensive hydraulic model was also developed by Gong et al. (2015a) to explain the relationship between internal pressure and deformation of concrete. According to Gong et al.'s model, to obtain the internal pressure with freeze-thaw cycles (FTCs), it is rational to apply the sum of the above three pressures. However, all of these models require the information of ice content as a known input, which still cannot be measured confidently during freeze-thaw cycles, even though some studies provide useful information by using differential scanning calorimeter (Johannesson, 2010, Sun and Scherer, 2010b), but it is limited to pore size from 4nm~100nm and the result would be complicated to interpret if there is solute in the pore liquid since the salt can change the heat flow state in concrete (Kjeldsen and Geiker, 2008).

Recently, using electrical measurements to investigate the micro-characteristics of cement-based materials has attracted more interest because of its high efficiency and easy application (Spragg et al., 2012). It seems also quite promising to use this method to study the frost damage of concrete, especially for the ice formation process (Perron and Beaudoin, 2002, Sato and Beaudoin, 2011). The electrical conductivity of concrete depends on five factors: porosity, connectivity, chemical composition of pore solution, saturation degree (moisture content) of concrete and temperature (Weiss et al., 2012). Generally, when the temperature is decreasing below the freezing point, the content of unfrozen water gradually decreases. According to existing understandings (Whittington et al., 1981, Katsura et al., 1996, Sato and Beaudoin, 2011, Spragg et al., 2013), both temperature and moisture content have a significant influence on the electrical conductivity of concrete. Weiss et al. (2012) suggested the relationship between electrical conductivity and degree of saturation of concrete under normal temperatures considering the porosity, connectivity of concrete and chemical composition of the pore solution (modified from the model of Archie (1942) in soil science). Effect of temperature on electrical conductivity of concrete has also been studied by applying Arrhenius's law (Chrisp et al., 2001, Liu and Presuel-Moreno, 2014). Wang et al. (2014a, 2014b) observed the electrical resistivity change in response to temperature and the change of ice nucleation temperature during FTCs. However, current studies only focused on the effect of either moisture content or temperature on the electrical conductivity of concrete (Villagrán Zaccardi et al., 2009). The combined effect of moisture content and temperature on electrical conductivity should be clarified firstly if one wants to monitor the ice formation process reliably based on the electrical measurements.

In terms of estimating ice content based on electrical measurement, Cai and Liu (1998) developed a simple model to predict the ice content by assuming that the electrical resistance of the pore solution is constant and is equal to the electrical resistance of the specimen, however, in reality, the resistance of the specimen varies against the temperature and moisture condition. McCarter et al. (2015) also proposed a model to predict the ice content based on electrical measurement with a similar equation to Cai and Liu's, but it considers the effect of

temperature on pore solution. Nevertheless, in their study the contributions of porosity and connectivity to the electrical conductivity of the specimen are ignored and the ice formation process is instant rather than continuous. Farnam et al. (2015) studied the electrical response of mortar under FTC to detect the phase change. In their study, a damage index based on the ratio of electrical resistivity before and after FTC was used to evaluate the frost damage of mortar with different degrees of saturation. A comprehensive relationship between the ice content and the electrical conductivity of mortar considering the combined effects of moisture and temperature has not been derived.

The purpose of this chapter is to derive a rational relationship between the ice content and the electrical conductivity of mortar and to understand the ice formation process in mortar under FTCs based on electrical measurements. A better understanding of combined effects of temperature and degree of saturation on electrical conductivity is to be achieved. In addition to the combined effects, with regard to serious damage of concrete after repeated FTCs, the model is extended to multiple cycles by considering the damage within each cycle. The results of this chapter are of significance in predicting the mechanical degradation of concrete under FTCs, as well as life cycle of concrete structures in cold regions. Furthermore, the knowledge of combined effects of temperature and degree of saturation can also be used to improve the understanding of hydration process of cement mortar by electrical monitoring the combined effects of temperature and moisture content.

2.2 THEORETICAL MODEL FOR THE COMBINED EFFECTS OF TEMPERATURE AND MOISTURE CONTENT

The degree of saturation is an important factor for electrical conductivity of concrete since it is related to the electrical conductivity of pore solution, water filled porosity and water connectivity, which are the dominant factors of electrical conductivity. Recently, Weiss *et al.* (2012) suggested a saturation function (Eq. (2.1)) to account for the electrical properties of partially saturated concrete based on the fact that the water filled porosity and water connectivity are proportional to a power law function of degree of saturation, which was originally developed in Archie (1942).

$$\frac{\sigma_c}{\sigma_{cs}} = S^n \quad (2.1)$$

where σ_c is the electrical conductivity of partially saturated concrete, σ_{cs} is the electrical conductivity of fully saturated concrete, S is the degree of saturation of concrete. n is the saturation coefficient which is simplified from term $n'+\delta-1$ for convenience. It is determined by two parts, the intrinsic properties of concrete such as porosity and connectivity (n') and chemical composition of pore solution ($\delta-1$) (Based on existing experimental data (Weiss *et al.*, 2012), for $w/c=0.5$, n of mortar approximately equals to 3.5). During freezing, water content loss due to ice formation, concentration and conductivity of the pore solution increases. Since the parameter ' n ' is related to pore solution composition which could account for the nonlinear relationship between conductivity and concentration, as discussed in Weiss *et al.* (2012), Eq. (2.1) can be used to estimate the degree of saturation change based on the change of electrical conductivity.

Temperature also has a significant effect on electrical conductivity of concrete because it can change the mobility of ions. Under high temperature, the ions are more active, consequently the electrical conductivity is higher and vice versa. Generally, researchers consider that the Arrhenius equation (Eqs. (2.2) and (2.3)) can be reliable in describing the

relationship between electrical conductivity and temperature (for temperature range of 0-50°C), and it is less temperature dependent when the temperature is higher than 50°C (Spragg *et al.*, 2013, Chrisp *et al.*, 2001, Liu and Presuel-Moreno, 2014). Moreover, with regard to recent research results (Panchmatia *et al.*, 2014), the equation is also applicable under a temperature of -18°C, therefore, it is possible to use it for investigating ice formation process.

$$\sigma = Ae^{-\left(\frac{E_a}{R_g T}\right)} \quad (2.2)$$

$$\frac{\sigma}{\sigma_{ref}} = e^{-\left[\frac{E_a}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]} \quad (2.3)$$

where σ is the electrical conductivity measured at the absolute temperature T (K), σ_{ref} is the conductivity at absolute reference temperature T_{ref} , the measured one and the reference one are the same degree of saturation, A is the nominal conductivity at infinite temperature ($T \rightarrow \infty$) in S/m, E_a is the activation energy for the conduction process in kJ/mol and R_g is the universal gas constant = 8.314 J/mol/K.

The activation energy of concrete (E_a) is the parameter that determines the sensitivity of electrical conductivity of concrete with regard to temperature. However, it is not a constant and increases with the decreasing of degree of saturation from existing experimental observations (Chrisp *et al.*, 2001). The value of E_a has been reported to range from 16.9 to 42.8 kJ/mol (Liu and Presuel-Moreno, 2014). In order to analyze the temperature effect on electrical conductivity of concrete quantitatively and accurately, it is necessary to clarify the relationship between the activation energy and the degree of saturation.

For the above purpose, as derived in the Appendix, the activation energy of partially saturated concrete can be written as the following equations

$$E_{a,s} = -\frac{R_g \ln\left(\frac{\sigma_{T,s}}{\sigma_{ref,s}}\right)}{\frac{1}{T} - \frac{1}{T_{ref}}} \quad (2.A.7)$$

$$E_{a,p} = E_{a,s} - R_g T_{ref} \ln(S^n) \quad (2.A.14)$$

where $E_{a,p}$ is the activation energy of partially saturated concrete for the conduction process and $E_{a,s}$ is the activation energy of fully saturated concrete for the conduction process. $\sigma_{T,s}$ is the electrical conductivity of fully saturated concrete at the absolute temperature T , $\sigma_{ref,s}$ is the electrical conductivity of fully saturated concrete at the reference temperature T_{ref} .

Based on the above equation, the normalized electrical conductivity (see Fig. 2.1) can be calculated as (see detailed derivation in appendix)

$$\frac{\sigma_{T,p}}{\sigma_{ref,s}} = e^{-\left[\frac{E_{a,s} - R_g T_{ref} \ln(S^n)}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]} \cdot S^n \quad (2.A.15)$$

By reversing Eq. (2.A.15), we have the relative content of unfrozen water (the same value as liquid saturation degree during freezing and thawing) as

$$S = \frac{n_{ref}}{n} \sqrt{\frac{\sigma_{T,p}}{\sigma_{ref,s}}} \cdot e^{\left[\frac{E_{a,s}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]} \quad (2.4)$$

During freezing the water transforms to ice. Since the conductivity coefficients of ice (solid) and vapor are very low compared to that of water ($\sigma_{liq}=1\sim 20$ S/m, $\sigma_{sol}\approx 10^{-9}$ S/m, $\sigma_{vap}\approx 10^{-15}$ S/m (Rajabipour and Weiss, 2007) and $\sigma_{ice}\approx 10^{-6}$ S/m (Petrenko, 1993)), the conductivity is mostly determined by the conductivity of pore solution. Therefore, the degree of saturation can be considered as relative content of unfrozen water. The relative ice content I is then determined as

$$I \approx S_0 - S \quad (2.5)$$

where S_0 is the initial saturation degree.

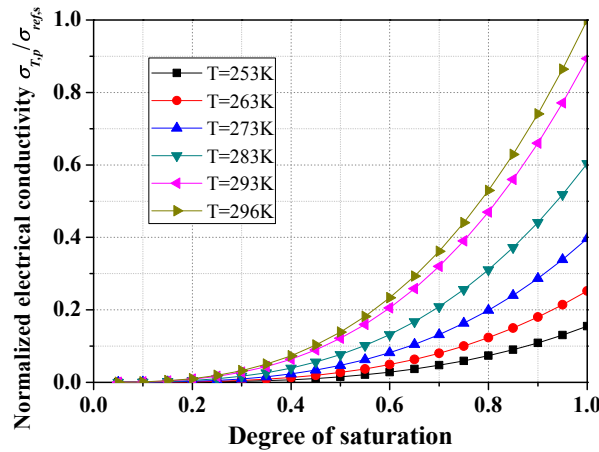


Fig. 2.1 The relationship between the electrical conductivity and degree of saturation

In addition, the frost damage may also affect the electrical conductivity by altering the porosity and connectivity of concrete, which makes the accuracy of the calculated ice content with FTCs reduced. However, at this stage, it is very difficult to quantitatively analyze the frost damage based on temperature change. The internal pore pressure in concrete can be calculated by ice formation along with temperature change which could be used for evaluating the damage, but once the damage developed, the ice content estimation would be affected, as a result, the damage cannot be evaluated accurately with temperature. According to Gong *et al.* (2015b), during freezing, damage increases, while during thawing the damage rather remains, therefore a possible simple solution is to differentiate the freezing and thawing process with and without considering damage evolution based on the damage mechanisms difference, respectively. In this case, the estimated ice content for multiple cycles would be more accurate. But this is only a simple approach for understanding the damage effect on ice estimation. In order to analyze the damage development quantitatively based on ice formation, it still needs further investigation. With regard to the damage development during freezing, the referenced electrical conductivity at i cycle may change with temperature after ice formation until it reaches the referenced electrical conductivity at $i+1$ cycle (see discussion in

Section 2.4.5) since it could be considered as a parameter to evaluate the damage (Farnam *et al.*, 2015). Thus, Eq. (2.4) is extended to the case of repeated freeze-thaw cycles as follows

$$S_{iF} = n \frac{T_{ref}}{T} \sqrt{\frac{\sigma_{T,p}}{\sigma_{ref_i,s} + \frac{T - T_F}{T_L - T_F} (\sigma_{ref_{i+1},s} - \sigma_{ref_i,s})}} e^{\left[\frac{E_{a,s}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]} \quad (2.6)$$

$$S_{iT} = n \frac{T_{ref}}{T} \sqrt{\frac{\sigma_{T,p}}{\sigma_{ref_{i+1},s}}} e^{\left[\frac{E_{a,s}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]} \quad (2.7)$$

where S_{iF} and S_{iT} are unfrozen water content during freezing and thawing at a certain i cycle, $\sigma_{ref_i,s}$ and $\sigma_{ref_{i+1},s}$ are the electrical conductivity of fully saturation concrete at the reference temperature before and after the i cycle. T_F is the freezing point and T_L is the lowest temperature (K).

2.3 EXPERIMENTAL METHODOLOGY

2.3.1 Specimen preparation

Mortar specimens were prepared. The mix proportion is based on ACI Committee 211 (1991), in which the coarse aggregate was not included. The w/c ratio is 0.5, water is 207 kg/m³, cement is 414 kg/m³ and fine aggregate is 990 kg/m³. The materials used were Ordinary Portland Cement with density 3.14 g/cm³, fine aggregate of 1.2 mm or less in size with density 2.67 g/cm³ and there is no admixture added. After proper mixing, the specimens were cast into $\varnothing 50$ mm $\times$ 100 mm cylinders and cured for 24 hours before demolding. Once the specimens were demolded, they were cured under water for 90 days at room temperature $23 \pm 2^\circ\text{C}$. The cured specimens were oven dried at 105°C for 24 hours in order to remove the evaporable water. Although there is possibility that the specimens have initial damage when the drying temperature was set 105°C , the oven-drying induced damage is insignificant compared with further frost damage according to the test results of Sicat *et al.* (2013). Therefore, the estimated ice content based on normalized electrical conductivity is still reasonable. Then the specimens were submersed in water until mass was constant to attain full saturation. Finally, the specimens were sealed with polyvinylidene chloride plastic (commonly known as Saran) and vinyl/mastic tape to prevent moisture loss. Before conducting the electrical measurements, the tape and Saran in the end of the cylinder specimen were removed and thus the specimen can contact with sponges.

2.3.2 Test method

In this test, we adopted end to end AC two point test and referred to the setup of Spragg *et al.* (2011), as shown in Fig. 2.2(a). The cylinder mortar was placed inside of the environmental chamber, two steel plate electrodes connect with the alligators of a commercial resistivity meter and the ends of the cylinder. The wet sponges, which were saturated with 20%wt NaCl solution to have high conductivity, were used between plate electrodes and cylinder specimen for better contact. Moreover, because the thinner the sponge is, the smaller the resistance would be, the thickness of the sponge in this test is about 2mm which is the thinnest found in the market (see Fig. 2.2(b)). To assure a good contact between electrodes and specimen, which may affect the resistivity measurement significantly, external pressure

of 6 kPa was applied as an external mass on the top electrode, as recommended by Newlands *et al.* (2008). Since the direct current causes polarization effect which increases the electrical resistivity, alternating current with a frequency of 1kHz was chosen for measurement, as the optimized frequency confirmed by McCarter *et al.* (2015). The uniaxial resistivity of specimen was measured continuously by the resistivity meter and the data was collected by computer automatically every 3 seconds. Three specimens at the same condition were used for testing and they were measured continuously for hours to get stable values for each designed temperature and obtain the exact value of activation energy of mortar at saturation. The electrodes were sandblasted before each measurement to assure that their resistance is the same for different specimens. The electrical resistance of the sponges was measured first because the resistance of the sponges during the FTCs may influence the total resistance.

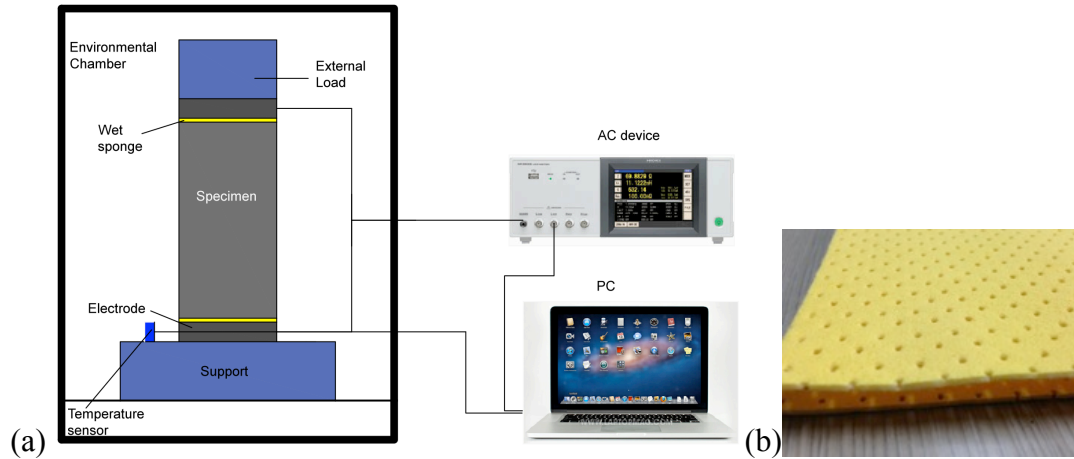


Fig. 2.2 Setup of the test (a) Test setup (AC device is a commercial resistivity meter) (b) Details of the wet sponge

2.3.2.1 Method of calculating the electrical conductivity

Resistance of mortar was calculated based on the method applied by Spragg *et al.* (2011). Since high external pressure was used in this test, there is not much difference between top and bottom sponge resistance and

$$R = R_{measured} - 2R_{sponge} \quad (2.8)$$

where R is the electrical resistance of mortar cylinder, $R_{measured}$ is the measured value of the whole system and R_{sponge} is the electrical resistance of sponge.

To consider the geometrical effect, the conductivity of the specimen is

$$\sigma = \frac{1}{\rho} = \frac{1}{KR} = \frac{L}{aR} \quad (2.9)$$

where ρ is the resistivity of the mortar, K is the geometrical parameter, a is the cross-sectional area and L is the length of the test specimen.

2.3.2.2 Freeze-thaw tests

As shown in Fig. 2.2, specimens were set in the environmental chamber, which can control temperature and relative humidity. The temperature history of the environmental chamber was measured by a temperature sensor recorded by computer. The temperature cycle

(Sicat *et al.* 2013) started at 10°C for 90 minutes, then decreased by 0.25°C per minute until it reached -28°C and remained constant for 90 minutes, and then increased by 0.25°C per minute until the maximum temperature 10°C. The FTC was repeated 3 times for three saturated specimens. The detailed temperature history of one cycle can be viewed from Fig. 2.4. The relative humidity in the chamber at 10°C is around 90%. Since the specimens were sealed during the test, the relative humidity controlled in the environmental chamber had insignificant effect to the electrical conductivity of specimens.

2.4 RESULTS AND DISCUSSION

2.4.1 The activation energy at full saturation

According to the theoretical model for calculating ice content (Eqs. (2.4) and (2.5)), only the activation energy at full saturation ($E_{a,s}$) and the saturation coefficient (n) are needed. The activation energy of the specimen is a parameter which can indicate the electrical conductivity's sensitivity to temperature, and highly depends on the degree of saturation of the specimen and the material properties. As shown in Fig. 2.3, although there is some difference between each specimen, the electrical conductivity and temperature show a linear relationship for all three specimens with similar slope values. The activation energies of the three specimens at full saturation are all about 16kJ/mol, which was calculated from Eq. (2.A.7) with regard to the measured electrical conductivity and temperature.

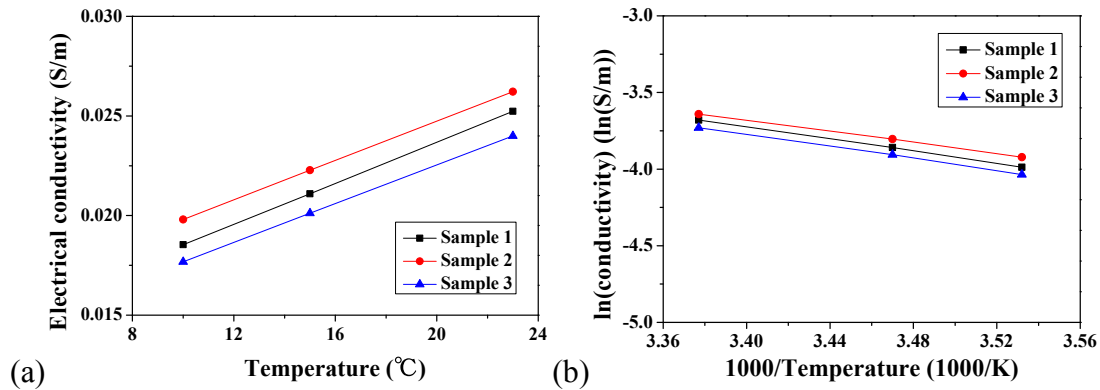


Fig. 2.3 Relationship between electrical conductivity and temperature at full saturation

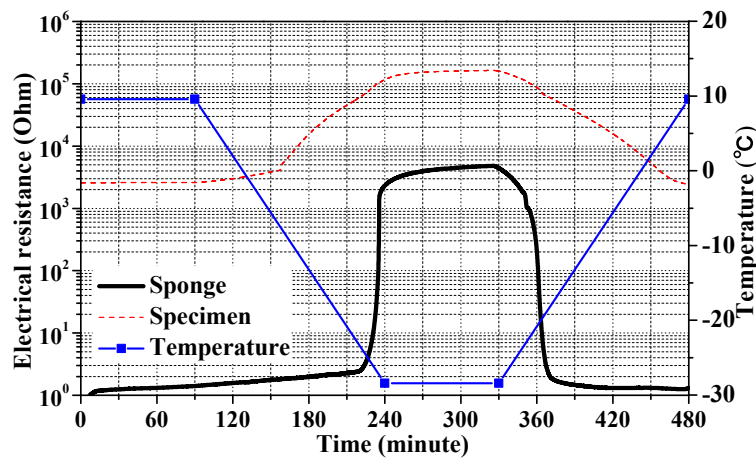


Fig. 2.4 Comparison of the electrical resistance of specimen and sponge under freeze-thaw cycle

2.4.2 The electrical resistance of sponge under FTC

As shown in Fig. 2.4, the electrical resistance of the sponge was not constant along with temperature change and it was observed negligible when the temperature is higher than -20°C . To be more exact, at temperature above zero, the electrical resistance of the wet sponge is less than $2\ \Omega$. Due to the ice formation in the sponge at temperatures below -20°C , the electrical resistance increased exponentially though it was still very small compared with the electrical resistance of mortar. By subtracting the electrical resistance of the sponge (Eq. (2.8)) from the measured total electrical resistance, correct electrical resistance of mortar under FTCs was obtained.

2.4.3 The electrical resistivity of specimen under FTCs

Due to complexity of measuring the inside temperature of samples, only the temperature of sample surface was measured, which was found to be the same as the set temperature. According to the study of Hasan *et al.* (2003), the temperature inside a concrete cylinder with size of $\phi 100\text{mm} \times 200\text{mm}$ was rather uniform. Therefore, the uniformly distributed temperature inside of the specimens was assumed in this paper because the sample size in this study is much smaller than Hasan's case. The resistivity of three specimens under three FTCs is shown in Fig. 2.5. The electrical resistivity of specimens changed dramatically in response to temperature change, especially under lower temperature. If the temperature variations are not the same during each cycle because of the change of thermal conductivity coefficient caused by frost damage, the electrical resistivity variations would be also very different. However, as can be seen in Fig. 2.5, the electrical resistivity becomes almost constant when the temperature becomes 10°C , which means that the temperature hysteresis change due to the frost damage was negligible. In addition, the temperature variation of concrete samples with FTCs was measured in (McCarter *et al.* 2015). Their temperature hysteresis results show little difference between two temperature cycles, which can also confirm that the change of thermal conductivity coefficient is not obvious after one cycle of frost damage. So it is reasonable to use the set temperature as the index of the temperature of the sample. Although there is a slight difference in resistivity between the three specimens at 10°C , their variation tendencies are almost the same, which means they have the similar ice formation process. The difference may be due to the testing scatter. The sample 3 may be slightly less porous or have lower degree of saturation than the other two. As a result, it has less frost damage and the difference becomes larger with increasing numbers of the cycles. Because the three specimens show very similar results, only the result of sample one is presented in detail in Fig. 2.6 for the electrical resistivity change during freezing and thawing process for each cycle. When the temperature is above 0°C , the logarithm of electrical resistivity is in linear relationship with temperature which means the change is simply due to the temperature variation, there is no ice formation. When the temperature drops below about -7°C , the resistivity starts to increase sharply. This turning point may be interpreted as the freezing point, while the turning point of resistivity with temperature increasing at the thawing phase can also be interpreted as the thawing point. For three freeze-thaw cycles, the freezing point increases with cycles while the thawing point decreases, which was also observed by Wang *et al.* (2014) (see details in the Fig. 2.7). Generally, the freezing point of mortar is below 0°C , which may be due to the supercooling nature of mortar (Sun and Scherer, 2010b). Because the supercooling phenomenon is a random phenomenon (Zeng *et al.*, 2015), from the statistical point of view, the freezing point change tendency needs further experimental confirmation. In a short temperature range after the freezing point, the logarithm of electrical resistivity is in linear increasing, which means the resistivity difference is mainly due to temperature change.

However, with further changing of temperature, the nonlinearity of resistivity curve is more obvious, which indicates that the ice formation is continuous under lowering temperature due to pore radius variation (water filled in smaller pores has lower freezing point) resulting in continuous decrease in liquid saturation rate. If the ice formation is instant at a certain temperature rather than being continuous, after a sudden change of slope, the curve is supposed to be linear. At the lowest temperature, the resistivity still increases to some extent, which may be caused by water re-distribution at the maintained temperature. Since the chemical potential difference caused by ice formation may induce the water to flow from smaller pores to bigger pores, the ice formation could continue even under the constant temperature. As a result, the electrical resistivity would increase due to the reduced liquid saturation degree. During the thawing process, the curve seems smoother than the freezing process because there is no supercooling effect, but the thawing point is higher than 0°C which may be due to the size of specimen. Owing to the temperature hysteresis, the smaller the specimen size, the closer of the thawing point to 0°C . This is because the heat needs time to be transferred, if the specimen is pretty large. It may take a certain time to achieve 0°C at the center of the specimen for thermal conducting. Therefore, the temperature at the surface of the specimen may be very different from 0°C .

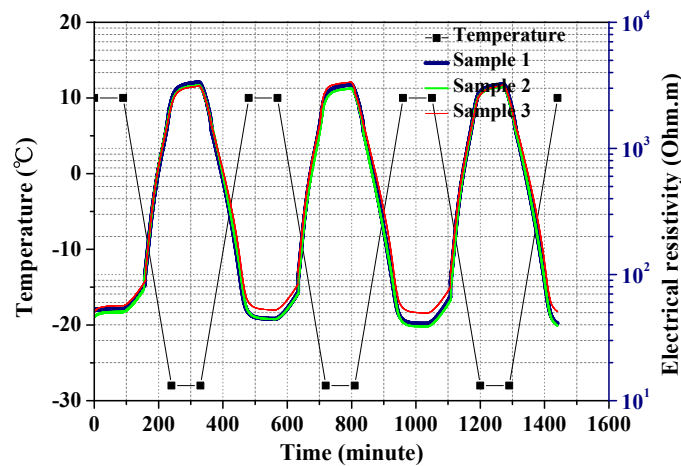


Fig. 2.5 Electrical resistivity changes under three freeze-thaw cycles

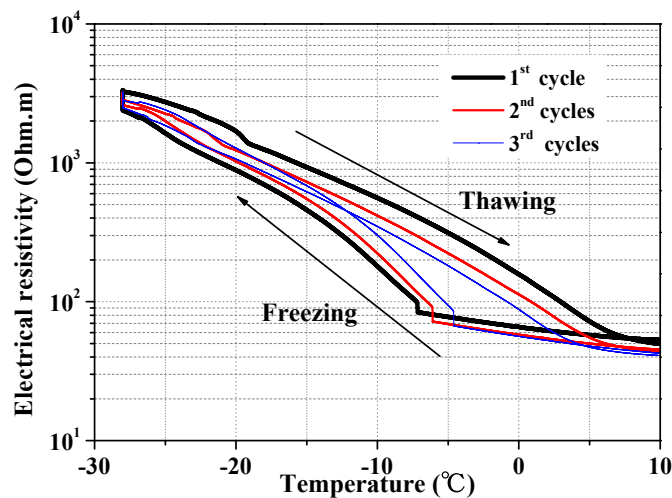


Fig. 2.6 Electrical resistivity changes under freezing and thawing

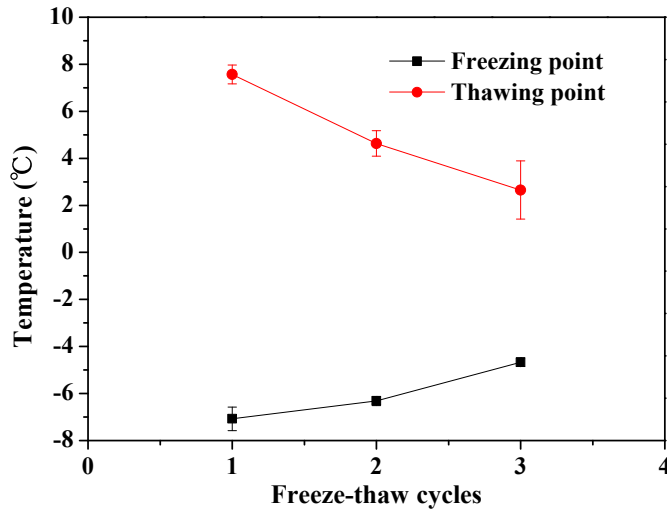


Fig. 2.7 Freezing and thawing points of specimens with FTCs

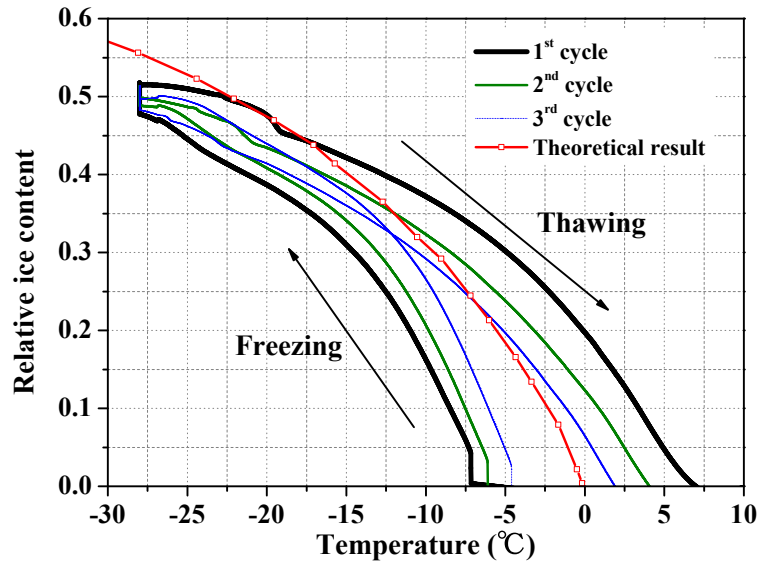


Fig. 2.8 Estimation of relative ice content in case of $n=3.5$ (Weiss *et al.*, 2012)

2.4.4 Estimation of ice content in mortar under FTCs

Eqs. (2.4) and (2.5) are used for calculation of ice content, in which the activation energy at full saturation (16kJ/mol) was obtained from our previous test as shown in Section 4.1 and the saturation coefficient approximates to 3.5 (referred to Weiss *et al.* (2012)). From the results shown in Fig. 2.8 and Fig. 2.9, under freezing, the relative ice content increases continuously after ice formation starts, reaching around 0.5 at -28°C . When the temperature was kept at -28°C , the ice content still has a slight rise. This is mainly due to the unfrozen water redistribution as a result of the chemical potential difference in pores with ice formation. During the thawing, the amount of ice content is higher than that of the freezing process at the same temperature, which is probably because of the natural supercooling effect of the porous medium. To be more precise, water in some of the pores reached the freezing point cannot form to ice due to lacking of ice nucleation crystals during freezing. However, this kind of phenomenon would not happen during thawing, which will result in the ice amount difference

between the two processes. The theoretical result from ice formation analysis (Gong *et al.*, 2013) based on thermodynamics and pore size distribution information of mortar (Gong *et al.*, 2014) is also presented in Fig. 2.8. It seems the theoretical result agrees reasonably well with the test results if we exclude the supercooling effect, which was not considered in the theoretical results in this study. The ice content variation with FTCs is shown in Fig. 2.9. From the results of the three specimens, they show almost the same change with temperature which confirms that the proposed method to estimate ice contents is reliable.

After revealing the ice formation process in mortar with electrical measurements, the results were compared with existing test results. Data from Sun and Scherer (2010b) was used for comparison. The study of Sun and Scherer applied a differential scanning calorimeter (DSC) to obtain the amount of ice formation in the mortar. It can be seen from Fig. 2.10 (a) that the shapes of results from Sun and Scherer and our test results are similar for freezing and thawing stages. The difference probably is due to different curing conditions and specimen sizes. Firstly, specimens from Sun and Scherer were immersed into limewater for six months before the test while our specimens were cured under tap water. This means our specimens would be more porous because of Ca^{+} leaching. Even though the w/c of Sun and Scherer's specimens is 0.55, the maximum value of ice content is still lower than our case (w/c=0.5). Secondly, the specimen Sun and Scherer used is 5 mm×5 mm×1 mm disk whereas our specimen is $\phi 50$ mm×100 mm cylinder. The reason why our specimen shows the greater difference between freezing and thawing points is the larger specimen size. The response to temperature difference, in other words, temperature hysteresis takes longer time. This point can also explain why there is slight increase in ice content during constant lowest temperature.

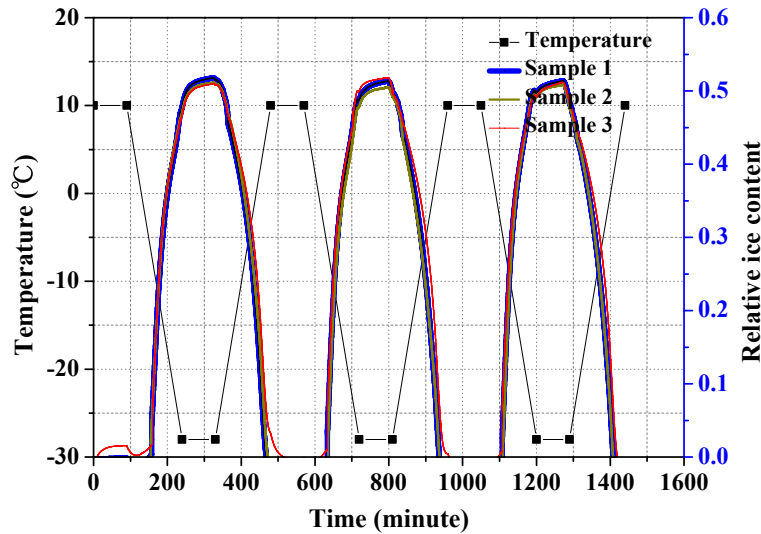


Fig. 2.9 Estimation of relative ice content with FTCs

In addition, the relative ice content of mortar specimens with different degrees of saturation under freezing and thawing from test results of Farnam *et al.* (2015) was calculated by the proposed model. Farnam *et al.* (2015) also tested the electrical response of mortar under FTC but they used a nickel conductive coating to reduce the interface effect between electrodes and specimen instead of wet sponges. Besides, by following ASTM C305-12, the mortar samples were sealed to cure for 28 days. Since they used relatively small size specimens (25.4 mm×25.4 mm×50.8 mm) in comparison with our specimen, the difference in relative ice content between freezing and thawing process is smaller than our case as shown in Fig. 2.10 (b). Because the energetic barrier to nucleation may vary with sample sizes (Sun and Scherer, 2010a), the ice formation processes varied accordingly. Although the shape and

the tendency of the curves are similar, the maximum relative ice content in Farnam *et al.*'s test is less than 0.5 for a fully saturated specimen. The reason may be explained by the lower water to cement ratio (0.42).

Furthermore, the calculated relative ice content of the different saturated specimens are shown in Fig. 2.11 (a) and compared to the theoretical results ($w/c=0.42$ was used) from Gong *et al.* (2013) in Fig. 2.11 (b) for the freezing process. It seems that the results have an acceptable agreement. Even though there is a slight difference at temperature near to the freezing point due to supercooling effect and lower than -20°C due to possibly ice percolation, the model can reasonably predict the ice formation in partially saturated cases.

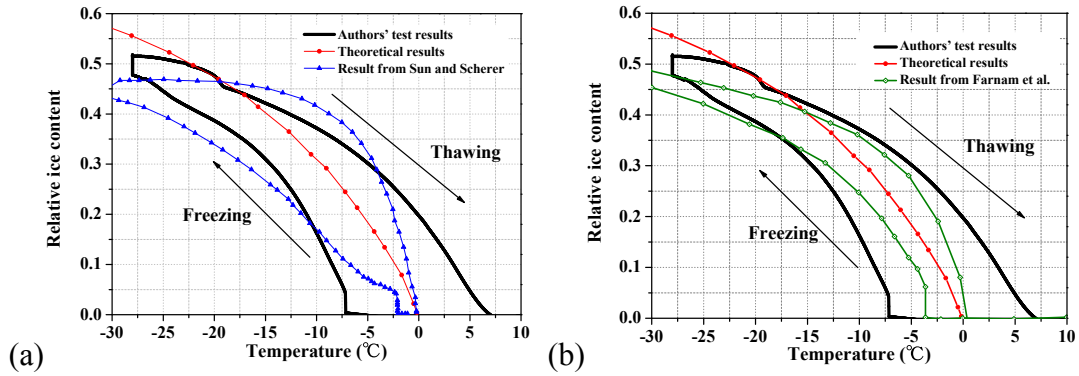


Fig. 2.10 Comparison ice content of mortar obtained from (a) electrical test (authors') and calorimetric test (Sun and Scherer, 2010) and (b) electrical test (authors' and Farnam *et al.*, 2015) (calculated by the author's model)

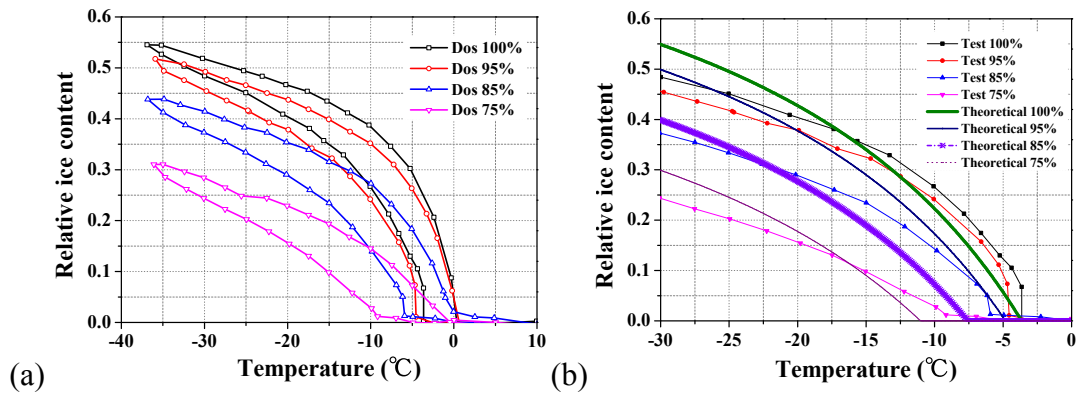


Fig. 2.11 Calculated relative ice content from electrical test results of Farnam *et al.* (2015) by using authors' model (a) Relative ice content of different degree of saturation under freezing and thawing (b) Comparison of the test results and theoretical results from Gong *et al.* (2013a)

2.4.5 Estimation of ice content with consideration of frost damage

It is common understanding that the frost damage may change the microstructural characteristics of mortar (eg. porosity and connectivity), therefore electrical resistivity of mortar may be affected as well. As a consequence, electrical conductivity of fully saturated mortar at the reference temperature $\sigma_{ref,s}$, activation energy of fully saturated concrete for the conduction process $E_{a,s}$ and saturation coefficient n (see Eq. (2.1)) would be different before and after FTC. Among them, $E_{a,s}$ and n are correlated with $\sigma_{ref,s}$. Therefore, the change of $\sigma_{ref,s}$ may represent the damage effect and this is the basic concept for Eq. (2.6). The frost damage does not suddenly happen but is accumulated with FTCs, which needs cycles to be serious. It may be ignored within one cycle for estimating relative ice content. As it is shown in Fig.

2.12 where the electrical data is cited from Farnam *et al.* (2015), and the damage evolution is assumed to be linear with temperature variation during freezing phase, the estimated relative ice content with and without considering frost damage does not show much difference within one cycle. To evaluate ice content more precisely during thawing process, we need for further experimentation to investigate the effects of damage on electrical conductivity. And further verification is necessary under multiple FTCs.

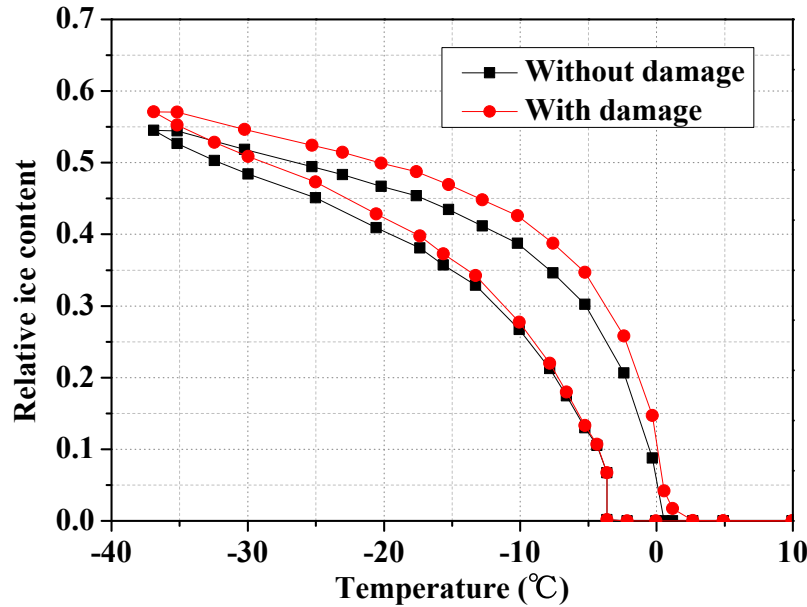


Fig. 2.12 Calculated relative ice content from test results (fully saturated case) of Farnam *et al.* (2015) by using authors' model with and without considering frost damage development

2.5 CONCLUSIONS

- (1) The combined effect of temperature and moisture content on electrical conductivity of concrete is explained from a theoretical point of view. Under freezing conditions, the two effects both play significant roles in the electrical behavior of concrete and the interactive effect is more obvious under higher temperatures and higher degrees of saturation. In this study, the relationship between the activation energy and the degree of saturation is derived. A method to estimate the ice content based on electrical measurements is proposed considering the coupled effect of temperature and moisture content. Although the ice formation in partially saturated specimens was calculated for one cycle based on the test results of Farnam *et al.* (2015), the proposed model still needs further experimental study with multiple FTCs for the verification of applicability.
- (2) Based on the proposed method, the relative ice content of mortar is estimated by conducting the electrical test. The test results of three samples during FTCs are consistent and the ice formation process is continuous with temperature variation, which means the proposed test method is reliable and repeatable. The freezing point of specimen is increasing with cycles while the thawing point has an opposite tendency. In addition, during FTCs, the relative ice content (the mass ratio of frozen water content to the total water content in mortar) during thawing is higher than that of freezing under the same temperature. The maximum value for the samples is around 0.5 at temperature -28°C. These results can be useful for the prediction of frost damage of concrete (Gong, *et al.* 2015a).
- (3) The calculated ice content from the developed model is compared with theoretical result

from thermodynamic analysis and found in acceptable agreement with each other. The calculated ice content is also compared with existing experimental results of other researchers', which were based on calorimetric test and electrical test data interpreted with this study's model. The shape of ice content and temperature curves looks similar. The difference in ice contents between our test and the existing tests can be explained by difference in material properties and curing condition. The frost damage of mortar to electrical conductivity is also discussed and concluded that the damage effect may be ignored within one FTC for estimating ice formation because the frost damage is cumulative and it is not so significant for a cycle. These verify the reliability and applicability of the proposed model.

APPENDIX. Normalized electrical conductivity ($\sigma_{T,p}/\sigma_{ref,s}$)

Normalized electrical conductivity $\sigma_{T,p}/\sigma_{ref,s}$ (electrical conductivity of partially saturated specimen at temperature T slash electrical conductivity of fully saturated specimen at reference temperature T_{ref}) is vitally important for estimating the ice content and it can be derived as following

$$\frac{\sigma_{ref,p}}{\sigma_{ref,s}} = S^n \quad (2.A.1)$$

$$\frac{\sigma_{T,p}}{\sigma_{ref,s}} = \frac{\sigma_{T,p}}{\sigma_{ref,p} \cdot S^{-n}} = \frac{\sigma_{T,p}}{\sigma_{ref,p}} \cdot S^n \quad (2.A.2)$$

where $\sigma_{ref,s}$ is the electrical conductivity of fully saturated concrete at the reference temperature T_{ref} , $\sigma_{ref,p}$ is the electrical conductivity of partially saturated concrete at the reference temperature (the same degree of saturation with measured one at temperature T (K)) and $\sigma_{T,p}$ is the electrical conductivity of partially saturated concrete at the absolute temperature T .

By substituting of Eq. (2.3) into (2.A.2), the normalized electrical conductivity would be

$$\frac{\sigma_{T,p}}{\sigma_{ref,s}} = e^{-\left[\frac{E_{a,p}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]} \cdot S^n \quad (2.A.3)$$

where $E_{a,p}$ is the activation energy of partially saturated concrete for the conduction process.

From Eq. (2.A.3), the activation energy of partially saturated concrete for the conduction process may be calculated as following

$$e^{-\left[\frac{E_{a,p}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]} = \frac{\sigma_{T,p}}{\sigma_{ref,s}} \cdot S^{-n} \quad (2.A.4)$$

$$\frac{E_{a,p}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right) = \ln(S^n) - \ln\left(\frac{\sigma_{T,p}}{\sigma_{ref,s}}\right) \quad (2.A.5)$$

$$E_{a,p} = \frac{R_g}{\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)} \cdot \left[\ln(S^n) - \ln\left(\frac{\sigma_{T,p}}{\sigma_{ref,s}}\right) \right] \quad (2.A.6)$$

When saturation degree $S=1$, then

$$E_{a,s} = - \frac{R_g \ln\left(\frac{\sigma_{T,s}}{\sigma_{ref,s}}\right)}{\frac{1}{T} - \frac{1}{T_{ref}}} \quad (2.A.7)$$

where $E_{a,s}$ is the activation energy of fully saturated concrete for the conduction process, $\sigma_{T,s}$ is the electrical conductivity of fully saturated concrete at the absolute temperature T .

Eqs. (2.A.6) and (2.A.7) are functions to calculate the activation energy only. Although there is a temperature parameter in the equations, it does not mean that the activation energy is dependent on temperature since $\sigma_{T,s}$ and $\sigma_{T,p}$ will change with temperature so the temperature parameter can be removed finally.

Besides, the normalized value $\sigma_{T,p}/\sigma_{ref,s}$ can also be calculated based on Eq. (2.2) directly:

$$\sigma_{T,p} = A_p e^{-\left(\frac{E_{a,p}}{R_g T}\right)} \quad (2.A.8)$$

$$\sigma_{ref,s} = A_s e^{-\left(\frac{E_{a,s}}{R_g T_{ref}}\right)} \quad (2.A.9)$$

where A_p is the nominal conductivity at infinite temperature at the measured degree of saturation, A_s is the nominal conductivity at infinite temperature at the fully saturation.

From Liu and Presuel-Moreno (2014), the value of A fluctuates with different degrees of saturation was found, but the difference was not significant (see details in (Wang *et al.*, 2014)). So this value is assumed to be constant. By dividing Eq. (2.A.8) with Eq. (2.A.9), if $A_p=A_s$ is assumed here, then

$$\frac{\sigma_{T,p}}{\sigma_{ref,s}} = e^{-\left[\frac{E_{a,p}}{R_g T} - \frac{E_{a,s}}{R_g T_{ref}}\right]} \quad (2.A.10)$$

By combining Eqs. (2.A.3) and (2.A.10), the relationship between activation energy for fully saturated and partially saturated specimen may be rewritten as following

$$e^{-\left[\frac{E_{a,p}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]} \cdot S^n = e^{-\left(\frac{E_{a,p}}{R_g T} - \frac{E_{a,s}}{R_g T_{ref}}\right)} \quad (2.A.11)$$

$$e^{-\left[\frac{E_{a,p}}{R_g T} - \frac{E_{a,s}}{R_g T_{ref}} - \frac{E_{a,p}}{R_g T} + \frac{E_{a,p}}{R_g T_{ref}}\right]} = S^n \quad (2.A.12)$$

$$e^{\left(\frac{E_{a,p}-E_{a,s}}{R_g T_{ref}}\right)} = S^n \quad (2.A.13)$$

$$E_{a,p} = E_{a,s} - R_g T_{ref} \ln(S^n) \quad (2.A.14)$$

Finally, by substituting Eq. (2.A.14) into Eq. (2.A.3), the normalized electrical conductivity is

$$\frac{\sigma_{T,p}}{\sigma_{ref,s}} = e^{\left[\frac{E_{a,s}-R_g T_{ref} \ln(S^n)}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]} \cdot S^n \quad (2.A.15)$$

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Chapter 3

ESTIMATION OF ICE FORMATION IN MORTAR SATURATED WITH NaCl SOLUTIONS

3.1 INTRODUCTION

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 cause 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 temperature, 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 pore pressures can be predicted correspondingly. Therefore, the ice formation information on the cementitious material's surface and pores is needed.

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

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

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

3.2 ESTIATION OF ICE FORMATION IN MORTAR SATURATED WITH NACL SOLUTIONS

3.2.1 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. 3.1). Based on solute mass conservation, the approach on how to calculate the volume fraction of ice with temperature change is derived as below and the results of certain concentrations and comparison with existing test results from Perovich and Gow (1996) are shown in Fig. 3.2 (a) and (b).

The regressed relationship for the freezing point of a certain concentration of NaCl solution can be expressed as Eq. (3.1) (Fig. 3.1(a)).

$$T_{c_0} = -0.0157N^2 - 0.5153N \quad (3.1)$$

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 regressed as Eq. (3.2) (Fig. 3.1 (b)).

$$N = -0.028T_{c_0}^2 - 1.6744T_{c_0} \quad (3.2)$$

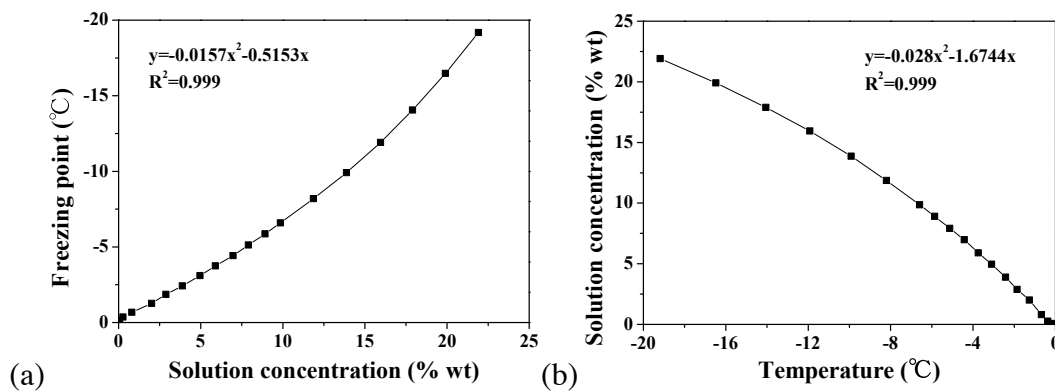


Fig. 3.1 Freezing point versus solution concentration by weight (Weast and Astle, 1981)

If the initial concentration of solution is $c_0\%$, once the temperature drops to its freezing point, the ice would form and then the concentration would change

$$T_{c_0} = -0.0157c_0^2 - 0.5153c_0 \quad (3.3)$$

Here we assume the mass ratio of ice is m_c , so the brine solution is $100-m_c$, and water is $100-c_0-m_c$, the new concentration of solution would be

$$c_1 = \frac{100c_0}{100-m_c} \quad (3.4)$$

In addition, current temperature T (°C) should be freezing point of c_1 concentrated NaCl solution. As a result, the new equilibrium can be

$$\frac{100c_0}{100-m_c} = -0.028T^2 - 1.6744T \quad (3.5)$$

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

$$m_c = 100 - \frac{100c_0}{-0.028T^2 - 1.6744T} \quad (3.6)$$

$$V_c = \frac{m_c / \rho_c}{m_c / \rho_c + (100 - c_0 - m_c) / \rho_w} \cong \frac{1.09m_c}{0.09m_c + 100 - c_0} \quad (3.7)$$

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. (3.6) into Eq. (3.7), there is

$$V_c = 1 - \frac{(0.028T^2 + 1.6744T + 100)c_0}{(100 - c_0)(-0.028T^2 - 1.6744T) - 9c_0} \quad (3.8)$$

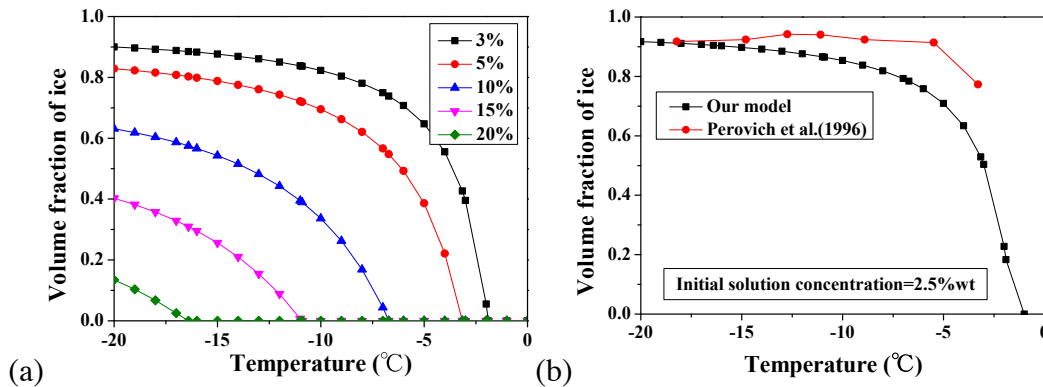


Fig. 3.2 Volume fraction of ice in solutions of NaCl versus temperature

The thermal stress develops in the ice depends on its stiffness, which will increase with the ice volume. When the stress exceeds the strength of ice, the cracks will occur. For the flexural strength and static elastic modulus, Sun and Scherer (2010) regressed the data from

existing tests and proposed model for estimation. The best available data for the flexural strength and static elastic modulus of frozen NaCl-water solutions are

$$\sigma_T (MPa) = 1.76 \exp(-5.88\sqrt{1-V_c}) \quad (3.9)$$

$$E (GPa) = 10 \exp(-7.1\sqrt{1-V_c}) \quad (3.10)$$

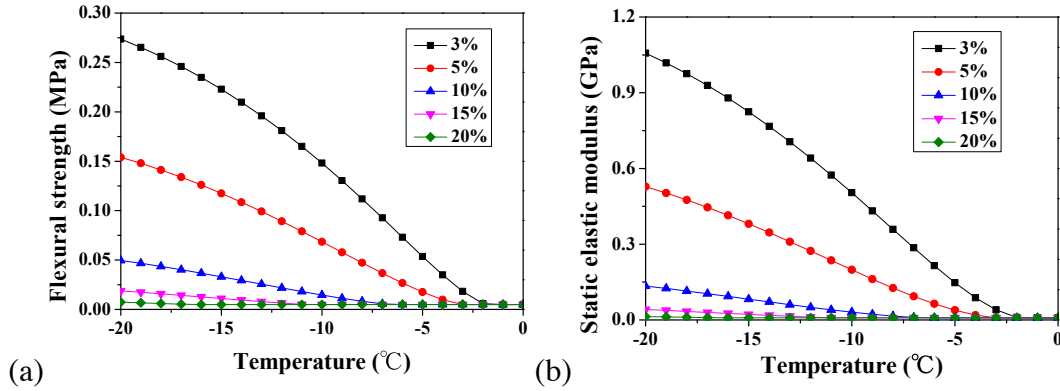


Fig. 3.3 Flexural strength and static elastic modulus of frozen solutions of NaCl (applied the model of Sun and Scherer, 2010)

Based on the model, mechanical properties of 3%, 5%, 10%, 15% and 20% NaCl solution are estimated, as can be seen in Fig. 3.3. It is clear that the flexural strength and stiffness of ice in high concentration solution are rather small compared with ice properties in low concentration solution. This can explain why the serious damage occurs at intermediate concentration solution (3~5%). Because high concentration solution, the ice is too soft to penetrate cracks into concrete while for low concentration, the ice is too strong to induce cracks.

3.2.2 Ice formation in cementitious materials saturated with NaCl solutions

3.2.2.1 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. 3.4). 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

$$v_c \gamma_{CL} \kappa_{CL} = -(S_L - S_C)(T - T_m) + RT \ln(a) \quad (3.11)$$

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 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

$$T_c = \frac{(S_L - S_C)T_m}{(S_L - S_C - R \ln(a))} - \frac{v_c \gamma_{CL} \kappa_{CL}}{(S_L - S_C - R \ln(a))} \quad (3.12)$$

If the ice crystal is in macroscopic, κ_{CL} is about zero, the second term of Eq. (3.12) become zero. In Eq. (3.12), the unit of temperature is K since the derivation is based on thermodynamics. Considering the temperature unit, then the freezing point (°C) of NaCl solution is

$$T_{c_0} = \frac{T_m(S_L - S_C)}{(S_L - S_C - R\ln(a))} - T_m \quad (3.13)$$

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

$$T_p = T_m - \frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}} - T_m = -\frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}} \quad (3.14)$$

where r_p is the radius of pore, δ is the thickness of the liquid film between the crystal and the pore wall, and $\Delta S_{fv} = (S_L - S_C)/v_c$ is the molar entropy of fusion. For ice, $\gamma_{cl} \approx 0.04 \text{ J/m}^2$, $\Delta S_{fv} \approx 1.2 \times 10^6 \text{ (J/m}^3\text{/K)}$, for water $\delta \approx 0.9 \text{ nm}$ (Scherer and Valenza, 2005). To combine with the regressed Eq. (3.1), we have

$$T_{c_0} = \frac{T_m(S_L - S_C)}{(S_L - S_C - R\ln(a))} - T_m = -0.0157N^2 - 0.5153N \quad (3.15)$$

$$S_L - S_C - R\ln(a) = \frac{T_m(S_L - S_C)}{(T_m - 0.0157N^2 - 0.5153N)} \quad (3.16)$$

Substituting of Eq. (3.16) into Eq. (3.12), and considering the pore curvature κ_{CL} in Eq. (3.12), $\kappa_{CL} = 2/(r_p - \delta)$, the freezing point of pore solution (K)(see Fig. 3.4) is

$$T_c = \frac{(T_m - 0.0157N^2 - 0.5153N)}{T_m} \left(T_m - \frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}} \right) \quad (3.17)$$

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

$$T_{cc} = \frac{(T_m - 0.0157N^2 - 0.5153N)}{T_m} \left(T_m - \frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}} \right) - T_m \quad (3.18)$$

Substituting Eq. (3.13) into Eq. (3.18), we can obtain the following equation.

$$T_{c_0} = \frac{T_{cc} + T_m}{T_m - \frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}}} T_m - T_m \quad (3.19)$$

For a certain temperature and a certain size of pore, the concentration of solution just reaches the freezing point is obtained from Eq. (3.18) as follows;

$$N = -0.028 \left(\frac{T_{cc} + T_m}{T_m - \frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}}} T_m - T_m \right)^2 - 1.6744 \left(\frac{T_{cc} + T_m}{T_m - \frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}}} T_m - T_m \right) \quad (3.20)$$

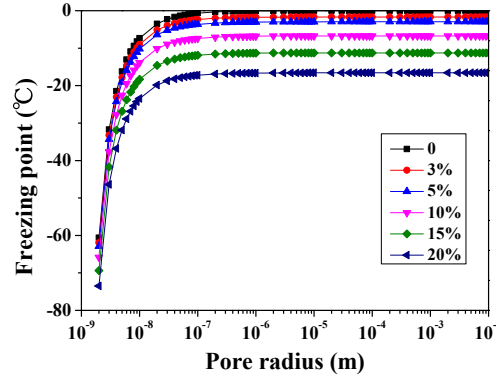


Fig. 3.4 Freezing point of solutions of NaCl versus pore radius (m)

3.2.2.2 Ice formation in cementitious materials with different NaCl solutions

For the initial concentration of solution with $c_0\%$, the ice would be formed once the temperature drops to its freezing point, T_{cc} (°C) as shown in Eq. (3.21) (see Eq. (3.18)).

$$T_{cc} = \frac{(T_m - 0.0157c_0^2 - 0.5253c_0)}{T_m} \left(T_m - \frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}} \right) - T_m \quad (3.21)$$

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

$$m_c = \int_{r_p}^{+\infty} m_c(r_p) v(r_p) dr \quad (3.22)$$

where $v(r_p)$ is the relative volume of pore with radius r_p . The brine solution is $100 - m_c$, and water is $100 - c_0 - m_c$, the new concentration of solution in the pore would be

$$c_1 = \frac{100c_0}{100 - m_c(r_p)} \quad (3.23)$$

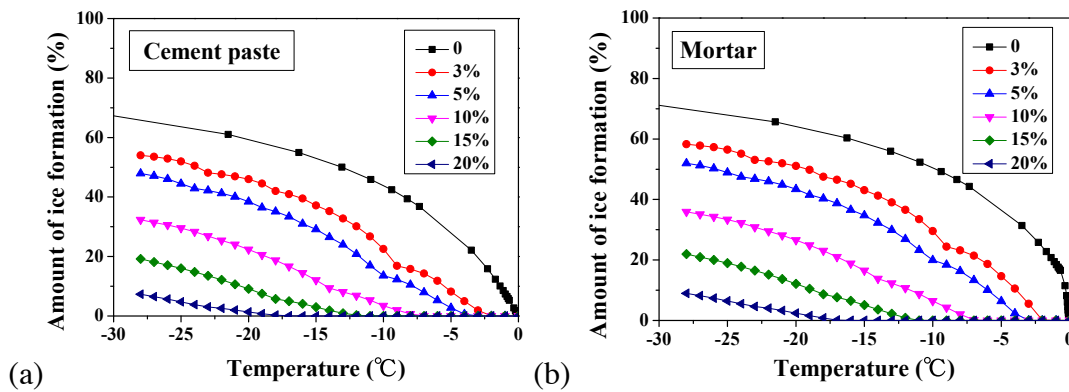
Current temperature should be freezing point of c_1 concentrated NaCl solution. As a result,

$$\frac{100c_0}{100-m_c(r_p)} = -0.028 \left(\frac{T_m(T+T_m)}{T_m - \frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}}} - T_m \right)^2 - 1.6744 \left(\frac{T_m(T+T_m)}{T_m - \frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}}} - T_m \right) \quad (3.24)$$

So the mass of ice in the pore would be

$$m_c(r_p) = 100 - \frac{100c_0}{-0.028 \left(\frac{T_m(T+T_m)}{T_m - \frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}}} - T_m \right)^2 - 1.6744 \left(\frac{T_m(T+T_m)}{T_m - \frac{2\gamma_{CL}}{(r_p - \delta)\Delta S_{fv}}} - T_m \right)} \quad (3.25)$$

As it is shown in Eq. (3.25), three parameters (initial solution concentration, temperature and pore size) are in need for calculating the ice content in a pore. To sum the ice content in all of the pores, we may get the ice content in bulk cement paste, mortar or concrete. For ice formation in cement paste, mortar and concrete, the difference is due to the pore size distribution and this can be calculated by an empirical model proposed by Gong et al. (2014). To be more precise, based on the empirical pore size model, we could get the volume density of each size of pores and the ice formation for different size of pores by Eq. (3.25). Combing the ice formation in each size of pores and pore size distribution with Eq. (3.22), the ice formation in cementitious materials can be obtained. As a result, the amount of ice forming for different concentration of NaCl solutions under different temperature is estimated (see Fig. 3.5). 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. Meanwhile, the ice amount in different size of pores and its static elastic modulus at -28 °C are also analyzed (see Fig. 3.6).



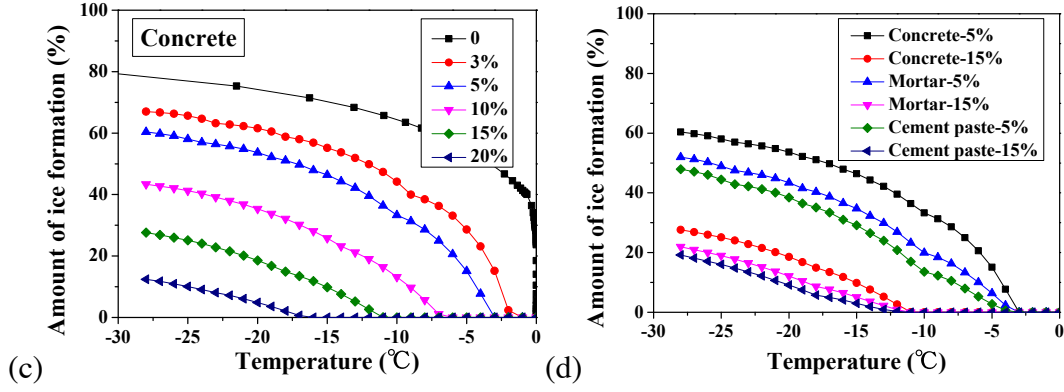


Fig. 3.5 Amount of ice content with different concentrations of NaCl solutions in (a) cement paste, (b) mortar, (c) concrete and (d) comparison of cement paste, mortar and concrete ($w/c=0.5$)

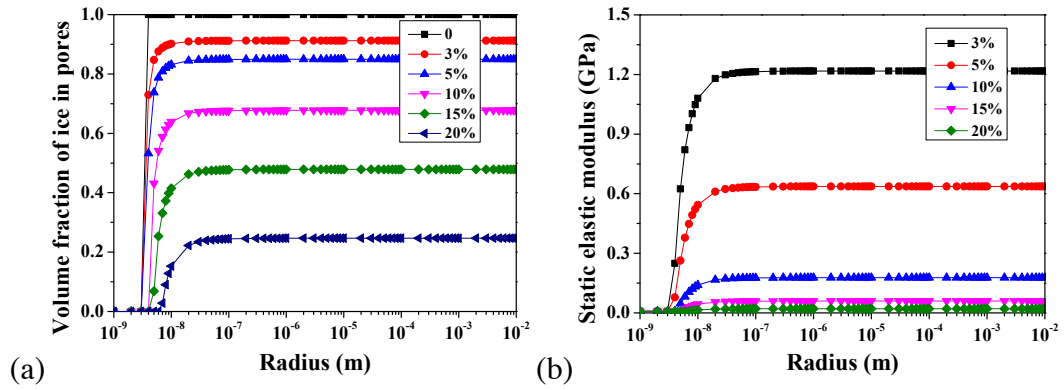


Fig. 3.6 Volume fraction of ice in pores and its elastic modulus for cementitious materials saturated with indicated concentrations of NaCl solution

3.3 THEORETICAL MODEL FOR ICE CONTENT ESTIMATION IN MORTAR SATURATED WITH NA CL SOLUTIONS BASED ON ELECTRICAL MEASUREMENTS

3.3.1 Moisture content

The ice content estimation model was preliminarily developed in chapter 2, which can be applied to specimen saturated with DI water. However, for specimen saturated with NaCl solutions, the model is not sufficient enough 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 in chapter 2, the moisture content can change the electrical conductivity of specimen significantly. The relationship can be presented as Archie's law (1949). In this chapter, the model was further derived to consider the pore solution concentration change. For cementitious materials, the electrical conductivity at full saturation is

$$\sigma_{ref,C,s,c_0} = F \cdot \sigma_{ref,p,s,c_0} \quad (3.26)$$

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)

$$\sigma_{ref,C,p,c_2} = F \cdot \sigma_{ref,p,p,c_2} \cdot f(S) \quad (3.27)$$

$$f(S) = S^n \quad (3.28)$$

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

$$\sigma_{ref,p,p,c_2} = \frac{\sigma_{ref,p,s,c_0}}{S} \quad (3.29)$$

Combining the Eqs. (3.26)-(3.29), the variation of electrical conductivity of cementitious materials based on changing of degree of saturation can be calculated as following

$$\frac{\sigma_{ref,C,p,c_2}}{\sigma_{ref,C,s,c_0}} = \frac{\sigma_{ref,p,p,c_2} \cdot f(S)}{\sigma_{ref,p,s,c_0}} = \frac{S^n}{S} = S^{n-1} \quad (3.30)$$

3.3.2 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. (3.31).

$$\sigma \propto \frac{I_M}{1 + G\sqrt{I_M}} \quad (3.31)$$

$$I_M = \frac{1}{2} \sum_{i=1}^N z_i^2 \cdot c_i \quad (3.32)$$

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. (3.32), 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

$$\frac{\sigma_{ref,p,p,c_1}}{\sigma_{ref,p,s,c_0}} = \frac{I_{M1}}{1 + G\sqrt{I_{M1}}} \cdot \frac{1 + G\sqrt{I_{M0}}}{I_{M0}} = \frac{c_1}{c_0} \cdot \frac{1 + G\sqrt{c_0}}{1 + G\sqrt{c_1}} \quad (3.34)$$

where I_{M0} and I_{M1} are the ionic strength of pore solution having concentration c_0 and c_1 respectively, namely $I_{M1}/I_{M0}=c_1/c_0$. 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. (3.34), the electrical conductivity of pore solution change due to drying or freezing can be simplified as (Weiss et al., 2012)

$$\frac{\sigma_{ref,p,p,c_2}}{\sigma_{ref,p,s,c_0}} = \frac{I_{M2}}{I_{M0}} \cdot \frac{1 + G\sqrt{I_{M0}}}{1 + G\sqrt{I_{M2}}} = \frac{1}{S} \cdot \frac{1 + G\sqrt{I_{M0}}}{1 + G\sqrt{I_{M0}/S}} \equiv S^{\delta_0-1} \quad (3.35)$$

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 in Weiss et al. (2012), the relationship between the correction term and ionic strength can be regressed as below

$$\delta_0 = 0.0565 \ln(I_M) + 0.213 \quad (3.36)$$

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

3.3.3 Temperature

As shown in chapter 2, temperature effect to electrical conductivity was usually described by Arrhenius equation (Chrisp et al., 2001) as follows

$$\frac{\sigma_{T,C,s,c_0}}{\sigma_{ref,C,s,c_0}} = e^{-\left[\frac{E_{a,s}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]} \quad (3.37)$$

where σ_{T,C,s,c_0} is the electrical conductivity of cementitious material specimen at fully 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 fully saturation with pore solution concentration equals to c_0 at the reference temperature, E_{a,s,c_0} 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. The investigation of saturation degree was presented in chapter 2, while the pore characteristics in Chapter 6. The combed effect of saturation degree and pore characteristics can be (see details in Chapter 6)

$$E_{a,p,c_1,a} = E_{a,s,c_0,0} - A \ln \left(\frac{\sigma_{ref,C,s,c_0,0}}{\sigma_{ref,C,p,c_1,a}} \right) + A \ln(S^{n_a}) - R_g T_{ref} \ln(S^{n_a}) \quad (3.38)$$

where $E_{a,s,c_0,0}$ and $E_{a,p,c_1,a}$ are the activation energy of fully saturated specimen before and after salt frost damage, A is the fitting parameter which can account to the effect of pore characteristics (about 15.313 from our regressed results) and n_a is the saturation coefficient after frost damage.

However, from our experimental results, the activation energy has no big variation with FTCs (see Section 3.4). To simplify the derivation at this stage, the effect of damage and ion concentration change during FTCs to activation energy was neglected. So the Eq. (3.38) was reduced to Eq. (2.A.14)

$$E_{a,p} = E_{a,s} - R_g T_{ref} \ln(S^{\delta_0^{-1}+n}) \quad (2.A.14)$$

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

3.3.4 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. (3.26)-(3.28) and (3.35), the variation of bulk conductivity of cementitious materials can be written as Eq. (4.39).

$$\frac{\sigma_{ref,C,p,c_2}}{\sigma_{ref,C,s,c_0}} = \frac{F \cdot \sigma_{ref,p,p,c_2} \cdot f(S)}{F \cdot \sigma_{ref,p,s,c_0}} = \frac{\sigma_{ref,p,p,c_2}}{\sigma_{ref,p,s,c_0}} \cdot S^n = S^{\delta_0^{-1}} \cdot S^n = S^{\delta_0^{-1}+n} \quad (3.39)$$

From the derivation, the saturation estimation equation was obtained as Weiss, et al. (2012) presented. Based on Eq. (3.39), the saturation degree of cementitious materials can be obtained by using the electrical conductivity results. The detailed discussion of this equation was shown in chapter 2.

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. (3.34) and (3.37), the electrical conductivity variation due to combined effects of concentration and temperature can be written as Eq. (3.40)

$$\frac{\sigma_{T,C,s,c_1}}{\sigma_{ref,C,s,c_0}} = \frac{\sigma_{ref,C,s,c_1} \cdot e^{-\left[\frac{E_{a,s}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]}}{\sigma_{ref,C,s,c_0}} = \frac{c_1}{c_0} \cdot \frac{1 + G\sqrt{c_0}}{1 + G\sqrt{c_1}} \cdot e^{-\left[\frac{E_{a,s}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]} \quad (3.40)$$

By reversing the Eq.(3.40), the pore solution concentration after salt crystallization can be

$$\frac{c_1}{1+G\sqrt{c_0}} = \frac{\sigma_{T,C,s,c_1}}{\sigma_{ref,C,s,c_0}} \cdot \frac{c_0}{1+G\sqrt{c_0}} \cdot e^{\left[\frac{E_{a,s}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]} \quad (3.41)$$

In order to simplify the derivation, here we may define the right term of Eq. (3.41), which is the known value, as follows;

$$a = \frac{\sigma_{T,C,s,c_1}}{\sigma_{ref,C,s,c_0}} \cdot \frac{c_0}{1+G\sqrt{c_0}} \cdot e^{\left[\frac{E_{a,s}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]} \quad (3.42)$$

Then, by substituting Eq. (3.42) into Eq. (3.41), Eq. (3.41) can be rewrite as

$$c_1 = a + aG\sqrt{c_1} \quad (3.43)$$

The Eq. (3.43) can be solved and the solution is as follows;

$$c_1 = \frac{2a + a^2G^2 + aG\sqrt{4a + a^2G^2}}{2} \quad (3.44)$$

$$\Delta c = c_0 - c_1 \quad (3.45)$$

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. (3.44), 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 are as below

$$\begin{aligned} \frac{\sigma_{T,C,p,c_2}}{\sigma_{ref,C,s,c_0}} &= \frac{\sigma_{T,C,p,c_2}}{\sigma_{ref,C,s,c_1}} \cdot \frac{\sigma_{ref,C,s,c_1}}{\sigma_{ref,C,s,c_0}} = \frac{\sigma_{ref,C,p,c_2}}{\sigma_{ref,C,s,c_1}} \cdot e^{\left[\frac{E_{a,p}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]} \cdot \frac{c_1}{c_0} \cdot \frac{1+G\sqrt{c_0}}{1+G\sqrt{c_1}} \\ &= \frac{c_1}{c_0} \cdot \frac{1+G\sqrt{c_0}}{1+G\sqrt{c_1}} \cdot S^{\delta_0-1+n} \cdot e^{\left[\frac{E_{a,s}-R_gT_{ref}\ln(S^{\delta_0-1+n})}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]} \end{aligned} \quad (3.46)$$

where

$$S^{\delta_0-1} \cong \frac{c_2}{c_1} \cdot \frac{1+G\sqrt{c_1}}{1+G\sqrt{c_2}} \quad (3.47)$$

The Eq. (3.47) was derived from Eqs. (3.34) and (3.35). Since Eq. (3.34) equals to Eq. (3.35), comparing the final term of the two equations, the Eq. (3.47) can be obtained.

Then by solving the Eq. (3.46), the saturation degree can be given as follows

$$S = (\delta_0 - 1 + n) \frac{T_{ref}}{T} \sqrt{\frac{\sigma_{T,C,p,c_2}}{\sigma_{ref,C,s,c_0}} \cdot \frac{c_0}{c_1} \cdot \frac{1 + G\sqrt{c_1}}{1 + G\sqrt{c_0}}} e^{\left[\frac{E_{a,s}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]} \quad (3.48)$$

Then relative ice content can be calculated as

$$I = S_0 - S \quad (3.49)$$

where S_0 is the initial saturation degree.

Considering Eq. (3.45), the amount of crystallized salt can be evaluated by

$$m_s = (c_0 - c_1) \cdot \phi_0 \cdot V_0 \quad (3.50)$$

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 Eq. (3.48) can be reduced to Eq. (2.4). The solution concentration change can be calculated based on Eqs. (3.34) and (3.35), as below

$$\frac{c_2}{c_0} \cdot \frac{1 + G\sqrt{c_0}}{1 + G\sqrt{c_2}} = S^{\delta_0 - 1} \quad (3.51)$$

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

The above equation can be rewritten as

$$\frac{c_2}{1 + G\sqrt{c_2}} = \frac{c_0}{1 + G\sqrt{c_0}} \cdot S^{\delta_0 - 1} \quad (3.52)$$

If we define

$$b = \frac{c_0}{1 + G\sqrt{c_0}} \cdot S^{\delta_0 - 1} \quad (3.53)$$

Then the Eq. (3.52) can be solved and the solution is

$$c_2 = \frac{2b + b^2 G^2 + bG\sqrt{4b + G^2 b^2}}{2} \quad (3.54)$$

Considering the case with salt crystallization, the solution concentration with freezing can also be calculated by Eq. (3.54). However, for calculating the parameter b in Eq. (3.53), c_0 should be represented with c_1 .

According to the study of Farnam et al. (2014), upon freezing, the salt crystallization would occur above the freezing point. The salt could be the reason for damage of specimen saturated with high concentration of NaCl solutions. In this case, the salt crystallization and ice formation processes are in separate stages. The amount of salt could be calculated with

regard to combined effects of ions concentration and temperature, while the ice amount involved the combined effects of saturation degree, ions concentration and temperature. Therefore, the pore solution concentration change and relative ice content during FTC could be obtained as follows;

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

$$c_1 = \frac{2a + a^2 G^2 + aG\sqrt{4a + a^2 G^2}}{2} ; a = \frac{\sigma_{T,C,s,c_1}}{\sigma_{ref,T,C,s,c_0}} \cdot \frac{c_0}{1 + G\sqrt{c_0}} \cdot e^{\left[\frac{E_{a,s}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]} \quad (3.55)$$

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

$$c_2 = \frac{2b + b^2 G^2 + bG\sqrt{4b + G^2 b^2}}{2} ; b = \frac{c_1}{1 + G\sqrt{c_1}} \cdot S^{\delta_0 - 1} \quad (3.56)$$

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

$$c_2 = \frac{2b + b^2 G^2 + bG\sqrt{4b + G^2 b^2}}{2} ; b = \frac{c_1}{1 + G\sqrt{c_1}} \cdot S^{\delta_0 - 1} \quad (3.57)$$

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

$$c_1 = \frac{2a + a^2 G^2 + aG\sqrt{4a + a^2 G^2}}{2} ; a = \frac{\sigma_{T,C,s,c_1}}{\sigma_{ref,T,C,s,c_0}} \cdot \frac{c_0}{1 + G\sqrt{c_0}} \cdot e^{\left[\frac{E_{a,s}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]} \quad (3.58)$$

Considering the effect of the salt frost damage on the electrical property of cementitious materials, the ice formation estimation model could be extended to the case of FTCs

$$S_{F,i} = (\delta_0 - 1 + n) \frac{T_{ref}}{T} \sqrt{\frac{\sigma_{T,C,p,c_{2,i}}}{\sigma_{ref,C,s,c_{0,i}} + \frac{T - T_{Fi}}{T_L - T_{Fi}} (\sigma_{ref,C,s,c_{0,i+1}} - \sigma_{ref,C,s,c_{0,i}})}} \cdot \frac{c_{0,i} (1 + G\sqrt{c_{1,i}})}{c_{1,i} (1 + G\sqrt{c_{0,i}})} \cdot e^{\left[\frac{E_{a,s,i}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]} \quad (3.59)$$

$$S_{T,i} = (\delta_0 - 1 + n) \frac{T_{ref}}{T} \sqrt{\frac{\sigma_{T,C,p,c_{2,i}}}{\sigma_{ref,C,s,c_{0,i+1}}}} \cdot \frac{c_{0,i} (1 + G\sqrt{c_{1,i}})}{c_{1,i} (1 + G\sqrt{c_{0,i}})} \cdot e^{\left[\frac{E_{a,s,i}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]} \quad (3.60)$$

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. (3.59) is applicable to the ice formation estimation for the freezing process while Eq. (3.60) 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. 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.

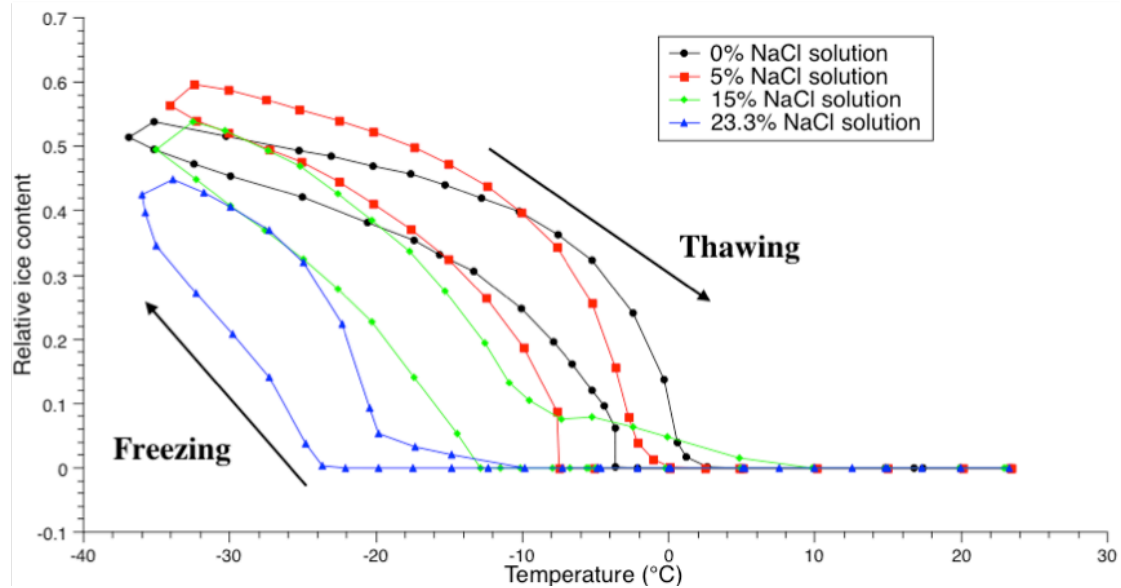


Fig.3.7 Relative ice content of different concentrations of NaCl solution saturated mortar under freezing and thawing (calculated from the data of Farnam et al., 2015)

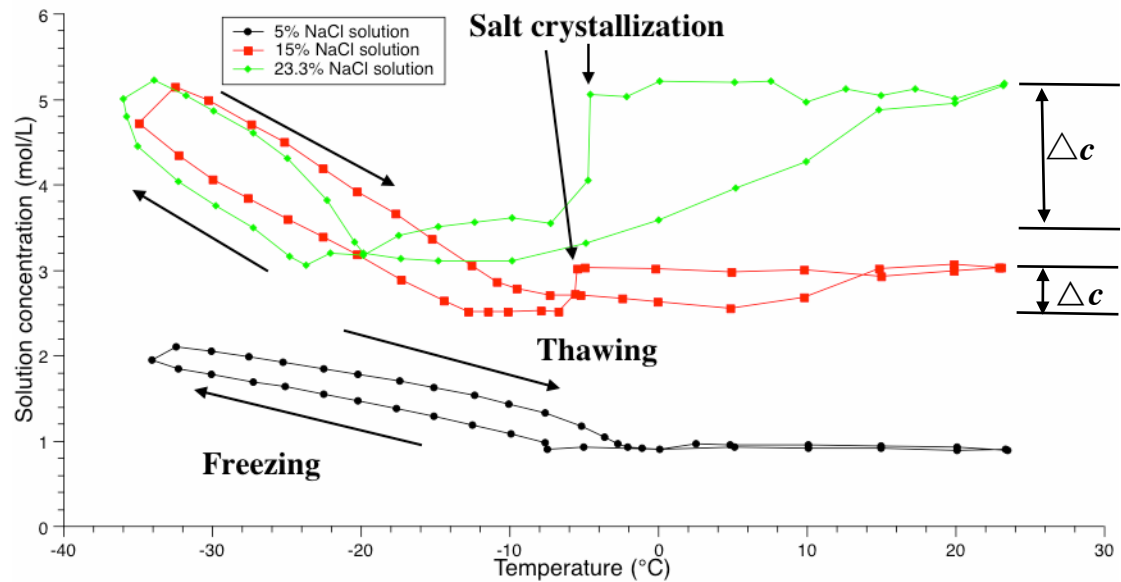


Fig. 3.8 Solution concentration change with temperature (calculated from the data of Farnam et al., 2015)

3.4 TEST PROGRAMS

3.4.1 Specimen preparation

Mortar specimens were used in this experimental program. Mix proportions with different water-to-cement ratio (w/c), excluding coarse aggregate, were based on ACI 211.1

(1991) design, as shown in Table 3.1 with different water-to-cement ratio (w/c), excluding coarse aggregate. The materials include ordinary Portland cement. The physical properties and chemical compositions are presented in Table 3.2. The size of fine aggregate is 1.2 mm or lesser and its density is 2.67 g/cm^3 . To promote frost damage, no air-entraining agent was incorporated. After proper mixing, it was cast into $40 \times 40 \times 160 \text{ mm}$ 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 $70 \times 30 \times 5 \text{ mm}$ after curing (see preparation details in Fig. 3.9). 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 preparation procedures of electrical test samples were shown in Fig. 3.10. Firstly, the electrodes were attached to mortar samples with conductive paste (see Fig. 3.10(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 (see Fig. 3.10(b)). 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 (see Fig. 3.10(b)) 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 insider. 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 (see Fig. 3.10(c)) 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. 3.10(d)).

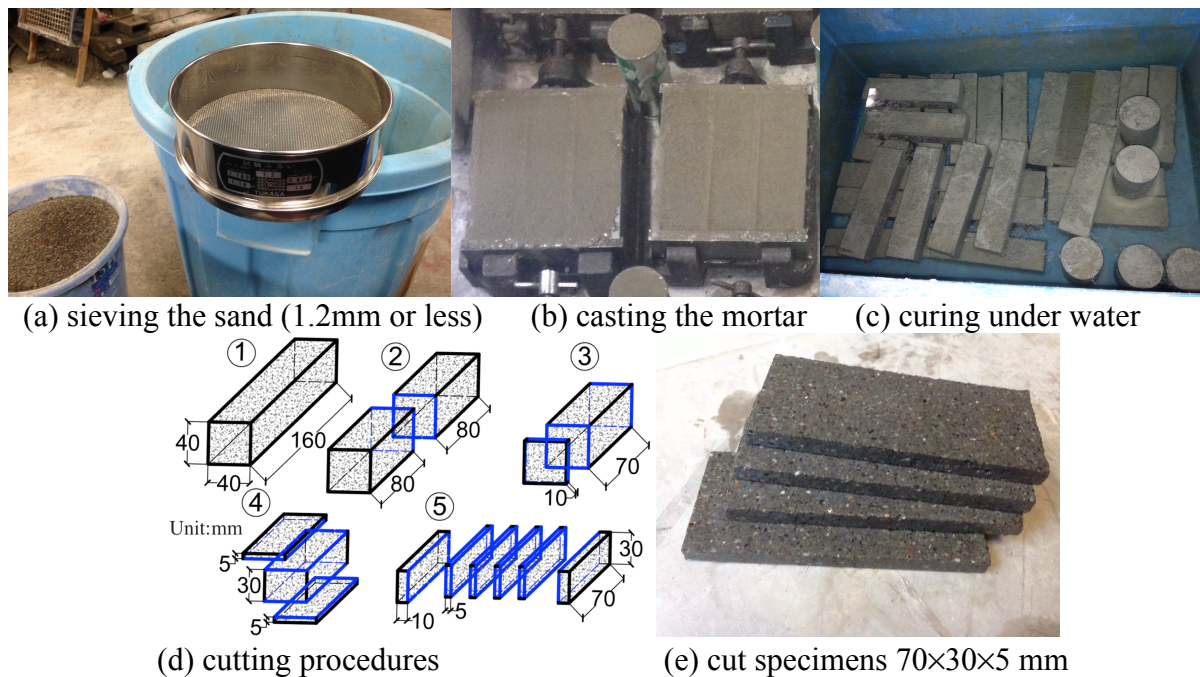


Fig. 3.9 Preparation of specimens

Table 3.1 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
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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 3.2 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

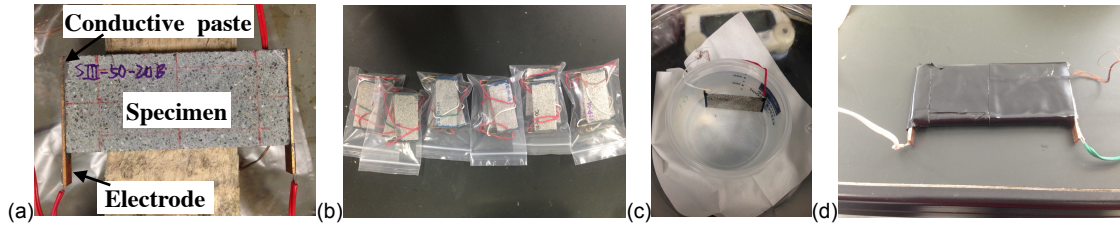


Fig. 3.10 Prepared specimen details 70 mm × 30 mm × 5 mm

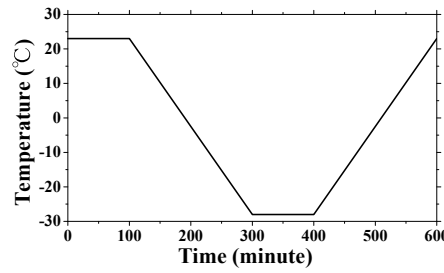


Fig. 3.11 Temperature history (one cycle)

3.4.2 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 (Chapter 2). The frequency of the alternating current is 1kHz 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 0.5Ω, which can be neglected compared with electrical resistivity of mortar samples. To consider the geometrical effect, the electrical resistivity of the specimen is

$$\rho = \frac{AR}{L} \quad (3.61)$$

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. 3.11. 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.

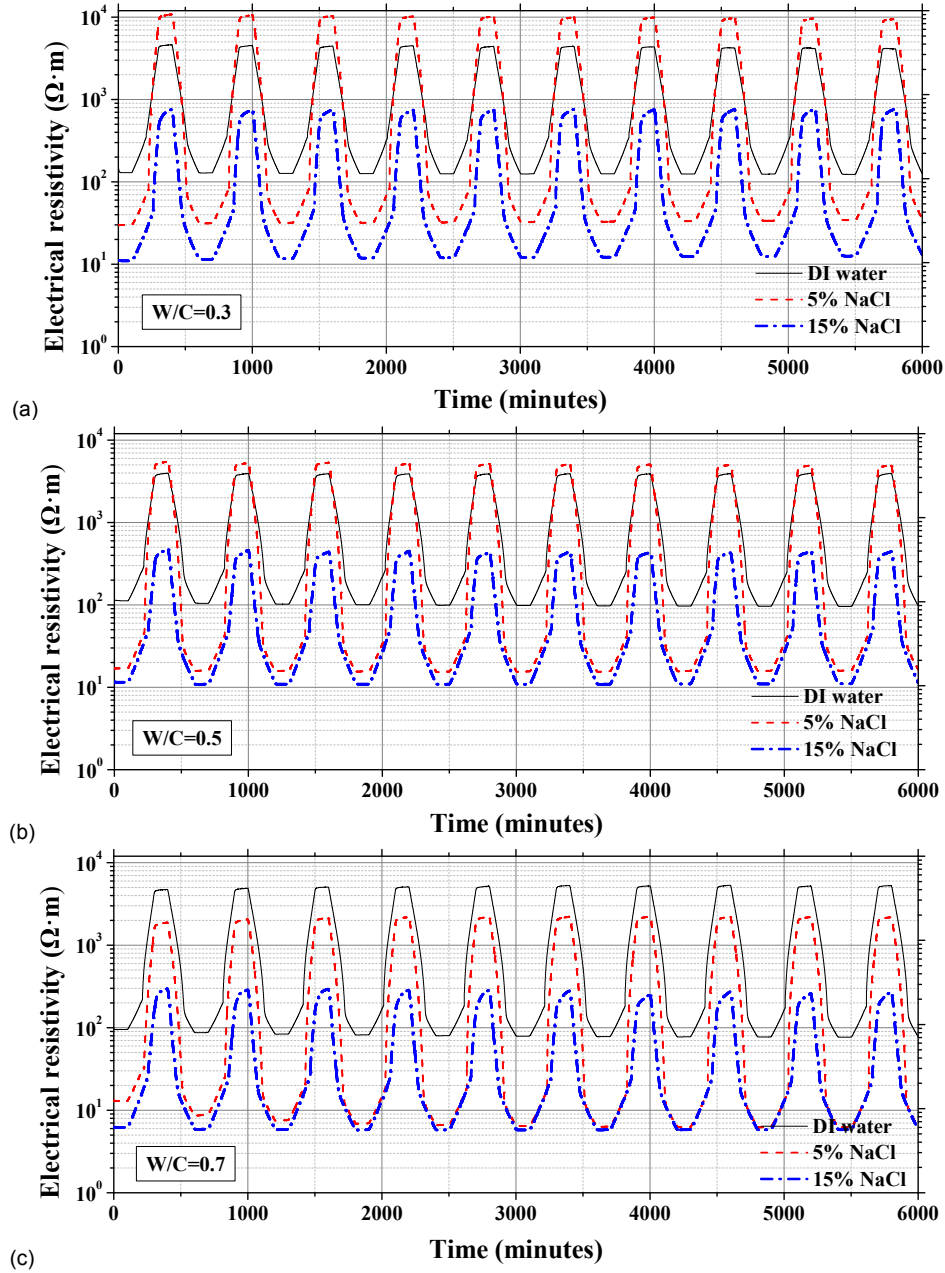


Fig 3.12 Electrical resistivity changes under freeze-thaw cycles (a) $w/c=0.3$ (b) $w/c=0.5$ (c) $w/c=0.7$

3.5 TEST RESULTS AND DISCUSSIONS

3.5.1 Electrical resistivity of specimen under FTCs

During FTCs, the electrical resistivity of specimens was changing with temperature. As shown in Fig. 3.12, 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. 3.13). 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. 3.13, 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 to 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.

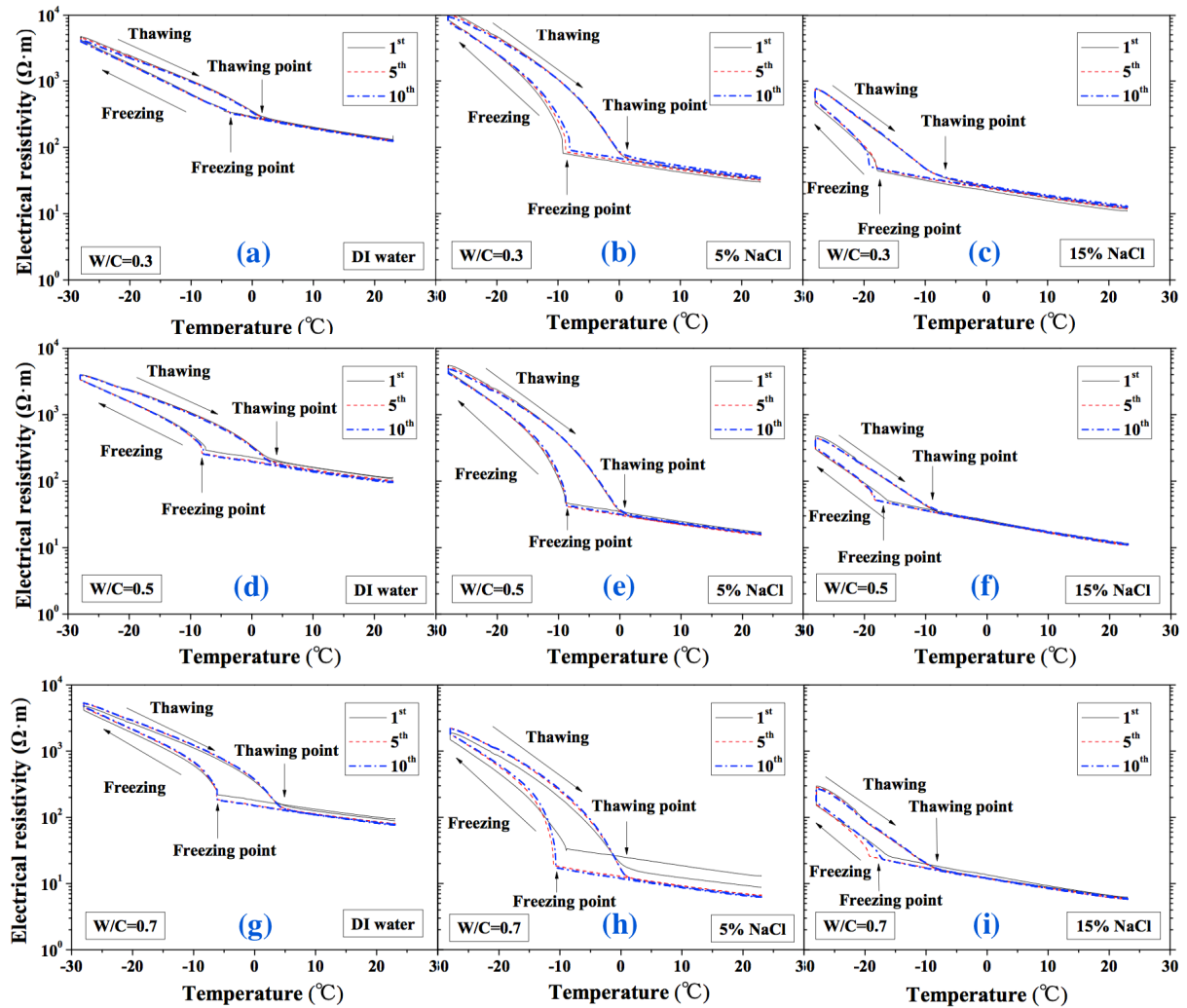


Fig. 3.13 Electrical resistivity changes with temperature

In addition, for each w/c samples, 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. This implies that the additional phase change depends on the chemical composition of cement pastes (Baroghel-Bouny et al., 2012), which needs further investigation. 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. 3.12, 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 salt crystallization may occur gradually at subzero temperature.

3.5.2 Electrical resistivity at reference temperature and lowest temperature

According to the study of Farnam et al. (2015), electrical resistivity at reference temperature can be used to evaluate the frost damage, whereas Wang et al. (2014) regarded the maximum electrical resistivity as the parameter of damage. Therefore, in this paper, as shown in Figs. 3.7 and 3.8, normalized electrical resistivity at temperatures 23°C and -28°C were considered, respectively. The normalized electrical resistivity means the ratio of electrical resistivity with FTCs to electrical resistivity at the first cycle. Electrical resistivity at reference temperature (23°C) and lowest temperature (-28°C) at first cycle were presented in Table 3.3. Figures 3.7 and 3.8 show that along with frost damage development, the electrical resistivity of mortar at 23°C and -28°C decreases. However, for 5% and 15% NaCl concentration solution exposed samples with $w/c=0.3$, contrary tendency were observed at 23°C. The increase tendency was also observed at -28°C in the case of DI water and 5% NaCl solution exposed samples with $w/c=0.7$. It indicates that the frost damages in the cases of 5% and 15% NaCl solution saturated samples with $w/c=0.3$ were not significant, because it has lesser amount of moisture and salt and higher strength than the cases of $w/c=0.5$ and 0.7. Besides, for the samples saturated with NaCl solutions, the chloride binding reduced the

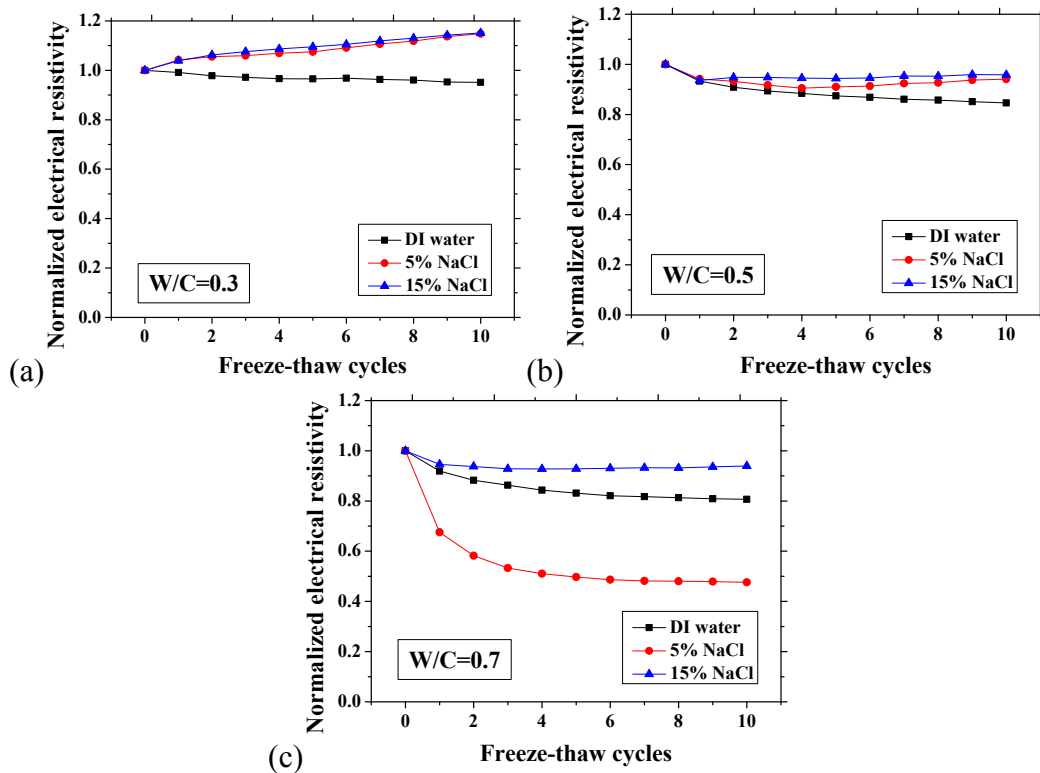


Fig. 3.14 Electrical resistivity at reference temperature (23°C) changes with FTCs (a) $w/c=0.3$ (b) $w/c=0.5$ (c) $w/c=0.7$

movable ions content and increased the electrical resistivity. For the samples with $w/c=0.5$ and 0.7 , even the chloride binding also occurs, the salt frost damage was more severe, so the electrical resistivity showed decrease tendency. However, for the case of DI water and 5% NaCl solution exposed samples with $w/c=0.7$, the increase of electrical resistivity at the lowest temperature was due to more severe frost damage. Although the frost damage can increase the connectivity and decrease the electrical resistivity, the sample with $w/c=0.7$ had good connectivity before frost damage, which made the effect of increased connectivity less on the change in electrical resistivity. Instead, because of the severe damage, the increasing of porosity yields the reduction of saturation degree, which increases the electrical resistivity.

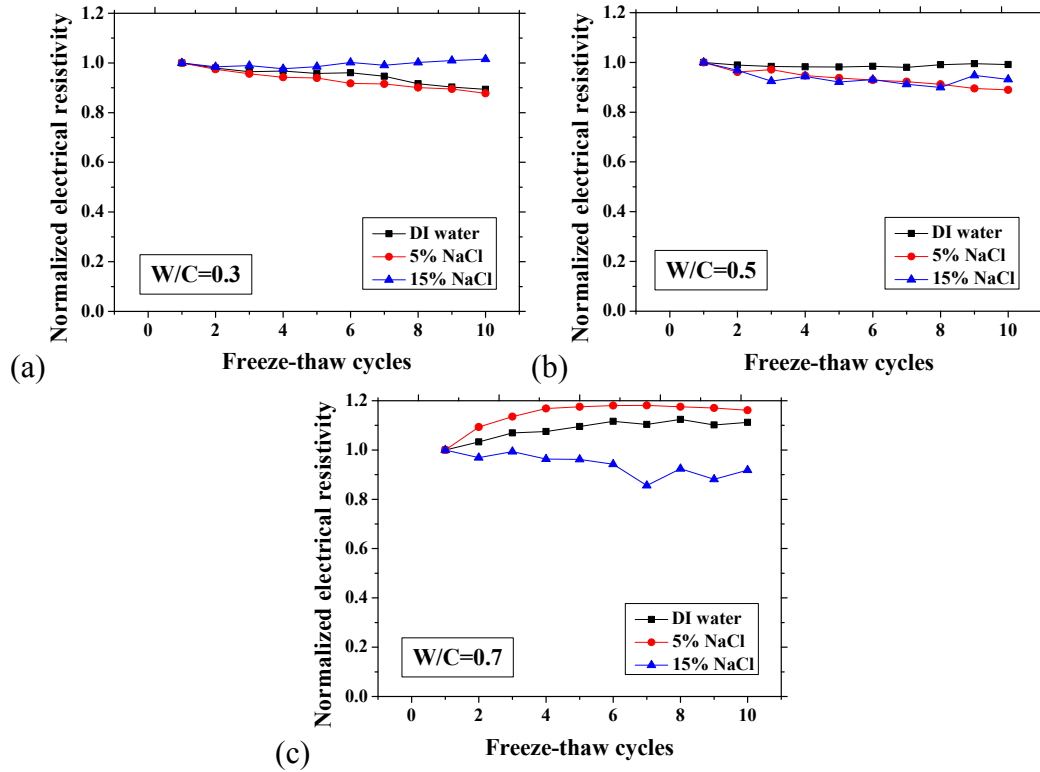


Fig. 3.15 Electrical resistivity at lowest temperature (-28°C) changes with FTCs (a) $w/c=0.3$ (b) $w/c=0.5$ (c) $w/c=0.7$

Table 3.3 Electrical resistivity at reference temperature (23°C) and lowest temperature (-28°C) at first cycle

	Electrical resistivity at temperature 23°C ($\Omega\cdot\text{m}$)			Electrical resistivity at temperature -28°C ($\Omega\cdot\text{m}$)		
	$w/c=0.3$	$w/c=0.5$	$w/c=0.7$	$w/c=0.3$	$w/c=0.5$	$w/c=0.7$
DI water	129.59	112.14	95.17	4622.47	3986.5	4745.47
5% NaCl	30.249	17.15	13.01	10835.95	5500.58	1879.03
15%NaCl	11.03	11.57	6.23	762.15	476.87	296.41

For fully saturated specimen, during freezing, the ice expansion can cause residual deformation, resulting in the increase in pore volume. And then the more unfrozen water from smaller pores will move to the ice front and have ice formation (see Fig. 3.16). With FTCs, the damage would develop, so the ice amount in the bigger pore increases and the bulk water amount in smaller pores decrease. Meanwhile, the specific surface of pores increases, then the

amount of water adsorbed at pore surface increases. The movable water at the lowest temperature is possible to reduce. With this regard, the electrical resistivity at lowest temperature may increase. However, because of the hydraulic pressure, not only the porosity increased, but also the connectivity of pores increases. So the electrical resistivity is possible to decrease.

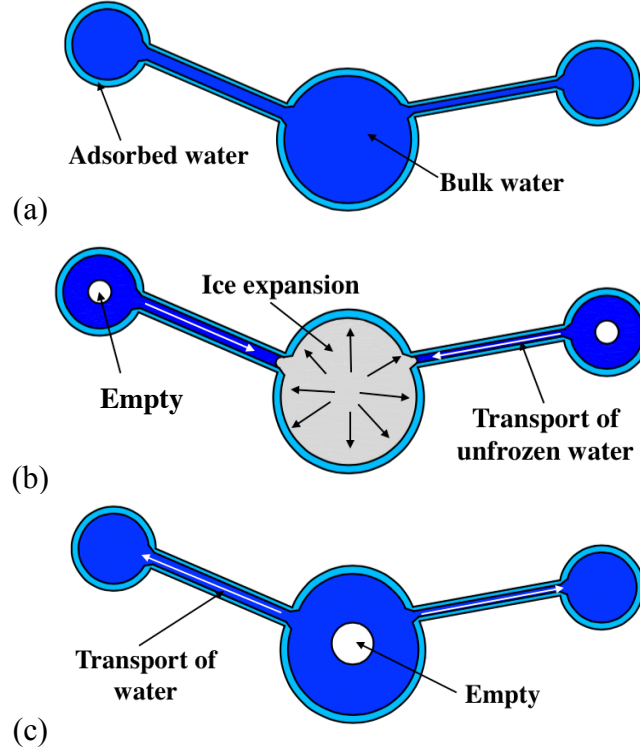


Fig. 3.16 Mechanism during FTC (a) before FTC (b) during freezing (c) after FTC

3.5.3 Activation energy changes with FTCs

Activation energy of mortar sample is a parameter to quantify the sensitivity of electrical resistivity to temperature and it is mainly correlated to the pore characteristics (Liu and Presuel-Moreno, 2014). The value of activation energy for fully saturated samples ($E_{a,s}$) can be calculated as Eq. (3.65) (Chrisp et al., 2001).

$$E_{a,s} = - \frac{R_g \ln \left(\frac{\sigma_{T,s}}{\sigma_{ref,s}} \right)}{\frac{1}{T} - \frac{1}{T_{ref}}} \quad (3.62)$$

The obtained activation energy results are shown in Fig. 3.17. The higher w/c is, the higher volume ratio of moisture, which samples can contain, is. For DI water cases, activation energy decreases with w/c . In the cases of $w/c=0.7$, the activation energy increases with NaCl solution concentration. The reason is due to formation of Friedel's salt which consumed water and movable ions. In particular, for higher concentration exposed samples, the absorbed moisture content is lesser because the formation of Friedel's salt can fill the pores and the amount of salt increases with NaCl concentration (see Chapter 4). Although the concentration of remaining pore solution is high, the sensitivity to temperature would increase. Besides,

because of less amount of Friedel's salt crystallization in the cases of $w/c=0.3$ and 0.5 , the activation energy of the two saturated with 5% NaCl are similar, but for 15% NaCl case, the differences become obvious due to the salt crystallization and total moisture amount. With frost damage development, both of porosity and connectivity of pores would increase. As a result, activation energy decreases with FTCs. When the porosity and connectivity increases, the electrical resistivity at reference temperature decreases. According to the study of Liu and Presuel-Moreno (2012), for DI water saturated concrete samples, there is a relationship between the activation energy and electrical resistivity at reference temperature. Once the electrical resistivity at reference temperature decreases due to the frost damage, the activation energy would decrease correspondingly. However, after frost damage, the degree of saturation would decrease since the deformation and cracks caused the connection of air voids and increase volume of air voids. Besides, it is known that the activation energy of mortar would increase with the reduction of water saturation degree (Chrisp et al., 2001). Therefore, as shown in Fig. 3.17, there is no general tendency for the activation energy changes with FTCs, which varies with w/c and NaCl solution concentration. According to the results, it seems that the variation of activation energy due to FTCs is not significant in the case of $w/c=0.3$ and 0.5 , but the decrease of activation energy in the case of $w/c=0.7$ and 15% NaCl solution saturated sample cannot be simply neglected.

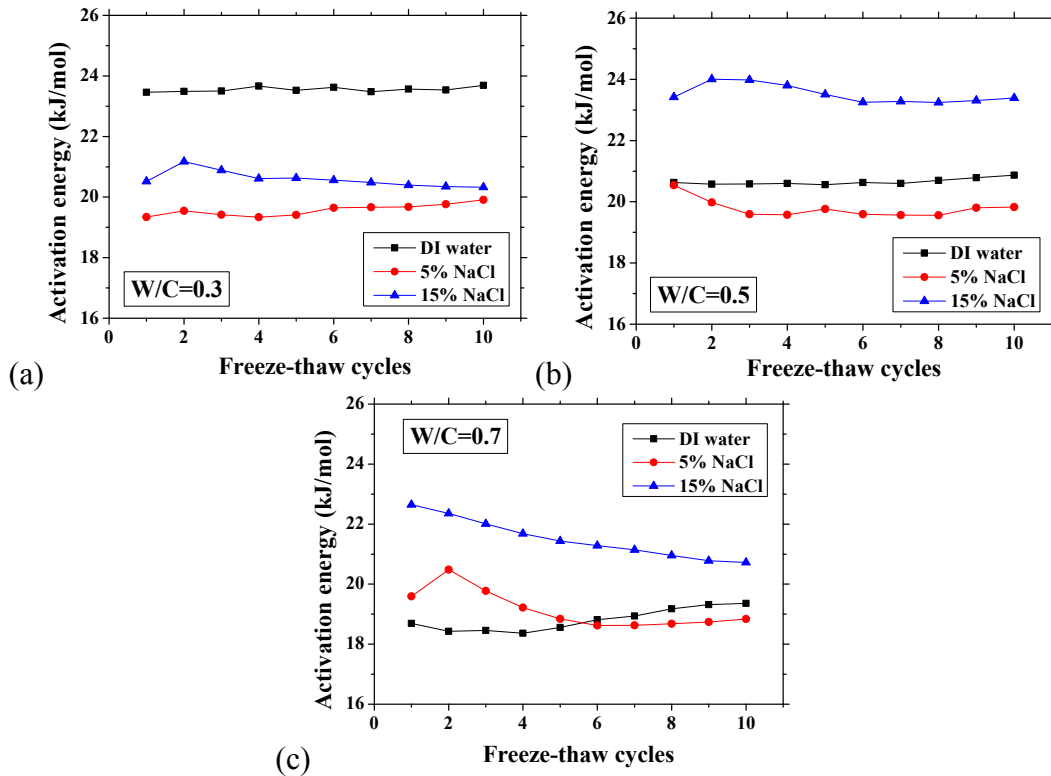


Fig 3.17. Activation energy of specimens changes with FTCs (a) $w/c=0.3$ (b) $w/c=0.5$ (c) $w/c=0.7$

3.5.4 Change in freezing and thawing points change with FTCs

With regard to Fig. 3.13, the freezing and thawing points with FTCs were detected and are shown in Figs. 3.18 and 3.19 respectively. The freezing point of solution in mortar depends on the pore size and solution concentration. After frost damage, the porosity and connectivity would increase, which means that the pore size can increase. Consequently, the freezing and thawing points may increase. However, as Fig. 3.18 shows, no obvious freezing point change tendency can be observed. The variation in freezing point with FTCs may be due

to the heterogeneous ice nucleation nature (Zeng et al., 2015). The freezing and thawing points decrease with the NaCl solution concentration. With different w/c , the trend is not clear. We can see that the case of $w/c=0.5$ has the lowest freezing point of the case of DI water, whereas the freezing points of 5% and 15% NaCl cases are similar amount different w/c .

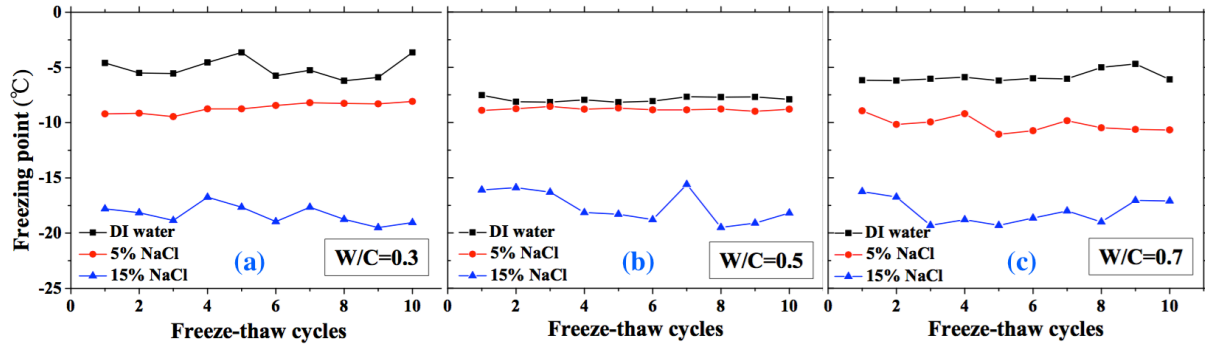


Fig. 3.18 Freezing point changes with FTCs (a) $w/c=0.3$ (b) $w/c=0.5$ (c) $w/c=0.7$

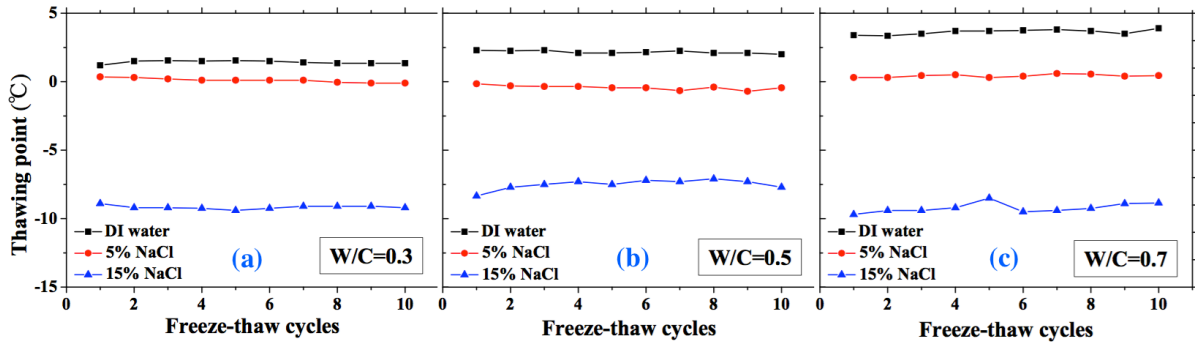


Fig. 3.19. Thawing point changes with FTCs (a) $w/c=0.3$ (b) $w/c=0.5$ (c) $w/c=0.7$

It seems that the thawing point of sample was steady compared with freezing point. For the DI water case, the thawing point increases with w/c , which means the macro pore size is bigger in higher w/c . But for 5% and 15% NaCl solution cases, this conclusion may not be appropriate because of the pore solution concentration and possible salt crystallization. When the NaCl penetrates into mortar, the formation of Friedel's salt could occur and fill the pores, altering the pore size of mortar (see Chapter 4). With increasing NaCl solution concentration and w/c , the amount of Friedel's salt increases (see Chapter 5). Therefore, for 5% and 15% NaCl solution saturated samples, the macro pore size is not bigger in higher w/c .

3.5.5 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 $\text{NaCl}\cdot 2\text{H}_2\text{O}$ would get crystallized when the temperature is below this point. The turning point due to this salt crystallization, however, was not found in the electrical results of this study. We may assume that the NaCl crystal was not precipitated at temperature higher than -28°C in this study, so only the ice formation needs to be considered. In this case, with regard to the frost damage to the electrical property, the ice formation could be estimated based on the model (Eqs. (3.59) and (3.60)), as shown in Fig. 3.20. Then the ice formation with 10 FTCs was further calculated and presented in Fig. 3.21. Similar to the results of Farnam et al. (2015), the ice amount of 5% NaCl case reached the highest. But there was no significant change in the ice content with FTCs. The experimental results of ice formation in mortar

($w/c=0.5$) saturated with NaCl solutions were compared with the theoretical results. As shown in Fig. 3.22, for 5% NaCl solution case, the experimental and theoretical results can basically reach an agreement. However, for 15% NaCl case, the predicted results have an acceptable agreement with our test results, but slightly lower than the results of Farnam et al. (2015)'s study.

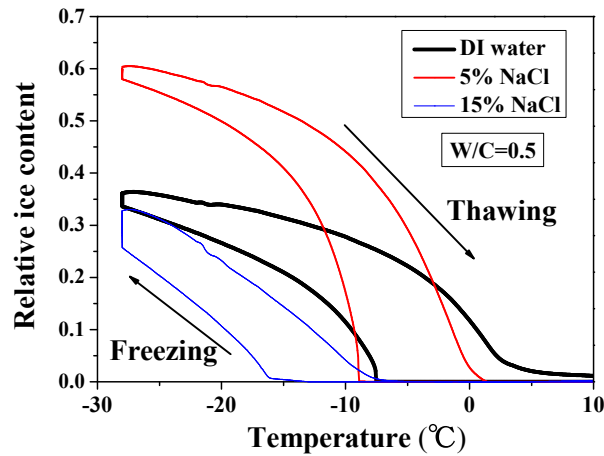


Fig. 3.20 Estimated relative ice content of specimen saturated with different NaCl solutions based on electrical measurement ($w/c=0.5$)

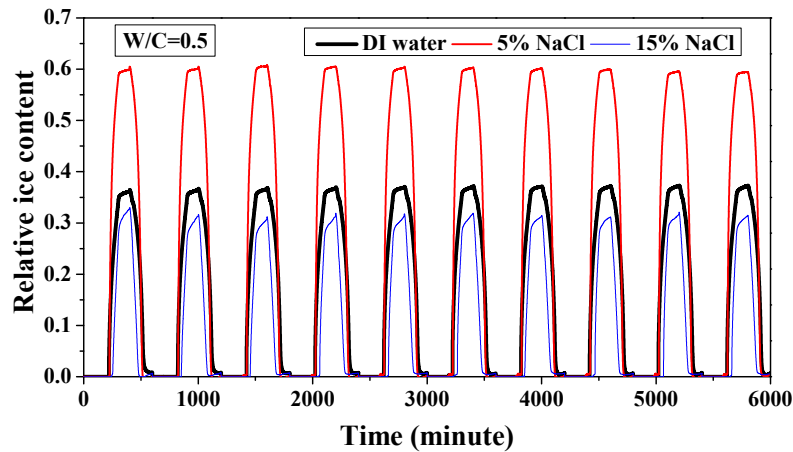


Fig. 3.21 Estimated relative ice content change with FTCs

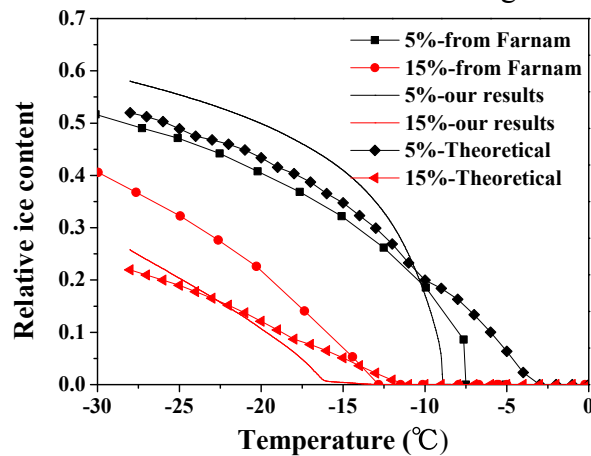


Fig. 3.22 Comparison the relative ice content from our theoretical calculations and experimental observations (during freezing process)

3.6 CONCLUSIONS

In this Chapter, the ice formation in cementitious materials with different concentration of NaCl solutions was theoretically investigated. Besides, 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.

(4) Both of the electrical resistivity at highest and lowest temperatures changes with the damage development, while activation energy does not show apparent relationship with frost damage development. Freezing and thawing points was detected from the relationship between electrical resistivity and temperature. From the previous report, the freezing point increases with FTCs. But in our meso-scale test results, such tendency was not observed.

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Chapter 4

MESOSCALE STUDY OF WATER TRANSPORT IN MORTAR INFLUENCED BY SODIUM CHLORIDE

4.1 INTRODUCTION

In cold and wet regions, frost damage of concrete is an important durability issue to concern, especially for the concrete structures exposed to deicing agents in winter (Valenza and Scherer, 2007). In order to predict the service life of concrete structures exposed to frost action, water transport properties were used as an index (Fagerlund, 1996). However, when the concrete is contaminated by the deicing salt, the transport properties of concrete would be very different with the one exposed to frost action only (Yang et al., 2006; Hashimoto and Yokota, 2013). Thus, the transport properties of concrete exposed to deicing agent need further investigation (Farnam et al., 2015).

When the chloride ion penetrates into concrete, on one hand, it binds to cement pastes by chemical reactions (salt crystallization) and physical adsorption (Baroghel-Bouny et al., 2012; Florea and Brouwers, 2012). The salt crystallization increases solids volume because the formation of Friedel's salt filling the voids may induce expansion (Valenza and Scherer, 2005) and consequently alters the pores diameter of mortar (Liu et al., 2014). On the other hand, when the concrete was exposed to salt solution, calcium hydroxide in concrete may dissolve into solution and leach out. In particular, with the presence of sodium chloride (NaCl), the process of calcium (Ca^{2+}) leaching may be accelerated and the porosity will increase correspondingly (Sato et al., 2015). Since the rate of liquid absorption is related to the diameter of each pore (Kelham, 1988; Martys and Ferraris, 1997; Liu and Hansen, 2015), if the pore diameter changed due to the salt crystallization or Ca^{2+} leaching, the solution transport will be affected. Therefore, by analyzing the liquid absorption, the salt effect on pore characteristics of concrete may be clarified.

Researchers have studied the liquid absorption for decades because it is an important parameter for durability of concrete (Hall and Tse, 1986; Wang and Ueda, 2011). Since the liquid absorption test was mainly conducted in macro scale (Chandra and Xu, 1992; Spragg et al., 2011), for the salt solution absorption, the pore solution concentration may vary from surface to depth of concrete (Wang and Ueda, 2013), which makes the salt crystallization effect on transport properties difficult to understand. So the specimen in small size is a good option for this study, but there are few studies concerning on the small scale. Although Macinnis and Nathawad (1980) developed meso-scale solution absorption testing method, their purpose was to measure the absorptivity and permeability of concrete. The absorption process difference with different concentration NaCl solutions was described, however, how the micro characteristics had been changed with different NaCl solutions and how the Ca^{2+} leaching and salt crystallization would affect transport properties of concrete were still not clarified.

In this paper, the main purpose is to understand how the combined salt crystallization and Ca^{2+} leaching alter the pore characteristics of mortar with different concentrations of NaCl solutions and then influence the water transport. Since the coarse aggregate has rather low permeability, the transport properties of concrete are mainly determined by mortar. The experimentation was conducted in meso-scale. In the meso-scale, which is in the order of five millimeters, the pore solution concentration in mortar could be considered as uniform (Valenza and Scherer, 2007), thus the salt effect can be analyzed by comparing the results of absorption of NaCl solutions and reabsorption of deionized (DI) water. Based on the solution

properties analysis and the proposed liquid transport model, the effect of salt crystallization and Ca^{2+} leaching to pore characteristics of mortar can be analyzed separately. The analyzed results such as relative absorbed water, matrix mass change and diffusivity change are discussed in detail in this paper.

4.2 TEST PROGRAMS

To understand the pore characteristics and transport properties change due to combined Ca^{2+} leaching and salt crystallization, the absorption test was adopted in this study by applying gravimetry. The microstructural alterations due to Friedel's salt formation and calcium leaching were observed through SEM images by Liu et al. (2014). In their study, immersed in DI water, the pore size of concrete increased due to calcium leaching, while it decreased with 5%wt NaCl solution because of formation of Friedel's salt. The research has qualitatively provided the information of microstructural alterations due to NaCl existence, and their results are consistent with our findings. Therefore, the SEM observation was not carried out in this study.

4.2.1 Specimen and solution preparation

Mortar specimens were used in this experimental program. The materials used were ordinary Portland cement with density of 3.16 g/cm^3 and fine aggregate which is 1.2 mm or less in size with density of 2.67 g/cm^3 without air entraining agent. Mix proportions are based on ACI Committee (1991) design, as shown in Table 4.1 with different water-to-cement ratios (w/c). The materials were mixed properly, and then cast into $40 \times 40 \times 160 \text{ mm}$ 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 . After curing, specimens were cut into meso-scale size of $70 \times 30 \times 5 \text{ mm}$ for absorption test. As can be seen in Fig. 4.1(d), the surface of mortar was removed and the core part was used for test. In this case, the property of samples can be assumed uniform. The details of preparation of specimens can be seen in Fig. 4.1. To obtain dry condition, specimens were put inside of oven for 24 hours at 105°C to remove evaporable water. After drying, they were sealed with saran carefully to prevent moisture transfer until measuring their weight under normal temperature and vacuumed chamber was used to store the dried specimens for test.

In order to get fully resolved solutions, the NaCl solute was stirred properly with deionized water in plastic container with volume of 4 liters. Sodium chloride solutions of 0, 3% and 20% by mass concentration were prepared 24 hours before testing.

The density and porosity of mortar were measured gravimetrically by immersing samples into DI water. First of all, the samples were dried by oven at 105°C and the mass was measured at normal temperature. Then the samples and DI water were put into vacuum desiccator separately for 15 minutes to remove the air inside of samples and DI water. After that, the samples were immersed into the DI water in a container. They were continuously kept in the vacuum desiccator for one hour until they were moved out, sealed and placed at room temperature 20 to 23°C . After immersing for 7 days, it was assumed that the samples were fully saturated and then measured the mass. The apparent volume of samples was obtained by suspending the sample into DI water. When the samples are suspended in the water, the measured mass change of water container (before and after the sample immersing into water) is equal to the mass of water flow away and this amount of water volume is the same as apparent volume of sample (apparent volume means including the pore inside since they were filled with water beforehand). Finally, the porosity and bulk dry density of samples were calculated based on the measured mass and volumes. Skeletal density was also calculated with porosity and bulk dry density subsequently. The results are presented in Table

4.1.

The test performed and number of specimens is summarized in Table 4.2.

Table 4.1 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 4.2 Summary of test performed and numbers of specimens

Test performed	Absorption test			Porosity
	DI water	3% NaCl	20% NaCl	
$w/c=0.3$	3	3	3	3
$w/c=0.5$	3	3	3	3
$w/c=0.7$	3	3	3	3

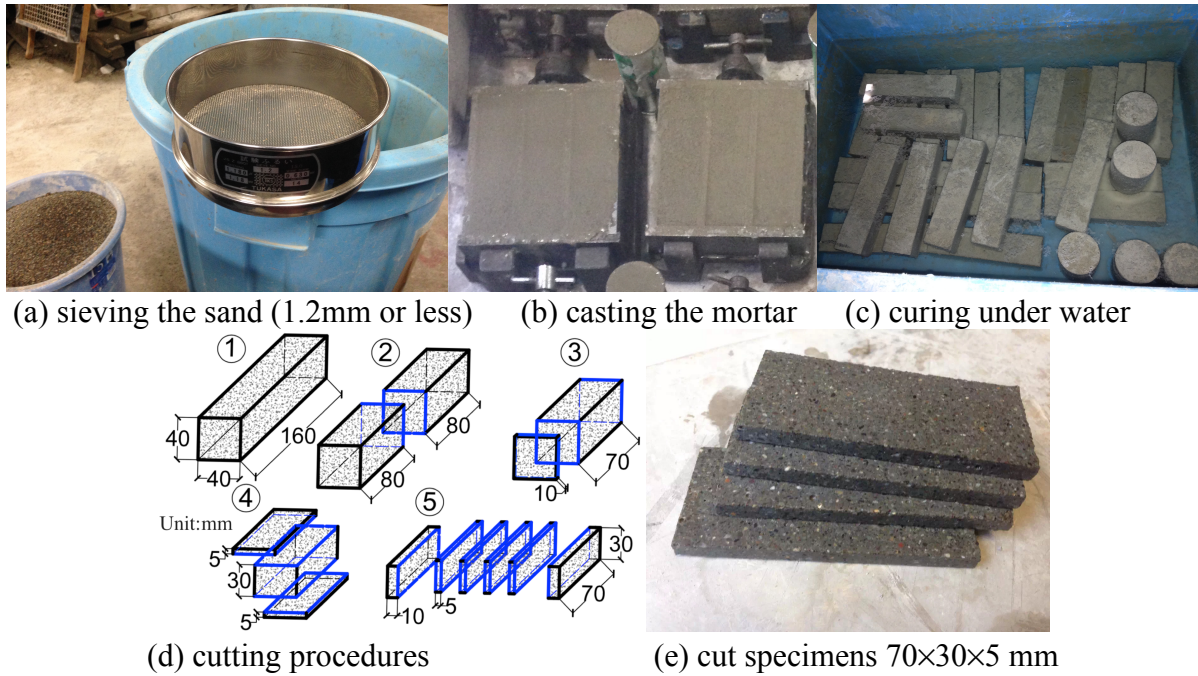


Fig. 4.1 Preparation of specimens

4.2.2 Absorption test procedures

Firstly, the dried weights of specimens were measured with scale (accuracy of 0.1mg). During the first one minute, the specimen was grasped by a tweezer. By doing so the specimen could be fixed to a certain place and easily taken out from solution. As a result, the time of specimen immersed into solutions can be exact as designed (see Fig. 4.2(a)). The first minute is highlighted because the immersion time at the initial stage is very sensitive to the absorption results. Based on the understanding of solution absorption (ASTM, 2004), the interval time of measurement is not constant, but increasing with absorption period (3s, 6s, 10s, 15s, 30s and 1 minute) since the solution absorption rate is not constant. After taking the specimen out of solution, the surface moisture of specimen was removed rapidly with towel paper and put on the scale to measure its weight immediately. To eliminate the effect of moisture evaporation, the whole measurement process was less than 30 seconds. Since the

sample is in meso-scale, though the evaporated water amount is small, it may be sensitive to the initial absorption results. When the absorption period is more than one minute, the specimen was put into solution with settled position by spacer. The measurement would continue with the steps described above except the interval time changes with the absorption period to 2, 3, 5, 10, 15, 20, 30, 40, 60 minutes, 8 hours and 1,2,3 days. In total, nine specimens (three of each for three different w/c) were tested in one container. The volume ratio of solution to samples was controlled over 40:1 (see Fig. 4.2(b)).

After the three days of absorption, the specimens were surface-dried by towel paper, and put into oven 24 hours with 105°C for drying again. When they were taken out of oven, again, the saran was used to prevent moisture transfer. Once the specimen's temperature decreased to normal temperature, the dried weight of dried specimens was measured again. As a result, the mass change of dry weight and water loss during drying were obtained. Containers of deionized water were prepared for reabsorption. Regardless of DI water or NaCl solutions absorbed in the first stage, all the specimens were put into DI water for reabsorption. During the initial solution absorption, calcium leaching and salt crystallization could occur to alter the pore characteristics. By conducting the water reabsorption test, the alteration in pore size distribution due to NaCl attack could be understood. Initially, the dried samples may contain NaCl salt if the sample was immersed in NaCl solutions. After re-immersing into DI water, water penetrates into the sample while NaCl salt dissolves into water. Considering the ionic exchange between pore solution and container water during the reabsorption, the process was prolonged to seven days to observe the moisture transfer equilibrium.

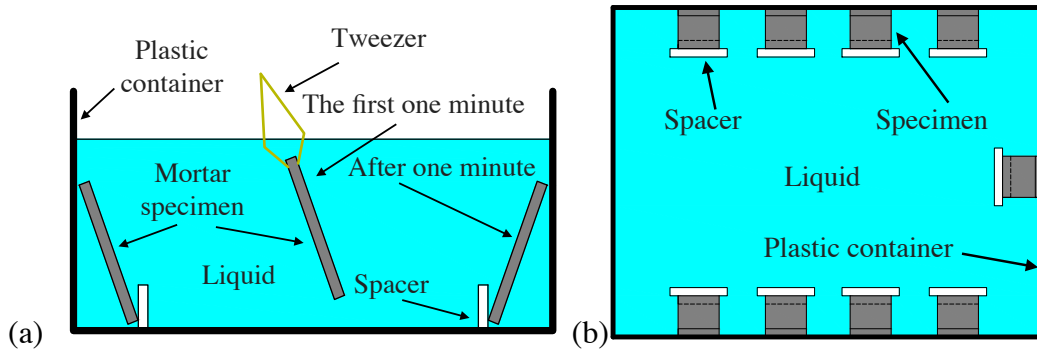


Fig. 4.2 Absorption test setup (a) side view (b) top view

4.3 THEORETICAL BACKGROUND

4.3.1 Two-stage absorption model

For one-dimensional liquid absorption, typically, the sorptivity of the sample can be obtained by fitting the following equation (Martys and Ferraris, 1997)

$$\frac{W}{A} = St^{1/2} + S_0 = C(1 - \exp(-St^{1/2} / C)) + S_g t^{1/2} + S_0 \quad (4.1)$$

where W is the volume of water absorbed, A is the cross-sectional area of the water exposed surface, C is the constant related to the distance of initial sorption, S_{g0} is the coefficient for the relaxation effect, S is the sorptivity and S_0 is the constant for initial water content. At long time absorption, the water absorption is dominated by the $S_{g0}t^{1/2}$ term (Martys and Ferraris, 1997). The relaxation effect means that after bulk water absorption, the air voids in small pores flow out and the pore characteristics may be changed due to Ca^{2+} leaching and salt

crystallization, which may promote further water ingress. However, these phenomena can also occur during the bulk water absorption, and they are related to the degree of saturation. Therefore, to have more accurate prediction, the coefficient of relaxation effect should be modified to consider the bulk water absorption, as below

$$S_g = \frac{S_{g0}}{C(1 - \exp(-St^{1/2} / C))} \quad (4.2)$$

However, for three-dimensional liquid absorption, the model is supposed to be modified based on the water absorption capacity to consider the size of samples and the solution uptake amount q (g/g) may be determined by the dried mass of the sample

$$q = \frac{m - m_d}{m_d} \quad (4.3)$$

where m is the mass of specimen having absorbed solution and m_d is the mass of dried specimen.

In three dimensions, the liquid exposed area could be considered as the exposed sample volume. If the sample is initially dried, the constant for initial water content S_0 is equal to zero. So Eq. (4.1) can be transformed to Eq. (4.4)

$$\frac{W}{V} = \frac{(m - m_d) \cdot \rho_b}{m_d \cdot \rho_l} = \frac{C}{h} (1 + S_g t^{1/2}) (1 - \exp(-St^{1/2} / C)) \quad (4.4)$$

where V is the apparent volume of the sample (the volume including the pore voids), ρ_l is the density of solution, ρ_b is the bulk dry density of sample, S_g is the modified coefficient for relaxation effect and h is the thickness of the sample.

Combing Eq. (4.3) and (4.4), yields

$$q = \frac{C \cdot \rho_l}{h \cdot \rho_b} (1 + S_g t^{1/2}) (1 - \exp(-St^{1/2} / C)) \quad (4.5)$$

Besides, a more general parameter to evaluate the moisture transport is the apparent moisture diffusivity D_0 , which can be estimated based on normalized sorptivity s (Wang and Ueda, 2013)

$$D_0 = s^2 / 123.131 \quad (4.6)$$

$$s = \frac{Sm_d \rho_l}{(m_{sat} - m_d) \rho_b} \quad (4.7)$$

$$S = \frac{11.1(m_{sat} - m_d) \rho_b \sqrt{D_0}}{m_d \rho_l} \quad (4.8)$$

where m_{sat} is the mass of saturated sample

After the initial sorption, the capillary pores are fully filled by solution. The sample is in a quasi-equilibrium condition, in which almost all the pores are occupied by liquid except small pores filling by air, so that the sample is very close to full saturation and the liquid

absorption rate becomes almost zero at that condition. It is reasonable to define the quasi-equilibrium solution uptake as:

$$q_{\infty} = (m'_{sat} - m_d) / m_d = C \rho_l / h / \rho_b \quad (4.9)$$

where m'_{sat} is the mass of quasi-saturated sample.

Therefore, the solution uptake could be described with the following two-stage model

$$q = q_{\infty} \left(1 + S_g t^{1/2} \right) \left(1 - \exp \left(-11.1 \left(\frac{D_0 t}{h^2} \right)^{1/2} \right) \right) \quad (4.10)$$

However, for different concentration solution, the solution mass gain may not show the transport characteristics very clearly. It is more realistic to normalize the solution uptake amount as Eq. (4.11)

$$Q = \frac{q \rho_b}{\rho_l} = \frac{(m - m_d) \rho_b}{m_d \rho_l} = \frac{V_l}{V} \quad (4.11)$$

where Q is the volume ratio of liquid volume to apparent volume of sample and V_l is the volume of liquid.

4.3.2 Relative sorptivity

Liquid absorption in mortar is mainly depending on liquid properties and pore structures. If the liquid properties change with solution concentration and temperature is known, the analysis of pore structure can be achieved based on the liquid absorption phenomenon.

For NaCl solution, three properties which may affect the solution absorption are surface tension, viscosity and density. Besides, all of them are sensitive to the solution concentration and temperature. Therefore, the relationships between the three solution properties and coupled concentration and temperature effect are supposed to be developed. Then the solution absorption with different concentration solutions and temperatures can be clarified and the salt crystallization can also be analyzed.

Surface tension of NaCl solution has been studied by Villani et al. (2014). By regressing the experimental results, they fitted the parameters of a semiempirical formulation proposed by Szyszkowski to calculate the surface tension with temperature and concentration as Eq. (4.12) (Villani et al., 2014):

$$\gamma = \gamma_{water,T} - RT \Gamma^{\infty} \ln \left(1 + \frac{c}{b} \right) \quad (4.12)$$

where $\Gamma^{\infty} = -3.86 \times 10^{-6} \text{ mol/m}^2$, $b = 16.11\%$, γ is the surface tension of solution at temperature T , $\gamma_{water,T}$ is the surface tension of water at the same temperature T of the solution and c is the concentration of solution (% by mass). At 25°C, the surface tension of water is 71.97 mN/m (wikipedia/Surface tension).

In the above equation, the effect of temperature on the surface tension of water is still not clear. The relationship between surface tension of water and temperature can be as Eötvös rule (Kensington, 1941)

$$\gamma_{water,T} = k(T_c - T) \quad (4.13)$$

where k is a constant (about 0.2056 mN/m/°C), T_c is the critical temperature of the surface tension of water/air reaching a value of 0 ($T_c=374^\circ\text{C}$).

Substituting Eq. (4.13) into Eq. (4.12), the surface tension could be a function of temperature and solution concentration as Eq. (4.14) and the predicted results of different temperatures are shown in Fig. 4.3(a).

$$\gamma = k(T_c - T) - RT\Gamma^\infty \ln\left(1 + \frac{c}{b}\right) \quad (4.14)$$

For the viscosity at normal temperature, Villani et al. (2014) also conducted test and predict it based on the equation proposed by Kaminsky as below (Villani et al., 2014)

$$\eta = \eta_{water} (1 + a_1 c^{1/2} + a_2 c + a_3 c^2) \quad (4.15)$$

where η is the viscosity of NaCl solution at a certain temperature and pressure (Pa.s), η_{water} is the viscosity of pure water at the same temperature and pressure, a_1 , a_2 and a_3 are constant parameters fitting by testing results and $a_1=0.1134$, $a_2=-0.0551$, $a_3=0.0027$.

The temperature effect on viscosity can be described with Arrhenius type of law as Eq. (4.16)

$$\eta = A \cdot \exp\left(\frac{E_a}{R_g T}\right) \quad (4.16)$$

From the test results of Villani et al. (2014), E_a is the activation energy which is around 20.9kJ/mol for NaCl solution. R_g is the universal gas constant (8.314 N.m/K/mol), and the parameter A is a constant changing with concentration of NaCl.

For the same concentration solution, the viscosity may be predicted based on the viscosity at reference temperature from Eq. (4.17)

$$\eta = \eta_0 \exp\left[\frac{E_a}{R_g} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad (4.17)$$

where η_0 is the viscosity at reference temperature T_0 .

Therefore, the viscosity of salt solutions with temperature and concentration change can be derived as follows

$$\eta = \eta_{water,T_0} \cdot (1 + a_1 c^{1/2} + a_2 c + a_3 c^2) \cdot \exp\left[\frac{E_a}{R_g} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad (4.18)$$

where η_{water,T_0} is the viscosity of pure water at the reference temperature. From Wikipedia (viscosity), at 25°C , the viscosity of water is 8.94×10^{-4} Pa.s. Based on Eq. (4.18), the viscosity is predicted as shown in Fig. 4.3(b).

The density of NaCl solution at 23°C is calculated as Eq. (4.19) (Yang, 2007)

$$\rho_l = 7.2011c + 997.83 \quad (4.19)$$

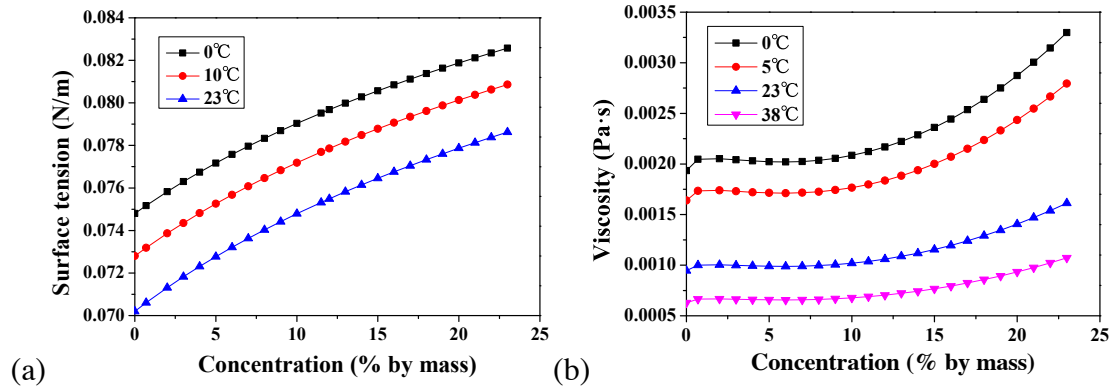


Fig. 4.3 Influence of temperature on NaCl solution properties (a) Surface tension and (b) viscosity

Following Hall and Hoff (2002), if samples share the same pore structure, then the solution absorption would vary with the ratio of surface tension and viscosity. The relative sorptivity can be defined as γ/η (Hall and Hoff, 2002), which is shown in Fig. 4.4. The relative sorptivity changes with temperature and concentration and it may reach the maximum value at intermediate concentration (3% to 10% by mass).

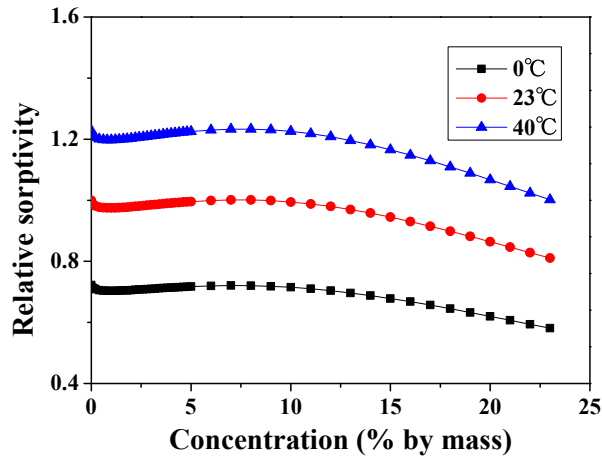


Fig. 4.4 Relative sorptivity change with solution concentration

4.4 RESULTS AND DISCUSSIONS

4.4.1 Absorbed water content during the first absorption

After 3 days immersion into solutions, the water absorbed was measured by gravimetric method. Theoretically, if there is no Ca^{2+} leaching and salt crystallization, the absorbed water content can be calculated based on total amount of absorbed solution and the concentration of pore solution. The total amount of absorbed solution can be known with the difference between the mass at fully saturation and initial dried of samples. Since the sample size is in meso scale in this study, the concentration of pore solution can be considered as the same with surrounding environment (solution concentration to which the sample was

exposed). Therefore, the absorbed water amount could be normalized to the dried mass of sample as Eq. (4.3), and the normalized absorbed water will be

$$m_w = q_{\max} \cdot (1 - c) \quad (4.20)$$

where $q_{\max}$ is the maximum normalized solution uptake.

Due to the possible Ca^{2+} leaching, the absorbed water content is not equal to the difference between the initial dried sample mass and saturated sample mass. Instead, it is more reasonable to calculate the absorbed water based on the difference between the re-dried sample mass and the saturated sample mass, considering the water absorption capacity difference, it can be normalized as below

$$m_w = \frac{m_{\text{sat}} - m_{\text{dre}}}{m_d} \quad (4.21)$$

where m_{dre} is the re-dried mass of sample.

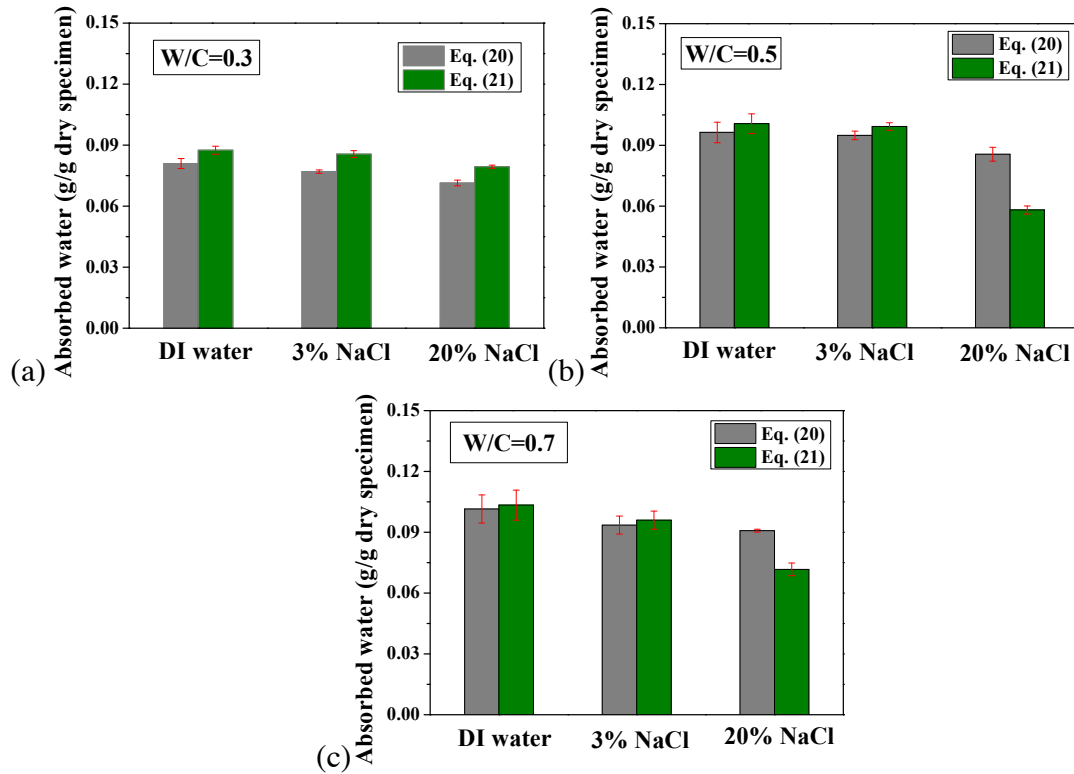


Fig. 4.5 Normalized absorbed water content with different w/c (a) 0.3 (b) 0.5 (c) 0.7

As shown in Fig. 4.5, samples exposed to DI water show that the absorbed water amount calculated by Eq. (4.21) is higher than Eq. (4.20), which means part of mortar matrix was replaced by water due to Ca^{2+} leaching. Clearly, samples exposed to 3% NaCl solution also show the tendency, in this case, the matrix mass change is dominated by Ca^{2+} leaching although it is co-existing with salt crystallization. However, samples exposed to 20% NaCl solution show different tendency compared with the two cases mentioned above except the $w/c=0.3$ case. This can be explained by the filling of pores by crystallized salt since the amount of crystallized salt increases with the increase of concentration of solution. However,

due to the less porous media in samples with $w/c=0.3$, the specific surface area is limited for salt crystallization to occur. As a result, the effect of salt crystallization cannot compensate the effect of leaching in the case of $w/c=0.3$. Also, it is interesting to note that the actual absorbed water content in samples exposed to high concentration solution is much lower than the one absorbed from DI water, which means that samples saturated with higher concentration solution may suffer from smaller internal stress induced by ice expansion. However, for intermediate concentration case (3% NaCl), in terms of absorbed water amount, there is no big difference compared with DI water. If the temperature decreases to subzero, the water would form to ice and the ice expansion could induce internal pressures to cause micro cracks and then macro cracks. At low temperature, the solubility of calcium hydroxide would be higher than at normal temperature since it increases with decreasing of temperature. In this case, NaCl may have reaction with the calcium hydroxide to form Friedel's salt. Because of the expansion of Friedel's salt, additional pressures will be induced. Therefore, the internal pressure due to the combined ice formation and salt crystallization during freezing is more severe than the pressure induced by ice formation alone in the case of DI water. This may imply the reason why the most destructive damage happens at the intermediate concentration case.

4.4.2 Mass change of mortar matrix after solution absorption

After the sample was exposed to solution, the mass of mortar matrix may be changed. In the case of DI water, the only possible mass change besides water uptake is the leaching of calcium hydroxide. However, for NaCl contaminated samples, in addition to the reduced mass due to leaching, the formation of salt and precipitation of NaCl can gain the mass. Since the mass increase contributed by NaCl precipitation is known, the proportion from crystallization can be estimated.

The amount of mass change can be calculated based on the difference between the initial dried mass and re-dried mass, considering the water absorption capacity difference, it can be normalized as below

$$\Delta m = \frac{m_{dre} - m_d}{m_d} \quad (4.22)$$

In addition, if there is no leaching or salt crystallization, the mass change is due to the precipitation of NaCl. Since the concentration of pore solution is known, the amount of mass gain can be estimated as following:

$$\Delta m_{NaCl} = \frac{(m_{sat} - m_d) \cdot c}{m_d} \quad (4.23)$$

As shown in Fig. 4.6, the matrix mass loss was observed in the case of DI water, and the amount reduces with the increasing of w/c . This phenomenon is corresponding to the amount of absorbed water and the reason is due to Ca^{2+} leaching as explained in the Section 4.4.1. With the increasing of solution concentration, the mass change increases gradually. It seems that the mass change tendency of the case 3% NaCl is from negative to positive with the increasing of w/c , which may indicate that the amount of crystallized salt is increasing with the porosity. More importantly, for the case of 20% NaCl, the mass change value from Eq. (4.22) is higher than the value from Eq. (4.23) for the case of $w/c=0.5$ and 0.7. It proves that there is formation of new salts (eg. Friedel's salt), which increased the matrix mass of sample in addition to NaCl precipitation. The difference between the two results could be contributed

to the newly formed salt (eg. Friedel's salt), and it is found that the amount of the salt is even higher than the precipitation of NaCl. In addition, it is worth noting that, for the case of $w/c=0.3$, the different tendency was observed. This implies that even under high concentration, the Ca^{2+} leaching phenomenon is still happening. Therefore, the actual crystalized salt amount is greater than the estimation and this amount of salt may have expansion enough to cause damage in the mortar specimen.

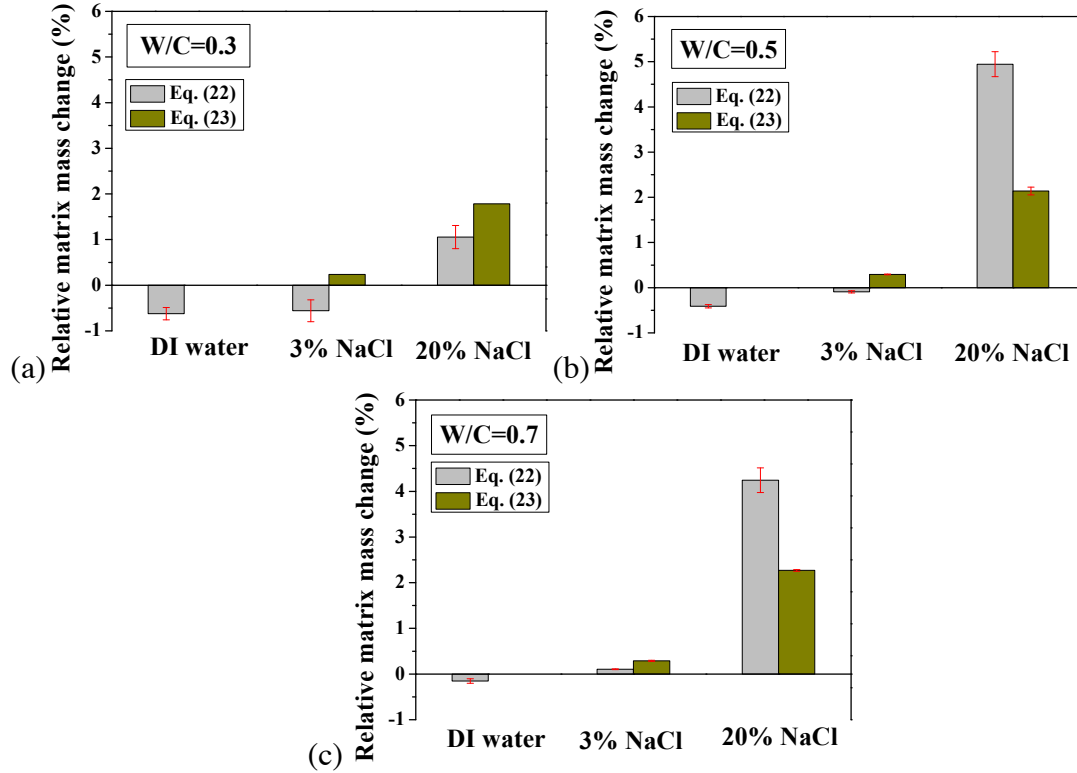


Fig. 4.6 Mass change of mortar before absorption and oven dried after absorption with different w/c (a) 0.3 (b) 0.5 and (c) 0.7

4.4.3 Solution absorption and water reabsorption of sample

For a short period of immersion (1 hour), the test results of cumulative solution absorption characteristics are presented in Fig. 4.7-10 with the square root of time. While for a longer period (7 days), as shown in Fig. 4.11, the absorption results are presented with the exponent of time. The absorption amount is analyzed based on Eq. (4.3), normalized by the dried mass of sample. As found in Fig. 4.7(a), the absorption process may be divided into two stages, initial absorption and long time absorption. The differences among the two stages are more obvious in Fig. 4.11. During the initial absorption, the mass of sample increased linearly and rapidly. This may be contributed by the capillary pore absorption. If the pores can be assumed to be continuous tubes for solution transport, the larger diameter can transport the solution more speedily (Kelham, 1988; Martys and Ferraris, 1997; Liu and Hansen, 2015). For the long time absorption, it is also linear (see Fig. 4.11). The gel pore solution absorption and filling of air voids may responsible for mass gain during this period. Due to the small size of gel pores, the solution transport inside could be rather slow, so it needs a long time to totally fill by water. In macro scale test in past study (Chandra and Xu, 1992), only the above two processes are obvious and it is a knee point separate them. However, in meso-scale absorption test, there is no clear knee point, instead, a transition region in a exponential relationship with time was observed, which is clearly shown in Figs. 4.7-10.

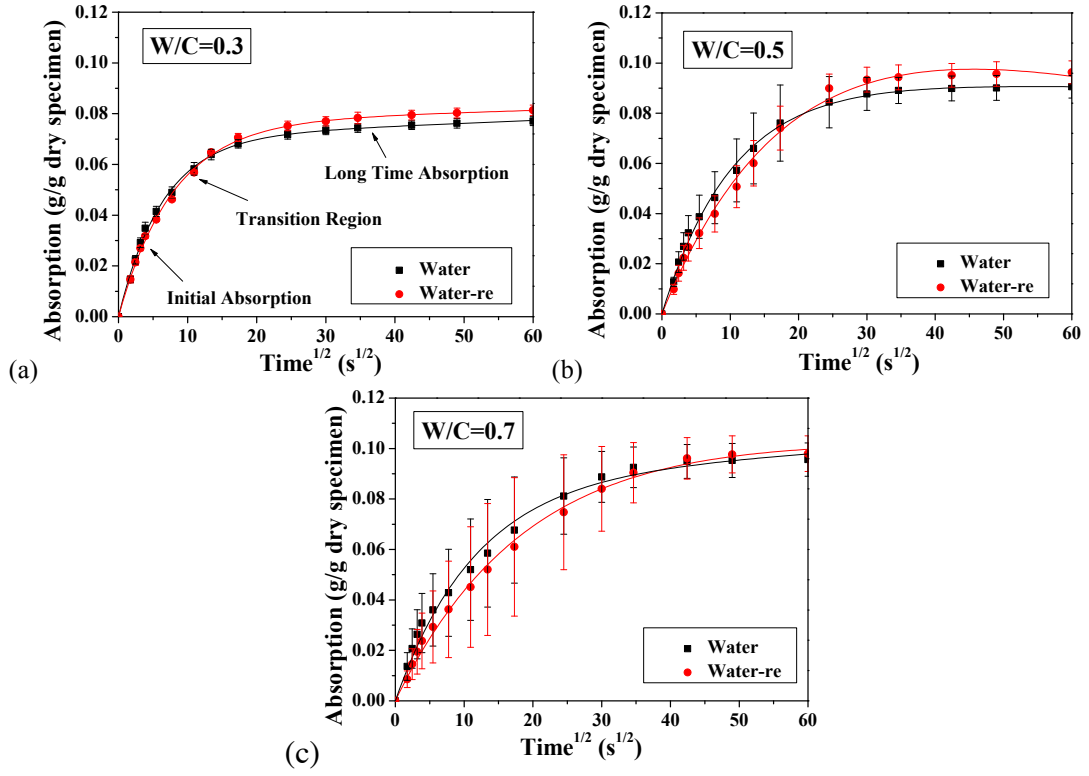


Fig. 4.7 Comparison of water absorption and water reabsorption mass in mortar within 60 minutes (a) $w/c=0.3$ (b) $w/c=0.5$ and (c) $w/c=0.7$

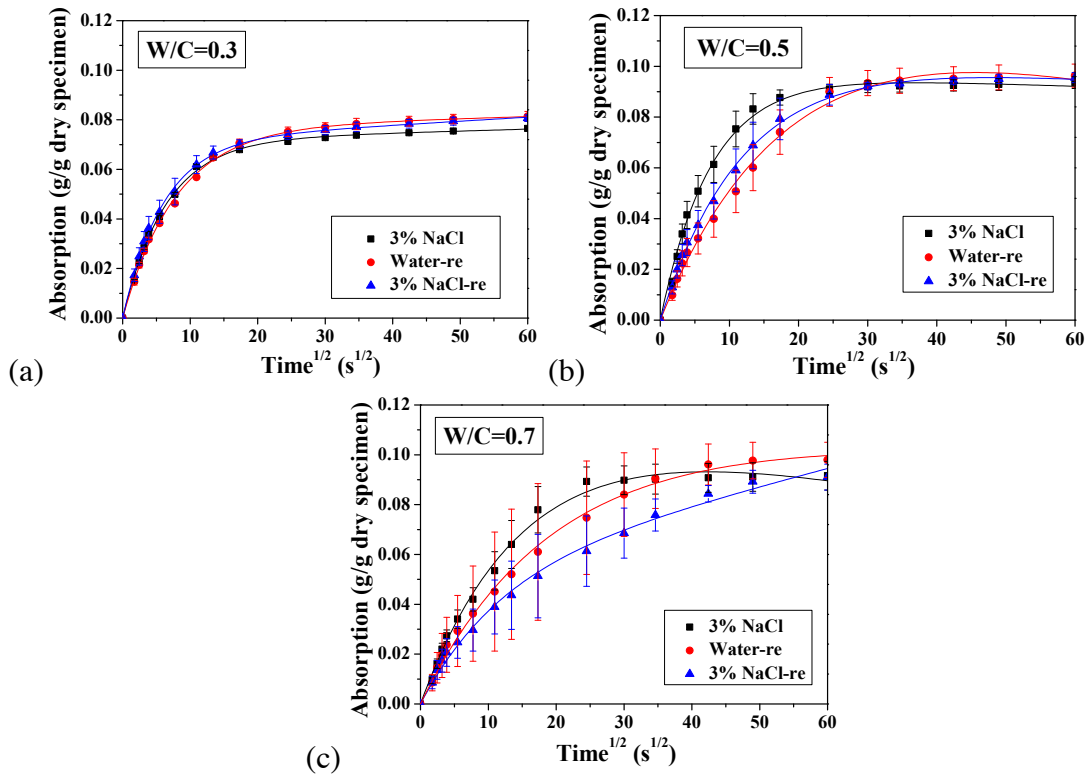


Fig. 4.8 Comparison of 3% NaCl solution absorption and water reabsorption mass in mortar within 60 minutes (a) $w/c=0.3$ (b) $w/c=0.5$ and (c) $w/c=0.7$

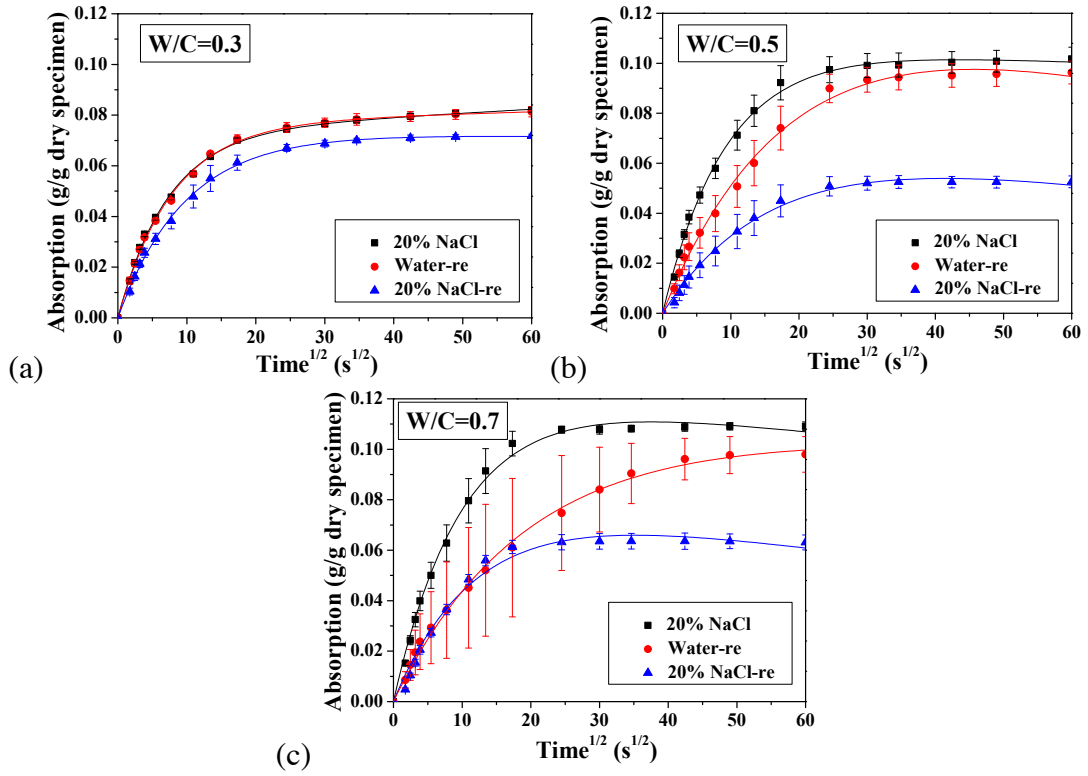


Fig. 4.9 Comparison of 20% NaCl solution absorption and water reabsorption mass in mortar within 60 minutes (a) $w/c=0.3$ (b) $w/c=0.5$ and (c) $w/c=0.7$

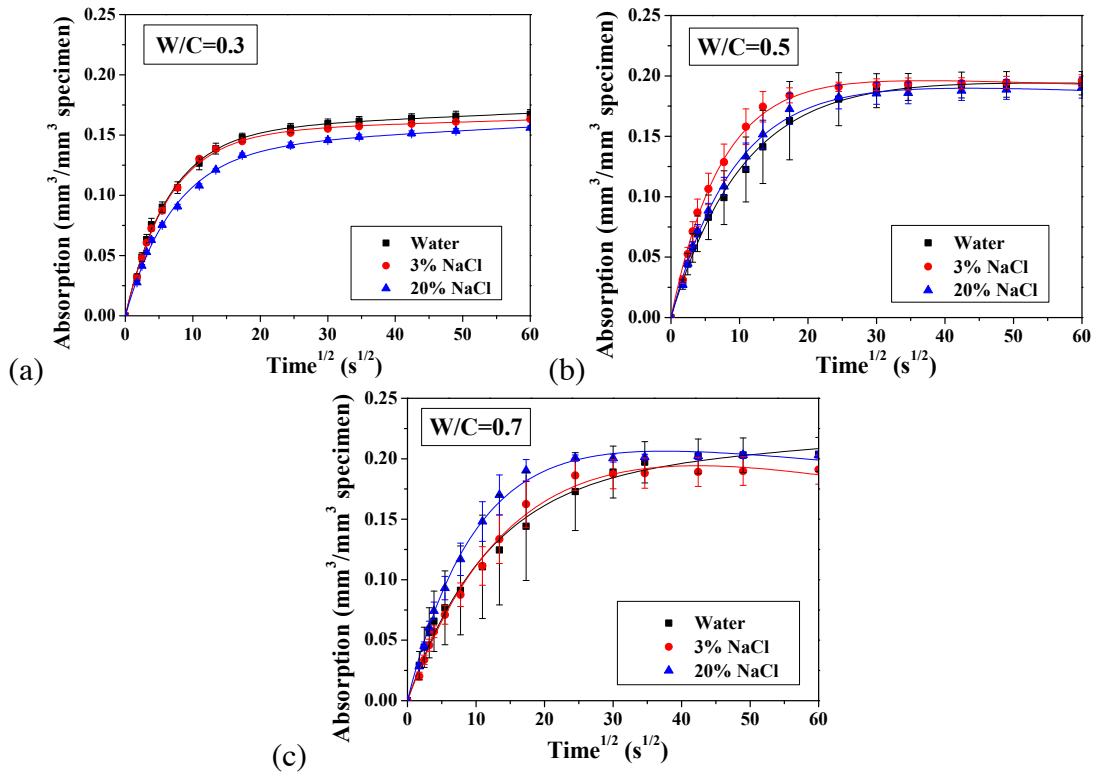


Fig. 4.10 Comparison of absorbed solution volume to sample volume ratio in mortar within 60 minutes (a) $w/c=0.3$ (b) $w/c=0.5$ and (c) $w/c=0.7$. Solid lines represent the curve fitting using the two-stage model.

In Figs. 4.7-9, the solution absorption is related to solution mass gain. Due to the solution density difference, the absorption amount in terms of volume for each concentration solution cannot be seen. In order to see the concentration effect, the absorbed solution volume to sample volume ratio, which was calculated based on Eq. (4.11), was compared among different concentration cases in Fig. 4.10. For different w/c , the absorption results are different. In the case of 20% NaCl solution, samples with $w/c=0.3$ has the lowest absorbed solution volume while it is increasing with w/c and becoming the highest for the sample with $w/c=0.7$.

The two-stage absorption model, which is shown by solid lines in Figs. 4.7-10, fit well the absorption processes of mortar samples ($w/c=0.3, 0.5$ and 0.7) in 0, 3% and 20% NaCl solutions and reabsorption processes in DI water (see Figs. 4.7-10). The parameters q_∞ , Q_∞ , D_0 and S_g are summarized in Table 4.3. Compared with water absorption and water reabsorption curves in Fig. 4.7, the slope during initial absorption becomes smaller in the reabsorption process, but the cumulative absorption amount exceeds the initial absorption at long time absorption period. Besides, in all 3% NaCl solution cases, parameters D_0 and S_g decreased during reabsorption while the parameters q_∞ and Q_∞ increased. This trend implies that the volume of capillary pores is reduced because the solution can be transported faster in capillary pores compared with in gel pores as aforementioned. The total pore volume is increased since the maximum absorption amount, which is determined by the total pore volume, is increased. The reduction of capillary pores may be caused by salt crystallization and the thermal shrinkage due to oven drying, whilst the increasing of porosity may be caused by the Ca^{2+} leaching and it mainly affects the gel pores.

Table 4.3 The fitted parameters during NaCl solution absorption or water reabsorption

	Absorption ($w/c=0.3$)				Reabsorption ($w/c=0.3$)			
Immersed solution	q_∞ (%)	Q_∞ (%)	D_0 ($\times 10^{-3} \text{mm}^2/\text{s}$)	S_g ($\times 10^{-3} \text{s}^{1/2}$)	q_∞ (%)	Q_∞ (%)	D_0 ($\times 10^{-3} \text{mm}^2/\text{s}$)	S_g ($\times 10^{-3} \text{s}^{1/2}$)
DI water	0.071	0.153	5.09	1.6	0.077	0.166	3.35	1.05
3% NaCl	0.072	0.153	4.93	1.09	0.071	0.155	5.71	2.26
20% NaCl	0.073	0.139	3.91	2.12	0.073	0.159	2.08	-0.31
	Absorption ($w/c=0.5$)				Reabsorption ($w/c=0.5$)			
Immersed solution	q_∞ (%)	Q_∞ (%)	D_0 ($\times 10^{-3} \text{mm}^2/\text{s}$)	S_g ($\times 10^{-3} \text{s}^{1/2}$)	q_∞ (%)	Q_∞ (%)	D_0 ($\times 10^{-3} \text{mm}^2/\text{s}$)	S_g ($\times 10^{-3} \text{s}^{1/2}$)
DI water	0.094	0.201	2.48	-0.52	0.139	0.298	0.65	-4.67
3% NaCl	0.097	0.204	4.86	-0.90	0.105	0.225	1.82	-1.48
20% NaCl	0.107	0.200	3.2	-0.99	0.074	0.158	0.94	-4.7
	Absorption ($w/c=0.7$)				Reabsorption ($w/c=0.7$)			
Immersed solution	q_∞ (%)	Q_∞ (%)	D_0 ($\times 10^{-3} \text{mm}^2/\text{s}$)	S_g ($\times 10^{-3} \text{s}^{1/2}$)	q_∞ (%)	Q_∞ (%)	D_0 ($\times 10^{-3} \text{mm}^2/\text{s}$)	S_g ($\times 10^{-3} \text{s}^{1/2}$)
DI water	0.088	0.187	1.59	1.96	0.109	0.231	0.55	-0.65
3% NaCl	0.121	0.254	0.89	-4.1	0.052	0.112	2.32	13.47
20% NaCl	0.125	0.232	1.77	-2.33	0.082	0.175	1.2	-4.26

In the case of 20% NaCl solution exposed samples, the reabsorption curves are very different from the samples exposed to DI water, especially for higher porosity samples. Besides, as shown in Table 4.3, the fitted parameter of quasi-equilibrium solution uptake and

relaxation parameter of 20% NaCl solution exposed samples are smaller while the apparent diffusion coefficient is higher except the case of $w/c=0.3$. Interestingly, for 3% NaCl solution, both of the apparent diffusion coefficient and relaxation parameter are the highest compared with other two solution cases. This is because the precipitated salt is insignificant to porosity alteration for the low concentration one and also the effect of leaching may compensate the effect of precipitated salt. However, the porosity is dramatically reduced for high concentration NaCl solution immersed samples, which means the leaching effect will not increase with solution concentration but the salt crystallization effect will. In addition, the porosity alteration is increasing with w/c . This is due to the possibility that more porous microstructural characteristics can promote the salt crystallization.

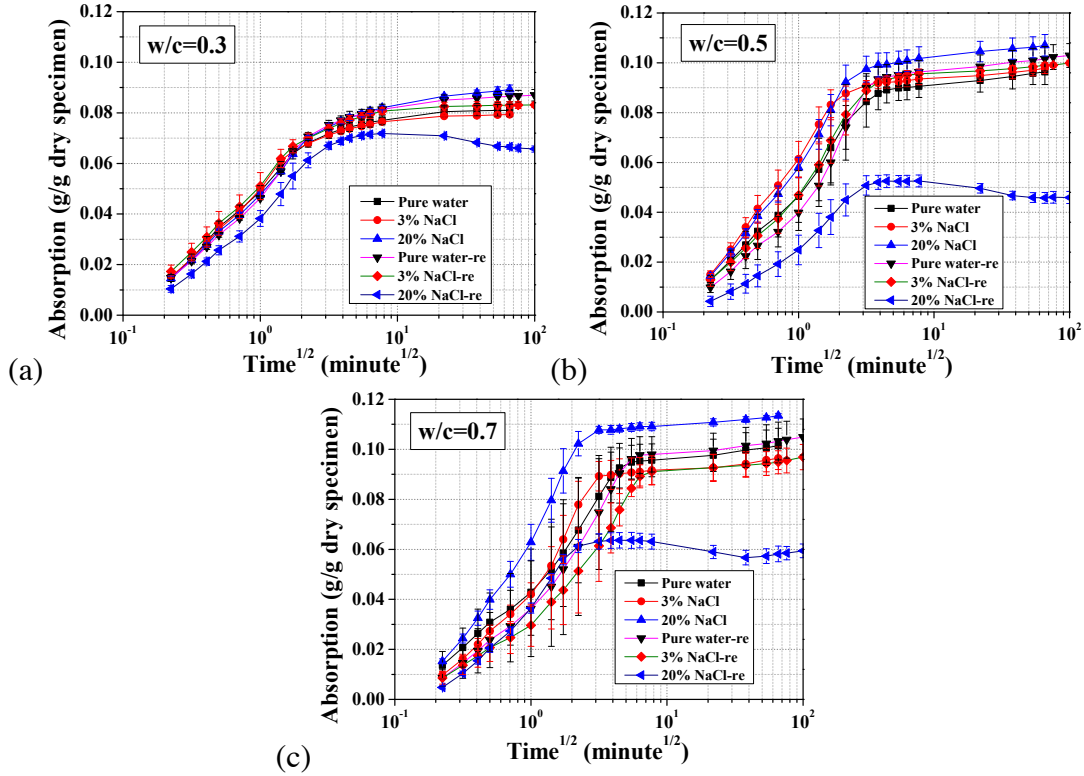


Fig. 4.11 Comparison of solution absorption and water reabsorption mass in mortar within 7 days (a) $w/c=0.3$ (b) $w/c=0.5$ and (c) $w/c=0.7$

4.5 CONCLUSIONS

Based on the proposed two-stage NaCl solution diffusion model, experimental results of mortar solutions absorption and water reabsorption can be described well. The following conclusions can be reached.

- (1) The solution transport depends on the pore characteristics of mortar. As a result, it varies with different w/c . The solution property change with solution concentration and temperature are analyzed and the relative sorptivity change with concentration is presented. The overall transport behavior difference with solute difference at 23°C can be explained by the difference in two phenomena, salt crystallization and Ca^{2+} leaching.
- (2) Exposure to intermediate concentration (3% by weight) solution, although the salt crystallization and Ca^{2+} leaching were co-existing, the sample absorbed almost the same amount of water as DI water case. When ice formation and salt crystallization occur at subzero temperature, the expansion due to ice and salt induce internal pressures. The

- pressure is more severe than the pressure in the DI water case, which is induced by ice formation alone, resulting in more destructive frost damage.
- (3) Exposure to high concentration (20% by weight) solution, the salt crystallization has greater effect on transport properties of mortar than Ca^{2+} leaching. The salt fills the voids or blocks the gel pores with solution transport. Subsequently, it reduced the further water penetration, so that the specimen would have less degree of expansion when the water transforms to ice.
 - (4) The rate of absorption in each stages is related to the pore diameters of mortar. By developing the model connected with pore diameter and absorption, the pore diameter change in each range may be understood accurately. This will be reported in the future study.

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Chapter 5

MECHANICAL DETERIORATION OF MORTAR SUBJECTED TO FREEZE THAW CYCLES AND SODIUM CHLORIDE ATTACK

5.1 INTRODUCTION

In cold and wet regions, concrete destroyed by freeze-thaw cycles (FTCs) and deicing agents is a serious durability problem to concern, especially for bridge deck and walkways (Litvan, 1976; Valenza and Scherer, 2007). Deicing agents such as sodium chloride (NaCl) can accelerate the frost deterioration, specifically, spoiling the appearance (surface scaling) and further reducing the strength and stiffness (internal damage) of concrete structures with FTCs (Penttala, 2006; Valenza and Scherer, 2007). Thus, there is in need to investigate the frost deterioration of concrete combined with salt ingress as it may threat to the safety of concrete structures. According to glue spall theory (Valenza and Scherer, 2006), the surface scaling is caused by the propagation of cracks in the ice on surface of concrete. The damage depends on not only the mechanical properties of ice on the concrete surface, but also the mechanical properties of surface concrete layer. In addition to the surface ice induced cracking, the mechanical properties of surface and internal concrete could be deteriorated by the combined salt attack and frost action as well. However, there is still no agreement about the combined damage mechanism until now (Liu and Hansen, 2015a,b).

In order to understand the mechanism of salt scaling, Valenza and Scherer (2005) observed swelling of cement paste exposure to NaCl brine, and the subsequent X-ray powder diffraction results revealed that the swelling was mainly contributed by the formation of Friedel's salt. In this case, the internal frost damage of concrete may be attributed to the combined ice and Friedel's salt formation (Wu et al., 2014; Farnam et al, 2014) since both of them can cause damage. Besides, if the lowest temperature is below -21 degree, the precipitation of NaCl crystal could also induce destructive damage of concrete when the specimen is in a supersaturated condition (Thaulow and Sahu, 2004; Lubelli et al., 2006). For frost damage of concrete due to ice formation alone, simulation model (Gong et al., 2015) based on ice content has already been well developed and the ice content can be estimated based on electrical measurements (Chapters 2 and 3). However, a comprehensive model explains the contributions by the combined ice and salt crystallization has not been developed yet. To achieve so, the understanding of the mechanism of combined effect to the mechanical properties of mortar is supposed to be sufficient.

For the damage effect of NaCl alone, Wang et al. (2006) studied the micro characteristics of concrete under 60 wetting-drying cycles by using X-ray diffraction (XRD) and scanning electron microscope (SEM), from which the effect could be attributed to the leaching of cement hydration products and salt crystallization. However, how the leaching and crystallization affect by NaCl concentrations has not been understood. In a sealed condition, the leaching is not likely to occur with FTCs since the solubility of calcium hydroxide is constant at a certain temperature. The salt crystallization may cause destructive damage, which was observed by Farnam et al. (2014) based on acoustic emission test. They found that the most severe damage is not happened at specimens saturated with NaCl solution around 3%wt but 15%wt due to a new phase transformation (eg. Friedel's salt). While from deformation measurements of Zeng et al. (2014), it seems there is no significant frost damage for cement paste saturated with high concentration NaCl solution because of lesser ice content at lowest temperature. With the NaCl salt presence, the freezing point of cementitious materials decreases, the ice content reduction could ease the pressures in pores. The damage

effect due to ice formation and salt crystallization may vary with the different concentration of salt solution. The results reveal that the damage process is much more complicated than what the existing models (Sun and Scherer 2010) explained and needs further investigation.

Recently, investigating the frost damage of concrete by electrical measurement was proposed as a great potential methodology (Sato and Beaudoin, 2011). This technique was applied to study concrete for decades (Whittington et al., 1981), moreover, it is believed that the electrical resistivity of concrete is related to the pore characteristics, pore solution composition, saturation degree and temperature (Weiss et al., 2012). Since ice formation is essential for understanding the frost damage of concrete (Gong et al., 2015), electrical measurements was applied to estimate the ice content below freezing point (Cai and Liu, 1998; Wang et al., 2016b). In addition, Wang et al. (2014) attempted to use the maximum electrical resistivity to evaluate the frost damage of cement paste immersed to water with FTCs. On the other hand, Farnam et al. (2015) studied the mortar saturated with different concentration NaCl solution and the electrical resistivity change at reference temperature (20°C) was considered to be the damage index, but only the first FTC was considered. Since they use the macro scale samples for testing, the salt frost damage may be not uniform along the depth of sample. So evaluation of salt frost damage of mortar with FTCs also needs further study.

In fact, the concentration of chloride ion in pore solution of concrete is not uniform along the depth from surface in macro scale, but varying from high to low due to the time dependence of ion penetration (Wang and Ueda, 2013). As a result, the damage is different for each layer of concrete. In order to predict the mechanical behaviour of concrete more accurately, meso-scale modeling (Gong et al., 2015) was applied in previous study. In meso-scale, the uniform moisture content, temperature and concentration of pore solution can be achieved, so the damage process of each layer could be known. Therefore, in this Chapter, to provide inputs for modeling, the meso-scale mechanical response of mortar samples suffered from FTCs with and without the presence of NaCl solutions was studied. Meanwhile, the chemical analysis was also carried out to clarify the damage mechanism of combined calcium leaching and salt crystallization (non-FTCs) and damage mechanism of combined ice formation and salt crystallization (with FTCs). To evaluate the salt frost damage under FTCs, a damage index was proposed to evaluate the frost damage of specimens. The results from three-point bending test of normalized elastic modulus were compared with the damage index from electrical measurements with FTCs.

5.2 TEST PROGRAMS

5.2.1 Specimen preparation

Mortar specimens were studied in this experimental program. Mix proportions were based on ACI Committee (1991), in which coarse aggregates were excluded, as shown in Table 5.1 with different water-to-cement ratios (w/c). Ordinary Portland cement was used and the physical properties and chemical compositions are shown in Table 5.2. The maximum size of fine aggregate was 1.2 mm and its density was 2.67 g/cm³. To promote frost damage, air-entraining agent was not added. The materials were mixed properly. Firstly, mortar specimens were cast into 40×40×160 mm form and cured for 24 hours prior to removing the form. After demolding, specimens were cured under water for 90 days at temperature of 23±2°C. With regard to the bleeding effect, the mortar surface was removed and the core part was cut into size 70×30×5 mm samples by using a wet saw (see Fig. 5.1). As discussed, the small size was chosen because the mechanical degradation mechanism of mortar due to different NaCl solution exposure and FTCs can be clear in meso-scale. To assure the sample pore solution has the same concentration as designed, specimens were initial dried by putting inside of oven for 24 hours at 105°C to remove evaporable water. The drying method was adopted because it can remove the water totally and has been verified by Sicat et al. (2013) that the drying

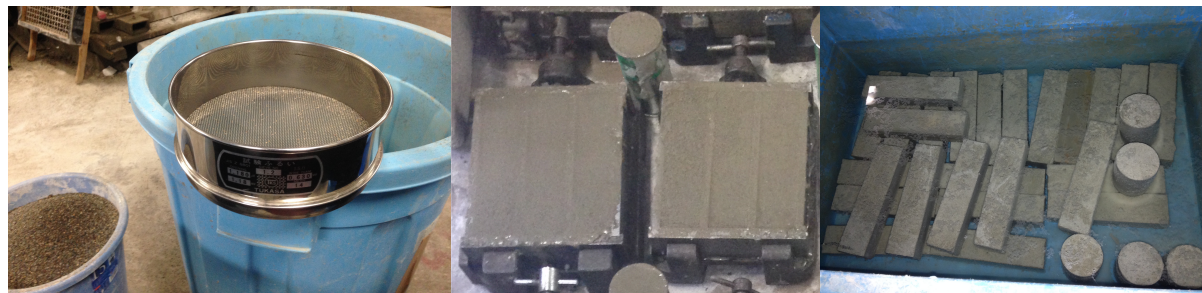
damage is insignificant compared with frost damage. After drying, they were sealed with polyvinylidene chloride plastic (Saran) carefully to prevent moisture transfer until storing them into vacuumed chamber. To get fully saturated samples, the NaCl solutions were first put into vacuum condition for deaeration, after 15 minutes, the mortar samples were immersed into solution and continuously staying in the vacuum condition for another one hour. Then the container with the salt solution and samples was taken out from the desiccator and sealed with its cap. After 7 days, it is assumed that the samples were full saturation and had the same solution concentration with the solution in container (Wang et al. 2016b). When the specimens were fully saturated, they were taken out from the NaCl solution and surface dried with paper towel in a short time. Next, Vinyl/mastic tape was applied for moisture sealing and the Saran was used again between the external sealing and the specimens to prevent damage during unsealing (Sicat et al. 2013). The density and porosity of mortar were measured gravimetrically by immersing samples into deionized (DI) water (Chapter 4). The results are also presented in Table 5.1.

Table 5.1 Mix proportions and properties of mortar

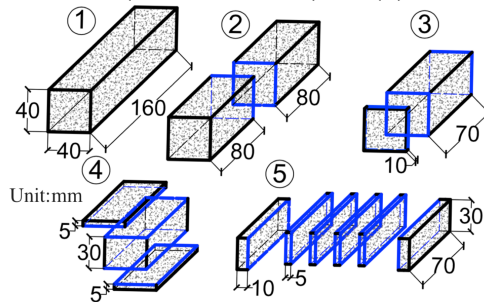
Water/Cement Ratio (w/c)	Water kg/m^3	Cement kg/m^3	Fine aggregate kg/m^3	Bulk dry density (ρ_b) kg/m^3	Skeletal density (ρ_0) kg/m^3	Porosity
0.3	207	690	755	2173	2676	0.188
0.5	207	414	990	2137	2688	0.205
0.7	207	296	1090	2125	2703	0.214

Table 5.2 Physical properties and chemical compositions of cement (OPC)

Physical properties	Specific gravity		Specific surface		Compressive strength (MPa)			
					3d	7d	28d	
	3.16		3350		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



(a) sieving the sand (1.2mm or less) (b) casting the mortar (c) curing under water



(d) cutting procedures



(e) cut specimens 70×30×5 mm

Fig. 5.1 Preparation of specimens

5.2.2 Freeze thaw test

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. 5.2. Since the specimens were sealed, the relative humidity has insignificant effect on the frost damage process, 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 -28°C and remained constant for 100 minutes, and then increased by 0.25°C per minute until the maximum temperature 23°C. After certain repeated FTCs, the specimens were taken out from the environment chamber and kept at room temperature before three-bending test. To understand the effect of NaCl to the mechanical properties of specimens, specimens from all three *w/c* cases were immersed into 0,3,5,10,15 and 20 %wt NaCl solution individually. More importantly, to understand the gradual mechanical degradation due to FTCs, specimens exposed to 0,5,15 and 20 %wt NaCl solution experienced 5,10 and 30 times FTCs, respectively. In addition, for *w/c*=0.5, to have more clear understanding of the frost damage process, specimens experienced 1 and 3 FTCs were tested additionally. There were three samples for each case.

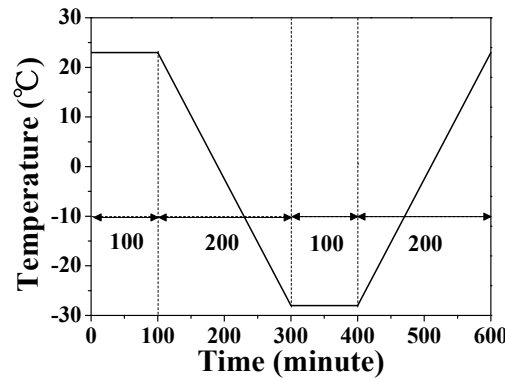


Fig. 5.2 Temperature history of one FTC

5.2.3 Three point bending test

After exposed to NaCl attack and FTCs, the specimens were unsealed. Then they were placed at vacuumed desiccator for three months until testing. As can be seen in Fig. 5.3(a), the bending span was set 50 mm and deflection was measured by LVDTs located at the centre of the specimens and supporting points (Sato et al., 2015). In addition, the loading rate was set as 0.001 mm/sec. Before the testing, the specimen was well labeled. To control the location of crack propagation, notch with 5mm depth were made in the two sides of specimen central cross-section (it becomes 70×20×5mm finally (Fig. 5.3(b))). Based on the test results, the load-deflection curve can be obtained, and then the flexural strength and elastic modulus can be analyzed as well.

The flexural strength (Eq. (5.1)) and elastic modulus (Eq. (5.2)) were calculated based on JCI standard 001 (2003), as following equations

$$\sigma = \frac{3Pl}{2bh^2} \quad (5.1)$$

$$E = \frac{P_{1/3} l^3}{4\delta_{1/3} bh^3} \quad (5.2)$$

where σ is the flexural strength (MPa), E is the elastic modulus (GPa), P is the maximum load in (N), l is the bending span (mm), b is the width and h is the thickness of the specimen (mm). $P_{1/3}$ is the one third of the maximum load (N), $\delta_{1/3}$ is deflection of specimen at one third of maximum load (mm).

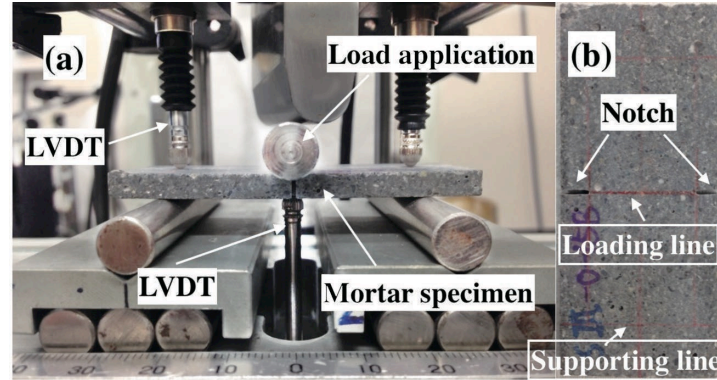


Fig. 5.3 (a) Setup of three-point bending test (b) Notched specimen

5.2.4 Test on Portlandite and Friedel's salt

Since the mechanical deterioration of specimen may involve the chemical phases change, the amount of Portlandite and Friedel's salt are important to clarify the frost damage mechanism with different NaCl concentrations. After three-point bending test, the specimens were crushed into pieces by hammer. Mixing with appropriate amount of acetone, with the aid of a ball mill device, the samples were further grinded into fine powder with size less than $150\mu\text{m}$. They were sealed with plastic bags after sieving. To get dried samples, they were placed in a vacuuming condition for 4 days. Then a vacuumed chamber was applied to store the powder samples until testing.

Although XRD was reported can be used to quantify the content of Friedel's salt (Ishida et al., 2008), thermogravimetry/differential thermal analysis (TG/DTA) test was applied in this study. Because it not only can estimate the amount of Friedel's salt (Csizmadia et al., 2001), but also the amount of Portlandite (Villain et al., 2007; Nguyen et al., 2016). As can be seen in Fig. 5.4, the internal reference material is alumina, the samples were involved in nitrogen atmosphere, the test includes heating and cooling which was program controlled by PC. The heating rate was $10^\circ\text{C}/\text{min}$, from 20 to 900°C . When the temperature cooled to room temperature, the powder sample was taken out and the container was cleaned with 0.1M HCl and ethanol sequentially. Besides, to avoid contamination, the container was kept in ethanol until using.

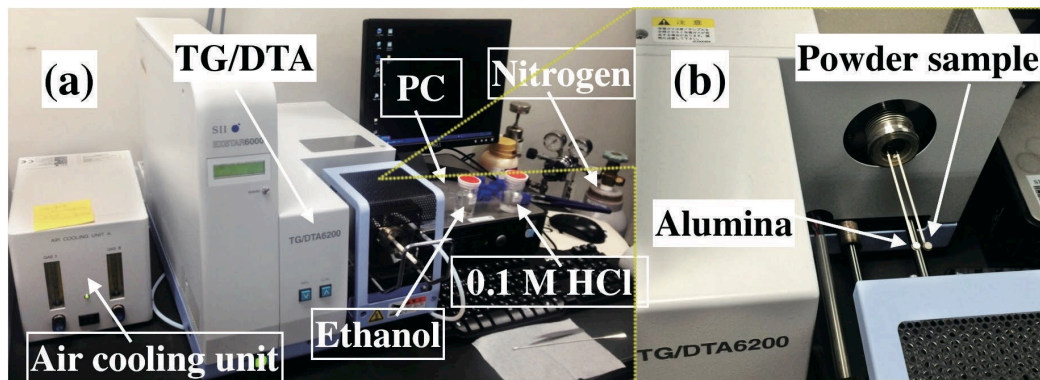


Fig. 5.4 Test setup of TG/DTA

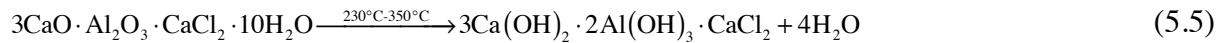
During heating, the mass of the powder sample loses gradually with temperature increase, which can be observed from TGA curve. Once the dehydration of Portlandite occurs, owing to its endothermal nature, a peak may be observed from DTA curve. Because of this phenomenon, Nguyen et al. (2016) calculated the content of Portlandite based on the gross mass loss around the peak. The mass loss of samples can be attributed to the evaporation of dehydrated water, the mass of Portlandite can be obtained by back analysis (see Eqs. (5.3) and (5.4)). However, due to the small amount of Portlandite, the DTA peak may not be observed clearly. It was reported that the DTG is more sensitive than DTA, which can be applied for computing the amount of Portlandite (Csizmadia et al., 2001; Villain et al., 2007). From our test results, the peak of DTA curve is corresponding to the peak of DTG curve when the Portlandite is hydrated at temperature around 370 to 450 °C (see Fig. 5.5(a)). For some test results, even though the peak of DTA is not clear (see Fig. 5.5(b)), the peak can be observed from the DTG curve. Therefore, in this study, the data of TG and DTG were applied together for calculating the amount of Portlandite (see Fig. 5.6). Although Villain et al. (2007) suggested that the mass loss of TG corresponding to DTG peak at temperature around 450°C is the water amount dehydrated from Portlandite, it is clear that the DTG value at the beginning and ending of the peak is not zero and the decrease tendency can also observed from TG curve. It seems that this amount of mass loss is not totally attributed to the loss of water, so it should be excluded from the calculation. Therefore, the following equation was proposed to calculate the amount of Portlandite



$$m_{CH} = \frac{M_{CH}}{M_{H_2O}} \cdot \left(m_{TGb} - m_{TGe} - \left(t \cdot \frac{m_{DTGb} + m_{DTGe}}{2} \right) \right) \quad (5.4)$$

where M_{CH} is molecular mass of calcium hydroxide (g/mol), M_{H_2O} is molecular mass of water (g/mol), m_{TGb} is mass of sample (TG) at the beginning of the peak (%), m_{TGe} is mass of sample (TG) at the ending of the peak (%), t is time range of the calcium hydroxide dehydration (min), m_{DTGb} is mass change ratio of sample (DTG) at the beginning of the peak (%/min) and m_{DTGe} is mass change ratio of sample (DTG) at the ending of the peak (%/min).

According to the study of Birnin-Yauri and Glasser (1998), 10 mol water of Friedel's salt will first lose 4 mol water at temperature around 290°C, and then further losing its 6 mol water at about 670°C. Since the decarbonation also occurs at temperature range 600 to 700°C, it is difficult to calculate the amount of Friedel's salt based on the high temperature range. Besides, it is clear that the dehydration of Friedel's salt caused obvious DTG peak at temperature from 230 to 350°C (see Section 5.3.1.2). Similar to Portlandite calculation, the equation to calculate the amount of Friedel's salt was proposed as below



$$m_{\text{Friedel}} = \frac{M_{\text{Friedel}}}{M_{H_2O}} \cdot \left(m_{TGb} - m_{TGe} - \left(t \cdot \frac{m_{DTGb} + m_{DTGe}}{2} \right) - m_0 \right) \quad (5.6)$$

where M_{Friedel} is molecular mass of Friedel's salt (g/mol) and m_0 is mass loss at the case of DI water.

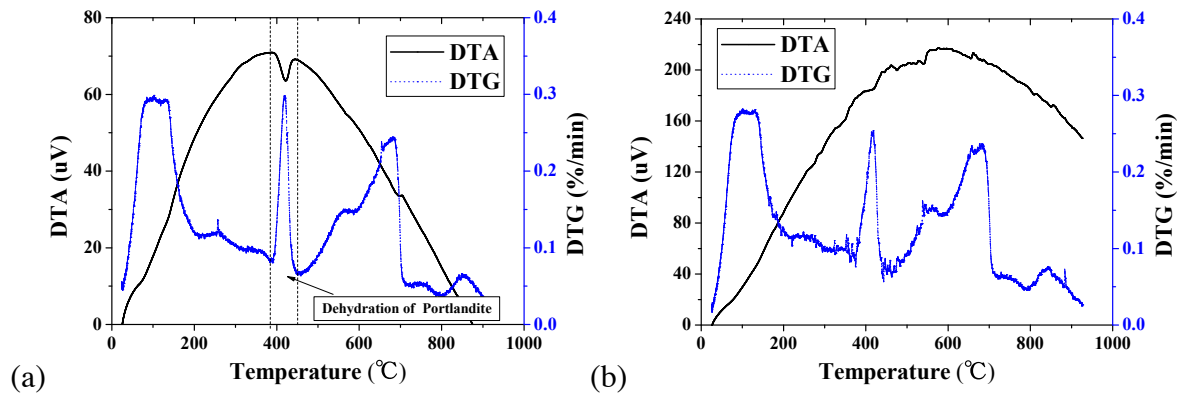


Fig. 5.5 DTG/DTA curve of sample immersed DI water

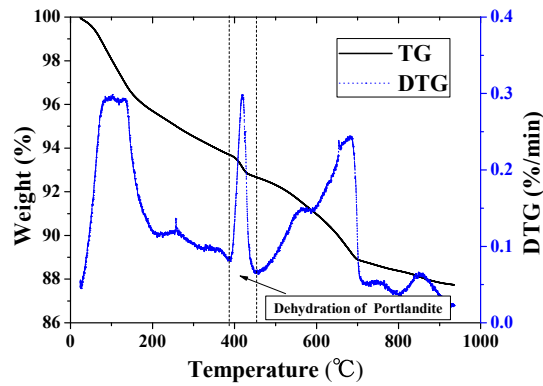


Fig. 5.6 TG/DTA curve of sample immersed DI water

5.3 TEST RESULTS AND DISCUSSIONS

The experimental program includes mechanical and thermal tests. The three point bending test was conducted to understand the mechanical response of mortar samples suffered from the combined effects. After the mechanical test, to further clarify the damage mechanism, the subsequent TG/DTA test was adopted to have chemical analysis.

5.3.1 Degradation of mechanical properties under the combined calcium leaching and salt crystallization

5.3.1.1 Mechanical properties before freeze-thaw cycle

In order to prepare the fully saturated specimens, the specimens have immersed into NaCl solutions for 7 days. During the immersing process, the pore characteristics of specimens could be altered due to calcium leaching and salt crystallization (Chapter 4). As a result, the mechanical properties of specimens could be changed as well.

Table 5.3 Average flexural strength and elastic modulus of samples before FTCs

Concentration (%wt)	Flexural strength (MPa)			Elastic modulus (GPa)		
	w/c=0.3	w/c=0.5	w/c=0.7	w/c=0.3	w/c=0.5	w/c=0.7
0	13.78	9.44	8.59	27.61	19.90	18.61
3	11.68	9.84	7.46	24.69	18.01	14.50
5	12.86	9.70	7.50	25.36	21.11	18.55
10	11.61	9.43	6.92	22.80	19.31	14.04
15	13.78	8.31	8.32	27.16	20.97	17.58
20	11.85	8.55	8.10	26.37	22.15	17.43

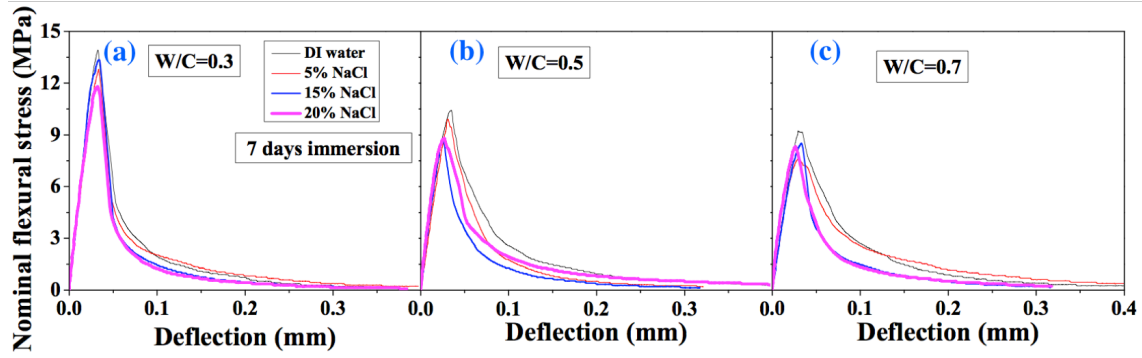


Fig. 5.7 Nominal flexural stress-deflection curve of 7 days immersed specimens

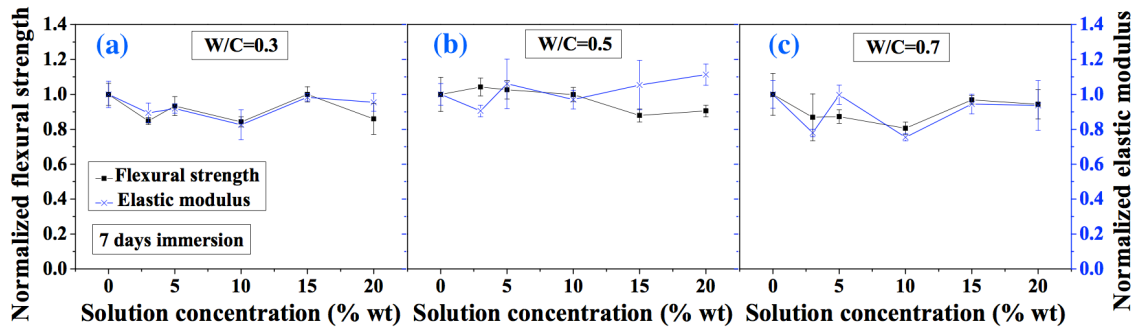


Fig. 5.8 Normalized flexural strength and elastic modulus of 7 days immersed specimens

Once the tensile stress of specimen reached its tensile strength, the crack at tip of the notch generated and propagated with further increase of load until final rupture. The nominal flexural stress (calculated by Eq. (5.1)) was adopted in this study. Since after specimen cracking, the specimen central area would reduce, so the flexural stress calculated by Eq. (5.1) is incorrect, we may call it nominal flexural stress. The nominal flexural stress-deflection curves were presented in Fig. 5.7 for the specimens immersed in 0, 5%, 15% and 20% by weight NaCl solution for seven days. The average flexural strength and elastic modulus of samples before FTCs were summarized in Table 5.3, while normalized flexural strength and elastic modulus (they were normalized with the case of DI water) were presented in Fig. 5.8. As shown in the results, the mechanical properties vary with NaCl solution concentrations. It is clear that the most severe mechanical degradation occurred at 3% and 10% NaCl solution exposed samples. For the specimens with $w/c=0.7$, they were less than 80% compared with DI water case.

5.3.1.2 Calcium hydroxide and Friedel's salt content before freeze-thaw cycles

The characteristic of DTG curve was clarified as Fig. 5.9(a). From 20-200°C, the mass loss is due to the evaporation of interlayer water, and then from 230-350°C, the peak can be explained by dehydration of Friedel's salt. After that, the third peak from 370 to 450°C is due to the dehydration of Portlandite. Next, from 500-700°C, the two peaks were accounted by decarbonisation. Meanwhile, from 500-750°C, further dehydration of Friedel's salt may also occur. As shown in Fig. 5.9, for different w/c specimens, the differential thermogravimetry result is different, especially for the peak at 370-450°C, which means the Portlandite amount varied significant. Another, at temperature range 500-750°C, there were two peaks for the case of DI water while only one peak was observed for the other cases, which is consistent with the report of Villain et al. (2007). In particular, the peak was much higher for the case of $w/c=0.5$, the reason may be due to improper procedure during the preparation of the

specimens. After cutting of the samples, the size of specimen was well measured and the surface of the samples was labeled (see Fig. 5.3 (b)). Since the number of specimens in the case of $w/c=0.5$ was double of others, the preparation process was more time-consuming. As a result, the carbonation was much more severe than the other cases because the specimens were exposed to air at that period.

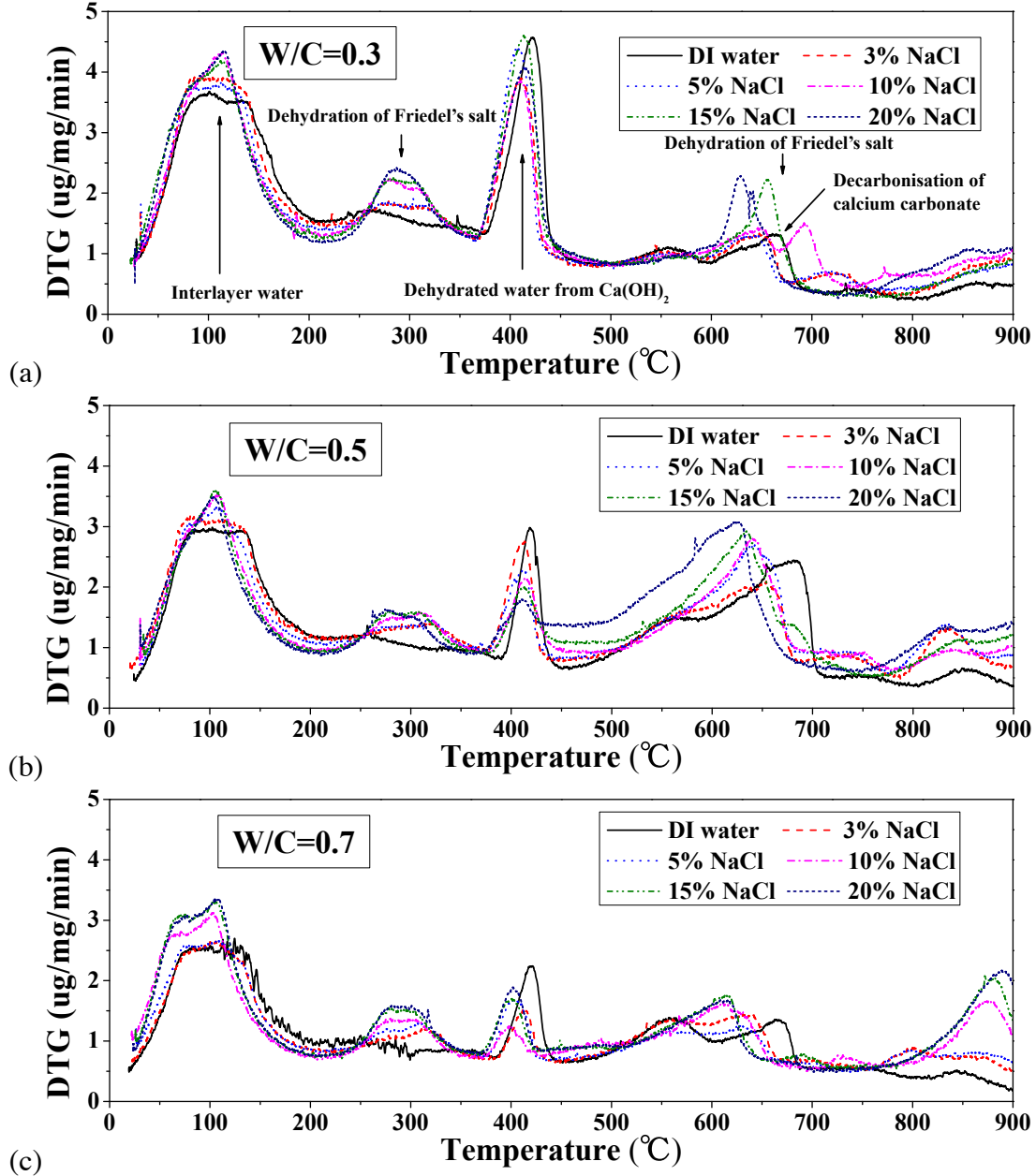


Fig. 5.9 DTG curves of samples immersed with different NaCl solutions (a) $w/c=0.3$ (b) $w/c=0.5$ (c) $w/c=0.7$

Based on Eqs. (5.4) and (5.6), the amount of Portlandite and Friedel's were calculated respectively. The results were shown in Fig. 5.10. While the amount of Friedel's salt was increasing with solution concentration, the amount of Portlandite was fluctuating. The cases of $w/c=0.3$ and 0.7 show the same tendency with regard to Portlandite amount, the difference between them and $w/c=0.5$ could be accounted as the effect of carbonation. In addition,

$w/c=0.5$ and $w/c=0.7$ cases show similar amount of Portlandite, although $w/c=0.5$ is supposed to have more Portlandite.

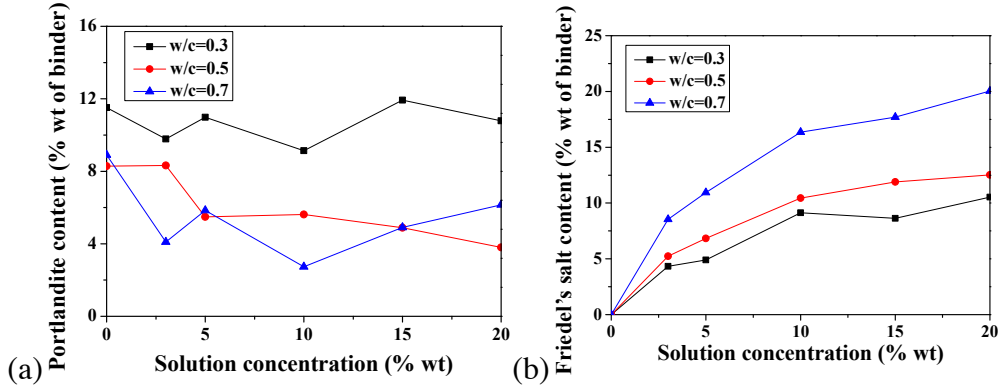


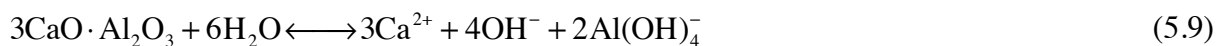
Fig. 5.10 Amount of (a) CH and (b) Friedel's salt variation with solution concentration

5.3.1.3 Damage mechanism of combined calcium leaching and salt crystallization

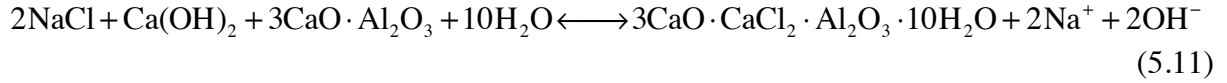
According to the existing study (Wang et al., 2006), exposed to NaCl solutions, the damage of mortar can be attributed to the combined effects of Ca^{2+} leaching and salt crystallization. With low concentration of NaCl solution, the Ca^{2+} leaching process can be accelerated. However, when the NaCl concentration is high, the leaching can be impeded (Chandra and Xu 1992) because of the lower Portlandite solubility. Therefore, there was severe degradation for 3% NaCl solution exposed specimens. As shown in Fig. 5.10 (b), the amount of Friedel's salt increases with increasing of solution concentration, regardless of w/c (Chapter 4). For specimens exposed to 10% NaCl solution, they had the most severe mechanical reduction (see Fig. 5.8) due to the combined leaching and salt crystallization effects except for the case with $w/c=0.5$. The difference may involve the severe carbonation in the case of $w/c=0.5$ because of longer time preparation.

5.3.1.3.1 Briefly review of the Friedel's salt formation mechanism

It is widely described that the chloride ion will physically bond to CSH and chemically react with hydrated products when it penetrates into concrete (Baroghel-Bouny et al., 2012). The Friedel's salt is the major product of the chemical reactions. The precise mechanism has not well understood yet, but the dissolution/precipitation and ionic exchange are generally considered responsible for the Friedel's salt formation (Suryavanshi et al., 1996; Birnin-Yauri and Glasser, 1998 and Jones et al., 2003). This formation process is often assumed instantaneous. The ionic exchange mechanism is the ion exchange between chlorides from the pore solution and sulfate ion from hydrated monosulfoaluminate, whereas the dissolution/precipitation mechanism is usually described as the reactions between sodium chlorides, calcium hydroxide and residual aluminates. With higher chloride concentration of the pore solution, the dissolution/precipitation mechanism plays more important role in Friedel's salt formation (Jones et al., 2003). Therefore, only the dissolution/precipitation mechanism was considered in this study.



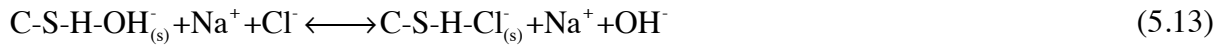
Overall, the mechanism can be expressed as below



Besides, the precipitation process depends on the solubility of Friedel's salt, and the solubility products K_{sp} was defined by (Birnin-Yauri and Glasser, 1998) as

$$K_{sp} = [\text{Ca}]^4 [\text{Al}(\text{OH})_4]^{-2} [\text{Cl}]^2 [\text{OH}]^4 \quad (5.12)$$

With regard to physical binding, it is also related to the ionic exchange, the mechanism is as below (Baroghel-Bouny et al., 2012)



From the above equations, we can see that no matter it is physical or chemical action, once the chloride is bonded, the hydroxide ion will be released. So this process on one hand it will consume the calcium hydroxide, on the other hand, it will reduce the solubility of calcium hydroxide and the kinetics depends on the concentration of chloride ion.

5.3.1.3.2 Solubility of calcium hydroxide in NaCl solutions

The calcium ion leaches out when the samples exposed to water. It is known that the existing of sodium chloride may accelerate the leaching process (Sato et al., 2015), however, this conclusion is based on the dilute sodium chloride solution. For higher concentration of NaCl solution, the leaching process may be impeded because the formation of Friedel's salt can release the hydroxide ion (Baroghel-Bouny et al., 2012; Duchesne and Reardon, 1995). Therefore, the solid-liquid equilibrium curve of calcium in NaCl solutions is essential to understanding the Friedel's salt formation and calcium leaching. According to Buil's et al. (1992) model, the solid-liquid equilibrium calcium can be depicted as three stages. Firstly, it is the rapid decreasing of calcium hydroxide. After the depletion of CH, the decalcification of CSH will occur slowly until the calcium ion concentration reduced to a certain amount. Finally, the remaining of calcium in CSH will leached fast. In cold regions, due to long time of freezing, leaching may be still limited to decalcification of calcium hydroxide, so only the first step is considered in this study. Since the dissolution rate of calcium ion is faster than the diffusion rate (Sugiyama et al., 2008), the calcium ion concentration in pore solution would keep constant and be fully saturated because the dissolution of CH could compensate the loss. The leached amount is determined by the diffusion ratio, which is related to the pore solution concentration. Thus, the solubility of calcium hydroxide is of significant importance.

According to Nakarai et al., (2006), the concentration of saturated calcium ions (c_{satu}) can be calculated from the solubility product (K_{sp}) as

$$c_{satu} = \frac{1}{2} \sqrt[3]{2K_{sp}} \quad (5.14)$$

Correspondingly, the solubility product is related to the concentration of calcium ion

$$K_{sp} = 4c_{satu}^3 \quad (5.15)$$

According to Thomas et al., (2003), with regard to the temperature effect, it may be described as the Arrhenius's equation

$$K_{sp,T} = K_{sp,ref} e^{\left[\frac{\Delta H_r}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right]} \quad (5.16)$$

where ΔH_r is a constant associated with each ion, for Portlandite, it is -17.88 (kJ/mol) (Parkhurst, 1995), R_g is the universal gas constant (8.314 J/mol/K), T_{ref} is the reference temperature (298.14K in this study) and T is temperature (K)

Combing Eqs. (5.14)-(5.16), the concentration of saturated calcium ion at temperature T is

$$c_{satu} = c_{satu,ref} \sqrt[3]{e^{\left[\frac{\Delta H_r}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right]}} \quad (5.17)$$

where $c_{satu,ref}$ is the concentration of saturated calcium ion at reference temperature.

In addition, when the calcium hydroxide mixed with NaCl solution, the solubility will vary with the concentrations of NaCl solutions. By regressing the data from (Duchesne and Reardon, 1995), the following equation can be obtained to calculate the concentration of calcium hydroxide based on sodium chloride concentration

$$c_{satu} = -3.211 \times 10^{-4} c_{Cl}^4 + 3.47 \times 10^{-3} c_{Cl}^3 - 1.351 \times 10^{-2} c_{Cl}^2 + 1.958 \times 10^{-2} c_{Cl} + 2.051 \times 10^{-2} \quad (5.18)$$

where c_{Cl} is the concentration of sodium chloride (mol/L).

So combined with temperature and NaCl effect, the full saturated calcium ion concentration is

$$c_{satu} = \left(-3.211 \times 10^{-4} c_{Cl}^4 + 3.47 \times 10^{-3} c_{Cl}^3 - 1.351 \times 10^{-2} c_{Cl}^2 + 1.958 \times 10^{-2} c_{Cl} + 2.051 \times 10^{-2} \right) \sqrt[3]{e^{\left[\frac{\Delta H_r}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right]}} \quad (5.19)$$

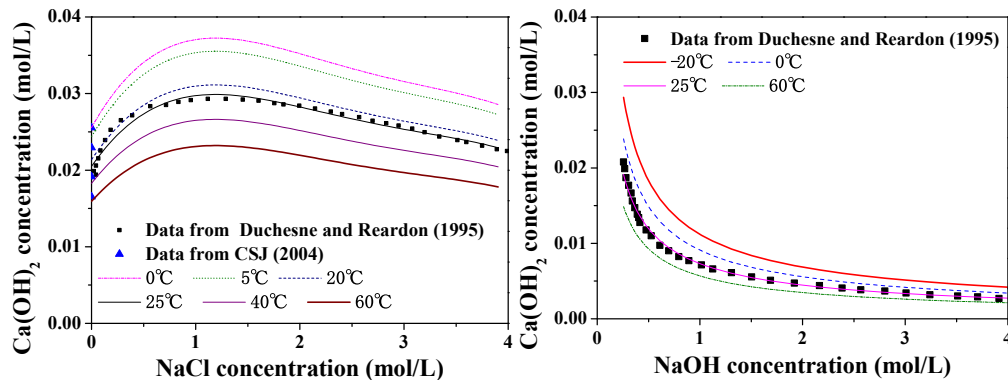


Fig. 5.11 Solubility of Portlandite in (a)NaCl solutions and (b) NaOH solutions

However, the existing of sodium hydroxide can also change the solubility of Portlandite dramatically. Since the formation of Friedel's salt will release the sodium hydroxide (Suryavanshi et al., 1996; Baroghel-Bouny et al., 2012), the concentration of hydroxide ion should be taken into consideration. From Eq. (5.11) and (5.13), one mole of sodium hydroxide can be released if one mole of chloride ion binds to hydrated products. As it was depicted in Baroghel-Bouny et al.(2012), the formation of Friedel's salt can be regarded to instantaneous, whereas the physical chloride adsorption is time dependent. Because the

specimens immersed into solutions for one week, only the formation of Friedel's salt was discussed. The following equation was regressed from the data provided in (Duchesne and Reardon, 1995)

$$c_{sat} = (0.0073c_{OH}^{-0.709}) \sqrt[3]{e^{\left[\frac{\Delta H_f}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right]}} \quad (5.20)$$

where c_{OH} is the concentration of sodium hydroxide (mol/L)

The solubility of Portlandite change with NaCl concentration and NaOH concentration is presented in Fig. 5.11, while the variation with temperature is presented in Fig. 5.12.

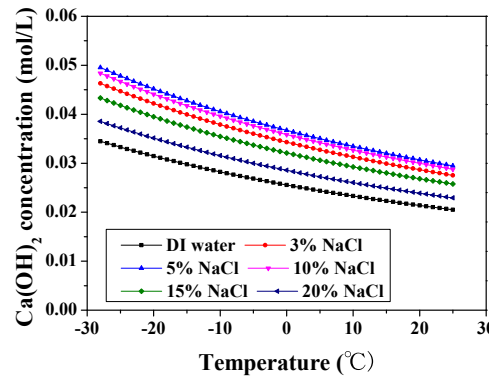


Fig. 5.12 Solubility of Portlandite in NaCl solutions change with temperatures

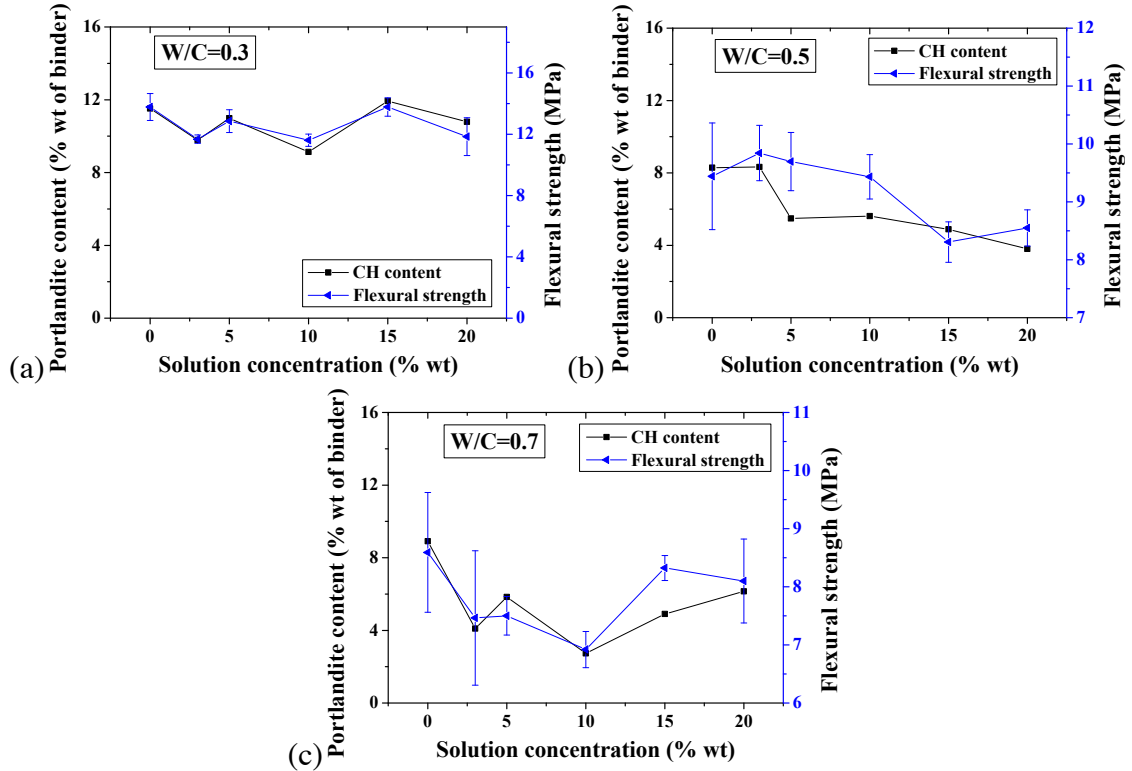


Fig. 5.13 Relationship of CH content and flexural strength

5.3.1.3.3 Mechanical properties change by combined calcium leaching and salt crystallization

The relationship between flexural strength, Portlandite content and NaCl solution concentration was shown in Fig. 5.13. It is obvious that the Portlandite content variation agrees satisfactory for $w/c=0.3$ and 0.7, especially for low salt concentration cases. As to $w/c=0.5$, acceptable agreement was observed, the different tendency could be attributed to severe carbonation. Therefore, the mechanical properties change is dominant by Ca^{2+} leaching. It is worth to note that the CH is the main contributor of mechanical performance for the case of $w/c=0.3$, while the CSH is more important for higher w/c . As shown in Fig. 5.13, for the case of $w/c=0.3$, the flexural strength is corresponding to the amount of CH, while for the other cases, the flexural strength is not change from zero with CH. It means that larger part of strength is attributed to CSH in these cases since total amount of CH and CSH generally can represent mechanical property of cement paste. Besides, the salt crystallization only contributes slightly at high concentration solution cases. Because of the crystallized Friedel's salt filling the pores, the strength and stiffness increased slightly, however, it reduced the mechanical properties with the concentration increases due to higher expansive pressure. The positive effect is more obvious in higher w/c case.

5.3.2 Degradation of mechanical properties under the combined ice formation and salt crystallization

5.3.2.1 Mechanical properties after freeze-thaw cycles

After FTCs, the mechanical properties will have further degradation due to the frost damage. The nominal flexural stress-deflection curves are presented in Fig. 5.14 ($w/c=0.3$) and Fig. 5.15 ($w/c=0.7$) for the specimens saturated with 0, 5%, 15% and 20% by weight NaCl solution suffered from 0, 5, 10 and 30 FTCs. Comparing the two cases, the reason of different change of their mechanical properties may be clarified. For the case of $w/c=0.3$, it is less porous than the case of $w/c=0.7$. Therefore, it has higher flexural strength and elastic modulus. The internal pressure may not be big enough to exceed its tensile strength to cause cracks. Interestingly, although the case of $w/c=0.3$ has no obvious difference at elastic region, the softening curve seems various. On the contrary, for the case of $w/c=0.7$, there is a good agreement for the final large deflection stage.

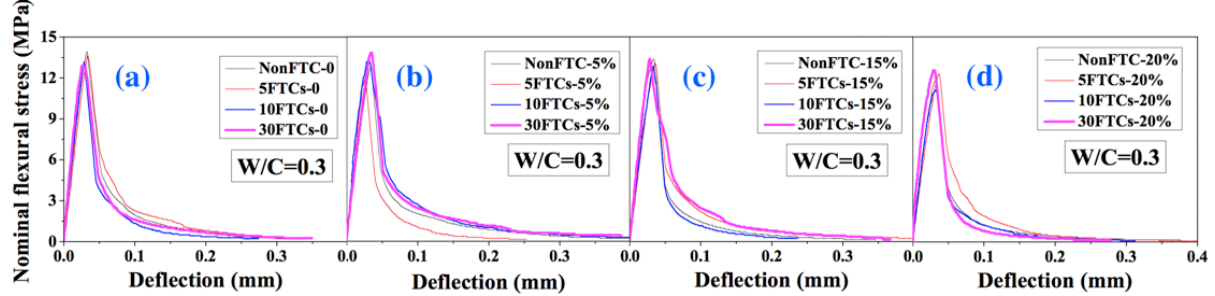


Fig. 5.14 Nominal flexural stress-deflection curve with FTCs ($w/c=0.3$)

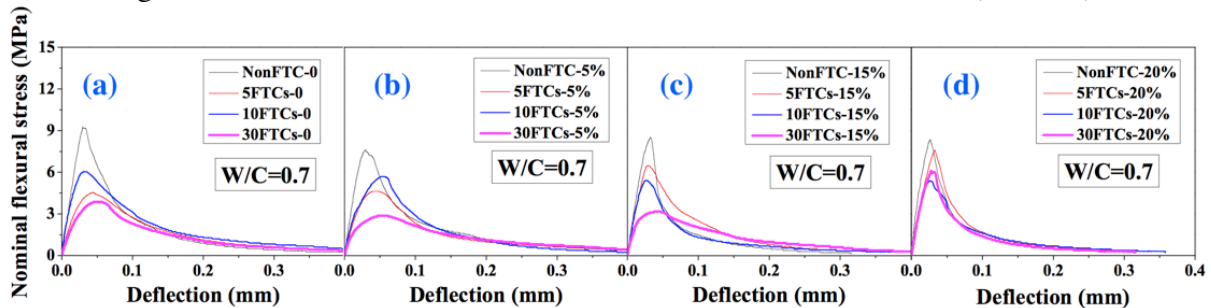


Fig. 5.15 Nominal flexural stress-deflection curve with FTCs ($w/c=0.7$)

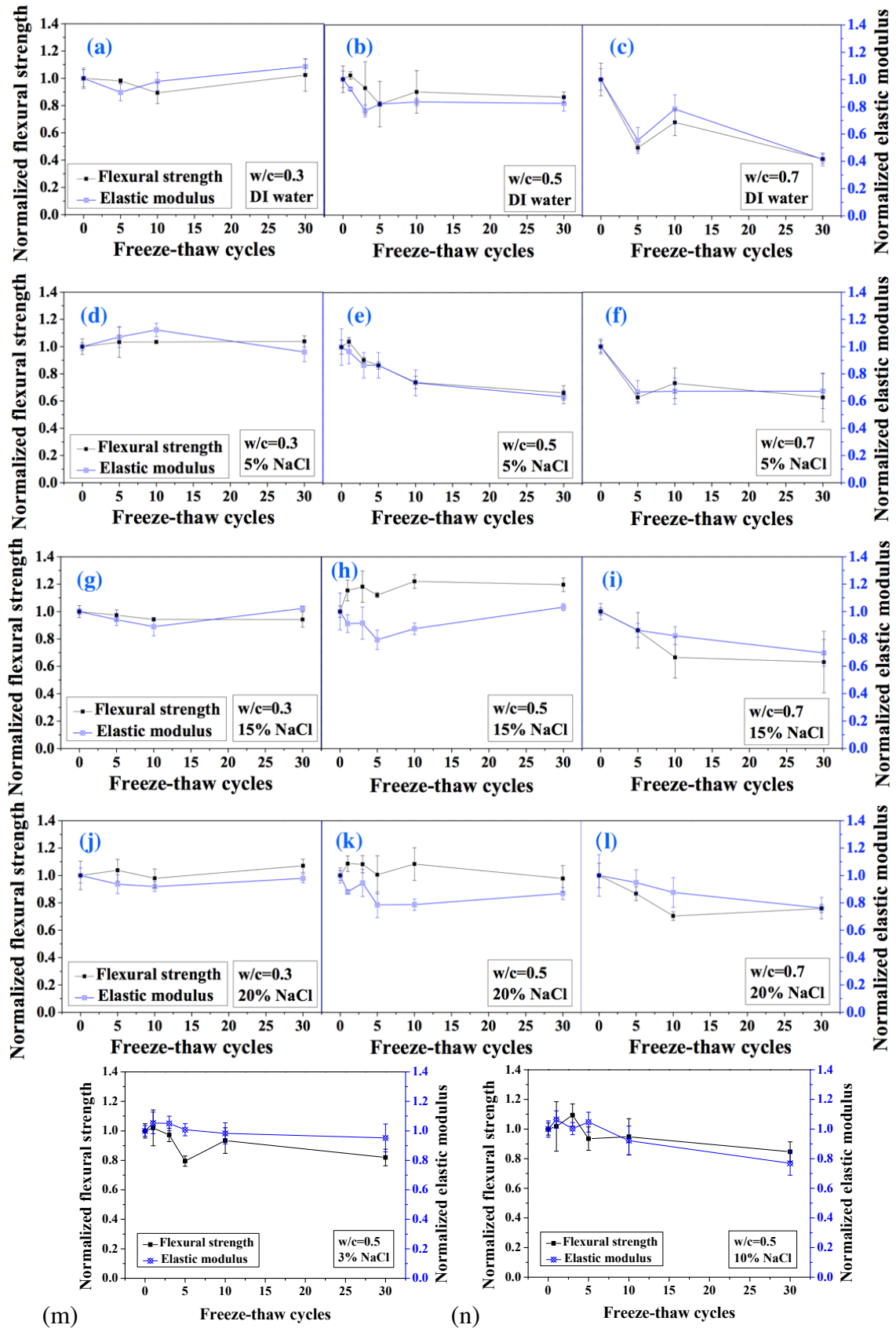


Fig. 5.16 Normalized flexural strength and elastic modulus change with FTCs

To evaluate the effect of FTCs, for each w/c specimens, the normalized flexural strength and elastic modulus with FTCs were presented in Fig. 5.16. For specimens exposed to each concentration NaCl solution, they were normalized to the values with Non-FTCs condition. As shown in Fig. 5.16, suffered from FTCs, the mechanical properties of specimens had further degradation after salt damage. For specimens with $w/c=0.3$, there was no obvious mechanical degradation can be observed for the samples exposed to different concentration of NaCl solutions. However, for the specimens with $w/c=0.5$ and 0.7 , the reduction of flexural strength and elastic modulus were significant, especially for specimens exposed to 5% NaCl solution. With higher w/c , the degradation was more severe because the specimen was more porous which could induce higher pore pressures and it has less strength and stiffness. As shown in Fig. 5.16 (e), the mechanical deterioration of specimens could be progressive. During freezing and thawing, ice and salt expansion in specimens cause residual strains and microcracks, which increase the pore size. Besides, the bigger pores can promote the ice formation and salt crystallization, because it has higher freezing point and the pore solution concentration can be increased after freezing. As a result, the damage can further develop if the space is not big enough to release the pore pressures.

In particular, for the specimens with $w/c=0.7$ exposed to higher concentration of NaCl solution, the mechanical property reduction with FTCs was also significant. With regard to the salt effect, in this case, the damage cause is not likely to be the ice formation alone because the amount of ice content is not enough to cause damage (Zeng et al., 2014). Besides, since there was enough space for the salt crystallization to occur, the pressures induced by the salt crystallization could be destructive. Under FTCs, it is known that the solubility of calcium hydroxide increases with lowering temperature, so the chemical equilibrium will be unachievable at low temperature and the Friedel's salt may form and resolve with FTCs. On the contrary, for the specimens with $w/c=0.7$ exposed to DI water, after first five cycles, the degree of frost damage was almost constant since the specimens were in sealed condition. As there was no further water supply, after frost damage, the expansive pressure due to ice formation could be released because the pore size become big enough.

However, it is worthy to mention that, there was different tendency for flexural strength and elastic modulus in Fig. 5.16 (h, k). The phenomenon appeared in specimens exposed to high concentration with $w/c=0.5$. At the first three cycles, the flexural strength increases with FTCs while the elastic modulus decreases until five cycles. In addition, the flexural strength showing larger degradation than elastic modulus was observed in the case of $w/c=0.7$, but the difference was not significant. The reason may be due to salt crystallization and carbonation, which still needs further investigation.

5.3.2.2 Calcium hydroxide and Friedel's salt content after freeze-thaw cycles

The DTG curve of samples suffered from the FTCs and different NaCl solutions are presented in Fig. 5.17. The results are very different for each w/c and salt concentration, however, there is no significant change for the reason of FTCs. As shown, the degree of carbonation, dehydration of CH and dehydration of Friedel's salt can be compared qualitatively. Among the peaks, the peak of $w/c=0.3$ cases reached the highest as dehydration of CH, regardless of solution concentration. For the same concentration, the peak due to dehydration of Friedel's salt reduces with increasing of w/c . In addition, obviously, the $w/c=0.5$ case is the most severe in terms of carbonation. Based on the data, the amount of CH and Friedel's salt are shown in Fig. 5.18 for each w/c case, the value is normalized with the nonFTCs case. No obvious chemical reactions were observed in the case of $w/c=0.3$ and 0.7 . It implies that there is almost no CH was consumed due to the formation of Friedel's salt with FTCs. Since Friedel's salt is a relatively stable material, the formation could be irreversible in this temperature range. So the contribution of salt to the damage is due to precipitation of

NaCl crystal instead of formation of Friedel's salt. Because severe damage was observed in the case of high concentration of NaCl solution immersed specimens. Another, the reduction of CH and increase of Friedel's salt were shown in the case of $w/c=0.3$ with 15% NaCl solution, which means that the salt crystallization is still possible to occur for specimen with affluent CH and NaCl. Also, irregular change of CH and Friedel's salt amount can be found in the case of $w/c=0.5$. It indicates that the carbonation can largely influence on the chemical reactions of mortar with chlorides.

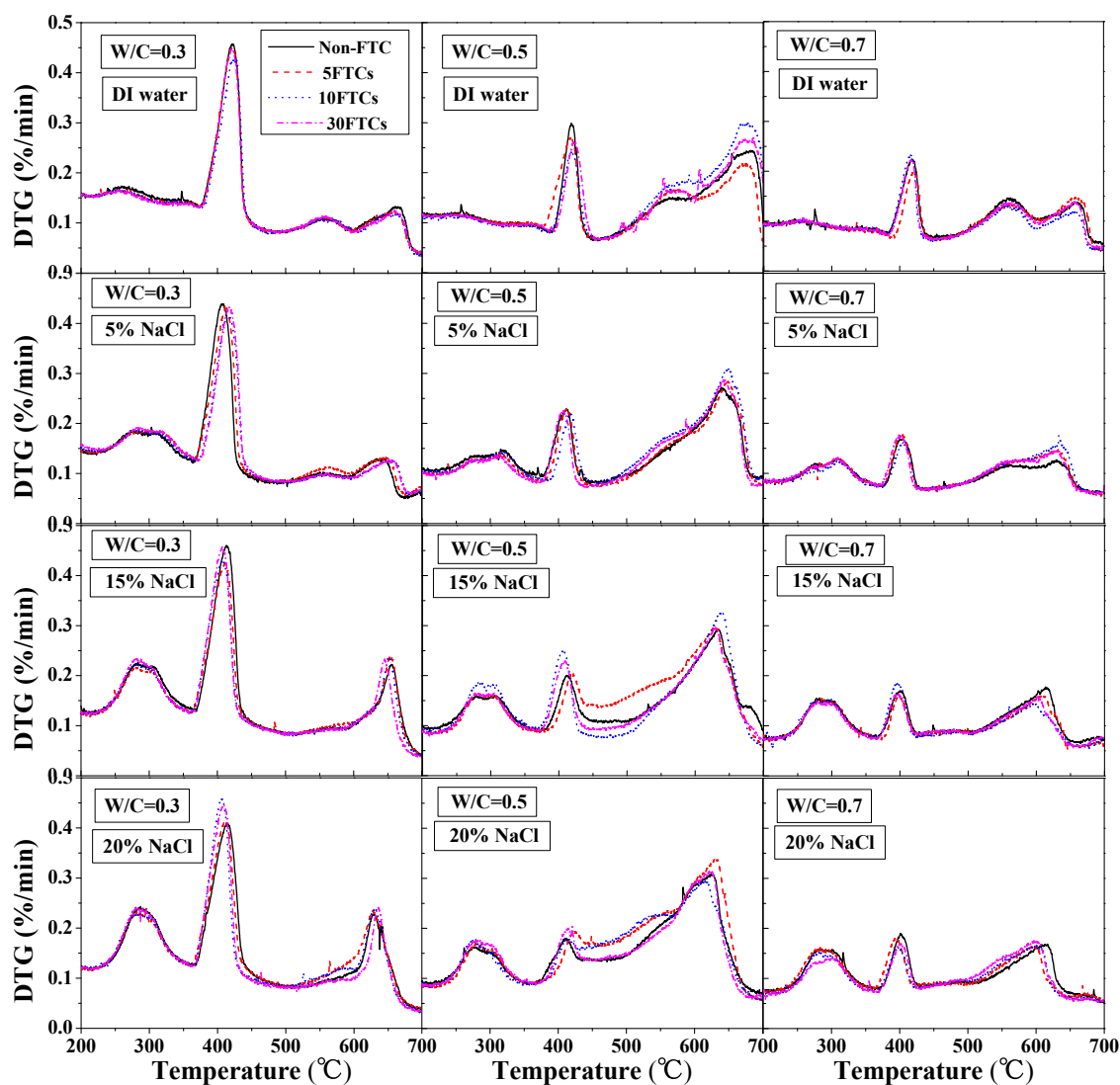


Fig. 5.17 DTG curves of samples suffered from FTCs and NaCl attack

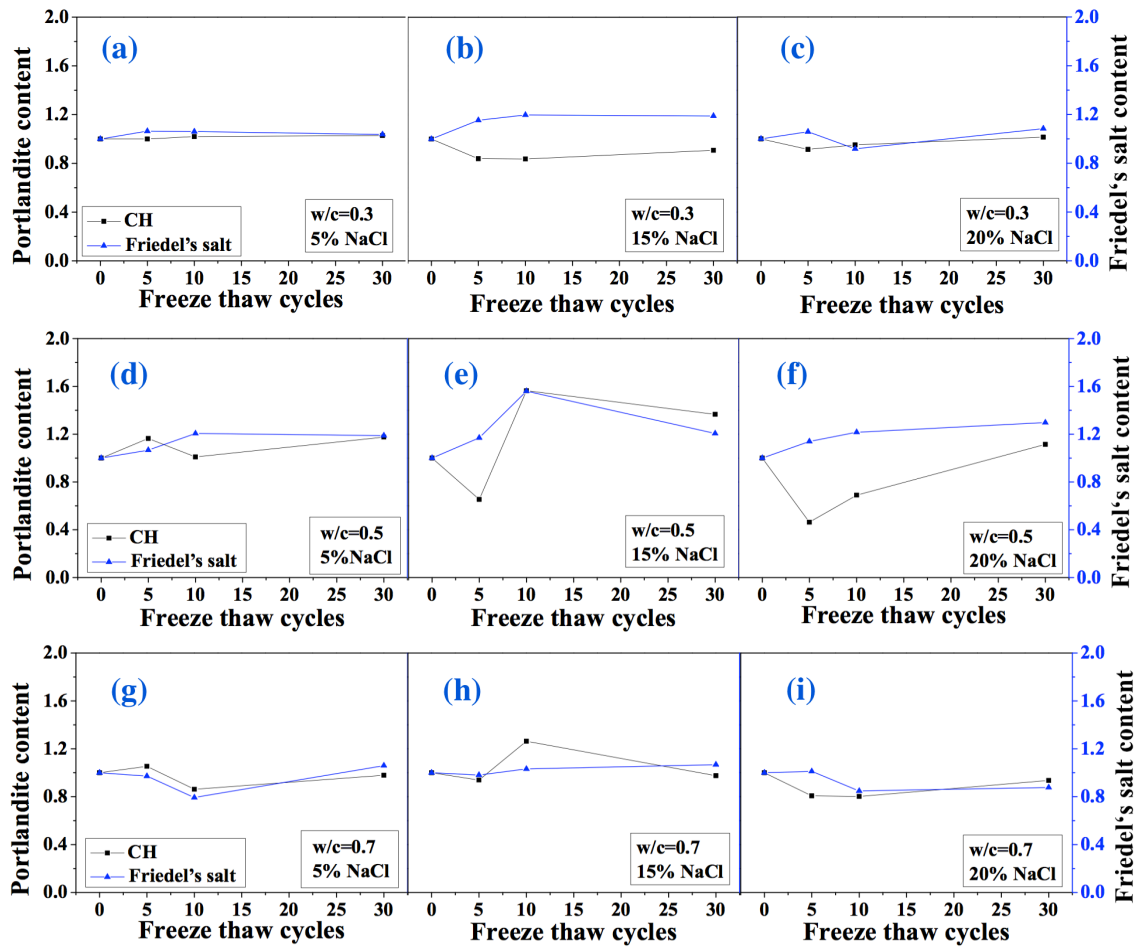


Fig. 5.18 Amount of CH and Friedel's salt variation with FTCs

5.3.2.3 Damage mechanism of combined ice formation and salt crystallization

From the meso-scale experimental results, one can conclude that the salt frost damage is due to the combined ice formation and salt crystallization. For each layer of concrete, the damage mechanism is different due to the difference in pore solution concentration and it is mainly due to the physical transformation instead of chemical reaction. Although no significant chemical component change with FTCs could be observed, but the mechanical properties reduced dramatically in the case of $w/c = 0.7$, regardless of solution concentration. So the precipitation of NaCl crystal rather than consumption of calcium hydroxide could be the reason. For intermediate concentration solution immersed specimens, the salt frost damage is the most severe because they contain almost the same level of water amount and have the extra contribution from salt crystallization, as it was reported in (Chapter 4). Compared with the cases of DI water and 20% NaCl, the pore pressures caused by ice formation is larger by salt crystallization since the samples saturated with DI water deteriorated more significantly with FTCs. Normally, the precipitation of NaCl has no relation with solution concentration, but could be affected by pore size since the eutectic point of NaCl in cement paste was observed to be around -25°C (Litvan, 1976) rather than -21.1°C in the air. Similar to the freezing point change with pore size, the eutectic point can be change as in Fig. 5.19. Considering the empirical pore size distribution model proposed by Gong et al. (2014), the normalized volume of pores reached eutectic point can be calculated as shown in Fig. 5.20, which is much larger than the ice volume (no consideration of salt

crystallization) estimated from Chapter 3. Therefore, theoretically, the sudden crystallization is enough to induce damage.

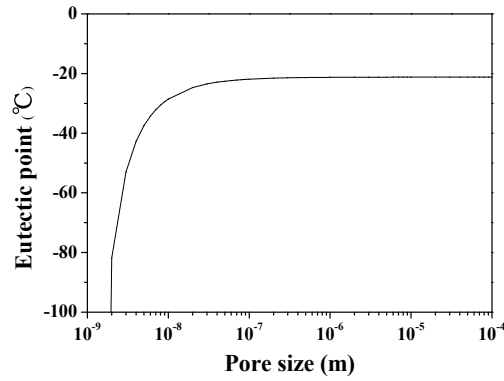


Fig. 5.19 Eutectic point of NaCl change with pore size

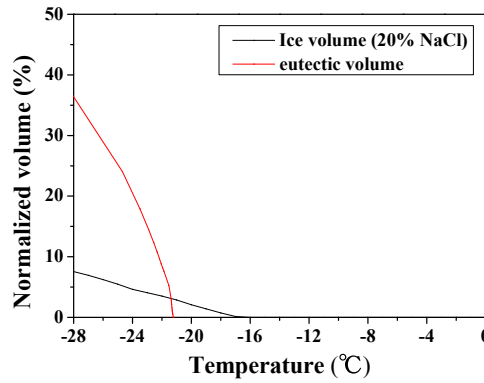


Fig. 5.20 Normalized volume of pores reached eutectic point and the corresponding ice volume ($w/c=0.5$)

5.4 PREDICTION MODEL OF MECHANICAL BEHAVIOR OF MORTAR UNDER FTCS AND NACL ATTACK

5.4.1 Prediction model for mechanical deterioration before FTCS

Before FTCS, the mechanical behavior of specimen was dominated by the amount of Portlandite. As described in section 5.3.1, the specimen's Portlandite amount varied with NaCl concentration due to leaching degree. By regressing the experimental results, for different w/c , the prediction model can be summarized as below

$$\frac{\sigma}{\sigma_0} = a_1 \frac{CH}{CH_0} + a_2 \quad (5.21)$$

$$\frac{E}{E_0} = b_1 \frac{CH}{CH_0} + b_2 \quad (5.22)$$

where σ/σ_0 and E/E_0 are normalized flexural strength and elastic modulus, respectively. CH/CH_0 is the normalized Portlandite amount. a_1 , a_2 , b_1 , b_2 are the fitting parameters for flexural strength and elastic modulus prediction model before FTCS, as presented in Table 5.4.

Table 5.4 Fitting parameters for flexural strength and elastic modulus prediction model before FTCs

Water to cement ratio (w/c)	Flexural strength			Elastic modulus		
	a_1	a_2	R^2	b_1	b_2	R^2
0.3	0.722	0.244	0.79	0.659	0.317	0.88
0.5	0.212	0.82	0.5	-0.269	1.214	0.66
0.7	0.253	0.755	0.67	0.38	0.67	0.69

Besides, the Portlandite amount change tendency with NaCl solution concentration can also be predicted as following

$$\frac{CH}{CH_0} = 0.117 \sin \left[\pi \cdot (c_{NaCl} - 4.617) / 3.84 \right] + 0.932 \quad (w/c=0.3, R^2=0.95) \quad (5.23)$$

$$\frac{CH}{CH_0} = 0.979 e^{-0.037 c_{NaCl}} \quad (w/c=0.5, R^2=0.84) \quad (5.24)$$

$$\frac{CH}{CH_0} = 0.361 \sin \left[\pi \cdot (c_{NaCl} + 0.723) / 2.97 \right] + 0.726 \quad (w/c=0.7, R^2=0.92) \quad (5.25)$$

where c_{NaCl} is the concentration of NaCl solution.

In this case, by substituting Eqs. (5.23)-(5.25) into Eq. (5.21) and (5.22), the flexural strength and elastic modulus can be evaluated based on the solution concentration directly. As shown in Fig. 5.21 and 5.22, the experimental and predicted values have an acceptable agreement.

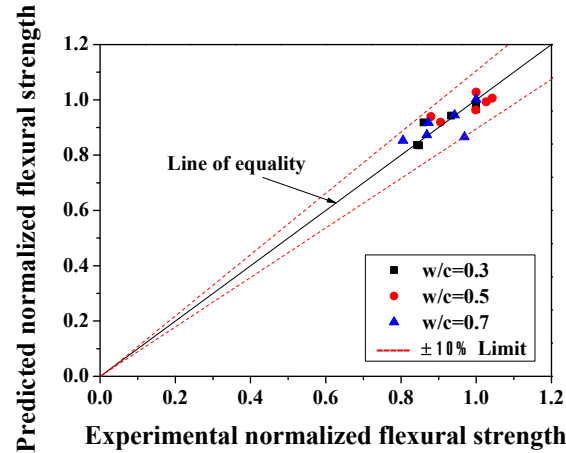


Fig. 5.21 Experimental and predicted normalized flexural strength before FTCs

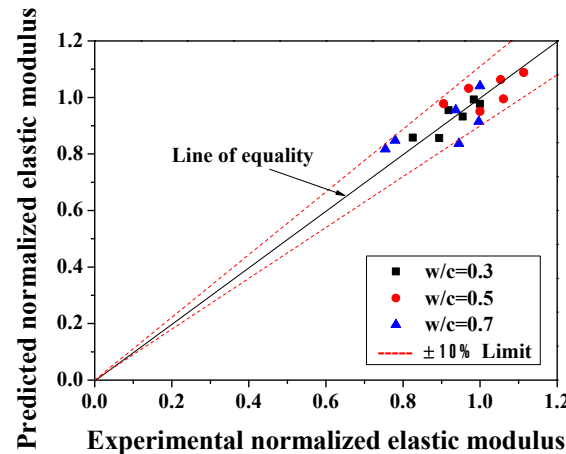


Fig. 5.22 Experimental and predicted normalized elastic modulus before FTCs

5.4.2 Prediction model for mechanical deterioration after FTCs

After FTCs, the mechanical performance of mortar specimen degraded. It seems that the damage level changes with the increase of FTCs gradually. As a result, the flexural strength and elastic modulus change can be predicted based on the following equations

$$\frac{\sigma}{\sigma_0} = c_1 N^2 + c_2 N + c_3 \quad (5.26)$$

$$\frac{E}{E_0} = d_1 N^2 + d_2 N + d_3 \quad (5.27)$$

where N is the number of FTCs, $c_1, c_2, c_3, d_1, d_2, d_3$ are the fitting parameters for flexural strength and elastic modulus prediction model under FTCs. For different w/c , the fitting parameters from regressing the experimental data were shown in Tables 6. 5 to 7, respectively.

After obtaining these fitting parameters, the mechanical performance of specimens under FTCs can be predicted quantitatively. As shown in Fig. 5.23 and 5.24, the comparison between experimental and predicted flexural strength and elastic modulus agreed acceptable.

Table 5.5 Fitting parameters for flexural strength and elastic modulus prediction model under FTCs ($w/c=0.3$)

Concentration (%wt)	Flexural strength				Elastic modulus			
	c_1	c_2	c_3	R^2	d_1	d_2	d_3	R^2
0	0.0005	-0.015	1.0128	0.85	0.0004	-0.007	0.9774	0.75
5	-0.0001	0.0048	1.0034	0.89	-0.0007	0.0189	0.9979	0.99
15	0.0002	-0.008	1.0019	0.99	0.0006	-0.0166	1.0027	0.99
20	0.0002	-0.003	1.0145	0.62	0.0004	-0.0122	0.9965	0.97

Table 5.6 Fitting parameters for flexural strength and elastic modulus prediction model under FTCs ($w/c=0.5$)

Concentration (%wt)	Flexural strength				Elastic modulus			
	c_1	c_2	c_3	R^2	d_1	d_2	d_3	R^2
0	0.0005	-0.02	1	0.51	0.0006	-0.0219	0.9352	0.47
3	0.0004	-0.017	0.9817	0.44	9E-05	-0.0054	1.0342	0.61
5	0.0008	-0.037	1.03	0.97	0.0007	-0.0325	0.992	0.98
10	6E-05	-0.008	1.0344	0.68	-2E-05	-0.0086	1.0411	0.89
15	-0.0006	0.0208	1.0647	0.58	0.0008	-0.0205	0.9557	0.7
20	-0.0003	0.0059	1.032	0.44	0.0008	-0.028	0.9636	0.67

Table 5.7 Fitting parameters for flexural strength and elastic modulus prediction model under FTCs ($w/c=0.7$)

Concentration (%wt)	Flexural strength				Elastic modulus			
	c_1	c_2	c_3	R^2	d_1	d_2	d_3	R^2
0	0.0012	-0.047	0.9137	0.58	0.0005	-0.0311	0.9109	0.64
5	0.001	-0.04	0.9413	0.67	0.0013	-0.0472	0.9621	0.84
15	0.001	-0.043	1.0149	0.98	0.0004	-0.0225	0.9896	0.98
20	0.001	-0.039	1.0112	0.98	0.0002	-0.0143	1.0042	0.99

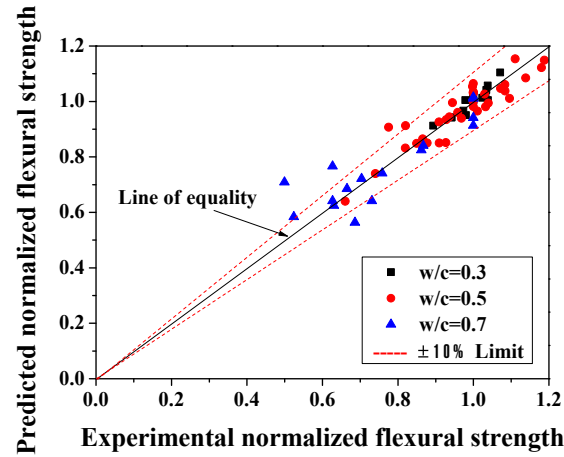


Fig. 5.23 Experimental and predicted normalized flexural strength after FTCs

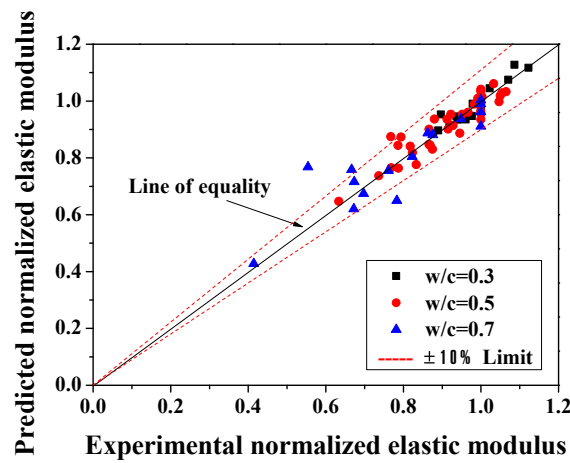


Fig. 5.24 Experimental and predicted normalized elastic modulus after FTCs

5.5 MECHANICAL EVALUATION MODEL BASED ON ELECTRICAL MEASUREMENTS

5.5.1 Theoretical model for the damage index

There are four kinds of water types in concrete. They are bulk capillary water, chemically combined water (a part of the gel), adsorbed water (about four molecules thick) and interlayer water (one molecule thick) (McCarter and Garvin, 1989). For the four parts, bulk capillary water and adsorbed water are considered as evaporable water while only the bulk capillary water can affect the resistivity of concrete significantly (Tashiro et al., 1987), as shown in Fig. 5.25. In addition, the adsorbed water was considered as semi-conductive, it also needs to concern when the saturation degree is low (Li et al., 2016). Li et al. (2016) believe that the electrical conductivity of pore solution equals to the sum of surface conductivity and electrical conductivity of bulk solution.

During the freezing, due to the ice formation, the micro cracks and cracks could be induced. As a result, the specific surface of pores increases. As shown in Fig. 5.25 (b), due to the characteristics of solid-liquid interface (physical interactions), the bulk water would move to the surface of pores to fulfill the adsorbed water layer first (Zeng et al., 2014). Therefore, the actual bulk water content would decrease. With this regard, the electrical resistivity of pore solution would increase because the adsorbed water is not as conductive as bulk water (Li et al., 2016). However, after the FTCs, the porosity and connectivity increase due to the

frost damage, which can decrease the electrical resistivity. Thus, the electrical resistivity change with FTCs is independent of porosity and damage degree of specimens.

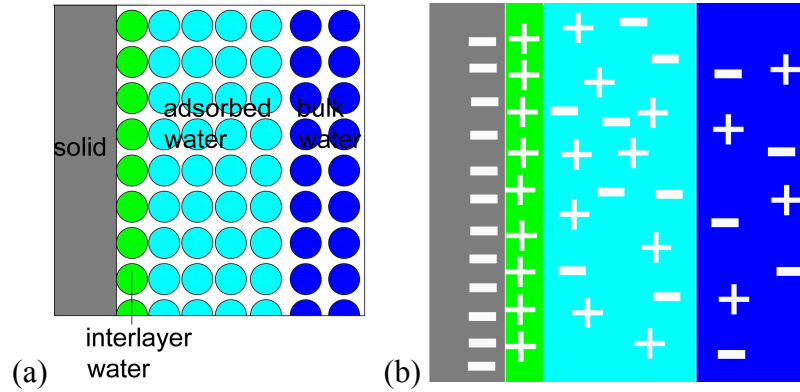


Fig. 5.25 the characteristic of solid-liquid interface (a) double layer water of solid-liquid interface (b) electrical behavior of solid-liquid interface (McCarter and Garvin, 1989)

5.5.1.1 Electrical resistivity at reference temperature

For fully saturated samples, before exposed to FTCs, the electrical conductivity of sample is determined by the electrical conductivity of pore solution and formation parameter (Weiss et al., 2012; Merioua et al., 2015), as below

$$\sigma_{ref,s,0} = \sigma_{ref,pore,0} / F_0 = \sigma_{ref,pore,0} \cdot \phi_0 \cdot \beta_0 = \sigma_{ref,pore,0} \cdot \phi_0^m \quad (5.28)$$

where $\sigma_{ref,s,0}$ is the electrical conductivity of sample before FTCs, $\sigma_{ref,pore,0}$ is the electrical conductivity of pore solution before FTCs, F_0 is the formation parameter before FTCs, ϕ_0 and β_0 are the porosity and connectivity of sample before FTCs, and m is a fitting parameter. Since the formation parameter is the reciprocal of porosity and connectivity of the sample and there is intrinsic relationship between porosity and connectivity. According to Archie's law (Archie, 1942), the formation parameter can be replaced by the porosity with power law. From Merioua et al. (2015), for mortar with $w/c=0.5$, m is about 3.

After frost damage, the porosity and connectivity increase, the degree of saturation would decrease, so the electrical conductivity of samples may increase as well. Therefore, the electrical resistivity change due to saturation should be excluded. Because of the increasing of porosity, the saturation degree of samples (S) decreases to

$$S = \frac{\phi_0}{\phi_a} \quad (5.29)$$

where ϕ_a is the porosity after frost damage and ϕ_0 is the original porosity of specimen.

The water saturation degree can affect the electrical resistivity significantly (McCarter and Garvin, 1989), and the relationship could be written as

$$\frac{\sigma_{ref,p,0}}{\sigma_{ref,s,0}} = S^{n_0} \quad (5.30)$$

$$\frac{\sigma_{ref,p,0}}{\sigma_{ref,pore,0}} = \frac{1}{F_0} S^{n_0} = \phi_0^m \cdot S^{n_0} = (\phi_0 S)^m \quad (5.31)$$

where n_0 is the saturation coefficient before FTCs (for mortar sample with $w/c=0.5$, n_0 approximately equals to 3.5 (Weiss et al., 2012)), which is determined by the porosity, connectivity and chemical composition of pore solution of sample. From Eq. (5.31), the m is equal to n_0 .

After the FTCs, by combine the Eqs. (5.28), (5.29) and (5.30), the measured electrical conductivity of sample is

$$\sigma_{ref,a} = \sigma_{ref,p,a} = \sigma_{ref,s,a} \cdot S^{n_a} = \sigma_{ref,pore,a} \cdot \phi_a^{n_a} \cdot S^{n_a} = \sigma_{ref,pore,a} \cdot \phi_a^{n_a} \cdot \left(\frac{\phi_0}{\phi_a} \right)^{n_a} = \sigma_{ref,pore,a} \cdot \phi_0^{n_a} \quad (5.32)$$

where $\sigma_{ref,a}$ is the electrical conductivity of specimen at reference temperature after FTCs, $\sigma_{ref,pore,a}$ is the electrical conductivity of pore solution at reference temperature after FTCs and n_a is the saturation coefficient after FTCs.

After the FTCs, for NaCl solution cases, there are chemical phase change in the sample during the FTCs, the electrical conductivity of pore solution would be changed. With regard to Eqs. (5.28) and (5.32), the measured electrical resistivity of sample is

$$\frac{\rho_{ref,a}}{\rho_{ref,0}} = \frac{\sigma_{ref,0}}{\sigma_{ref,a}} = \frac{\sigma_{ref,s,0}}{\sigma_{ref,p,a}} = \frac{\sigma_{ref,pore,0} \cdot \phi_0^{n_0}}{\sigma_{ref,pore,a} \cdot \phi_0^{n_a}} = \left(\frac{\sigma_{ref,pore,0}}{\sigma_{ref,pore,a}} \right) \cdot \phi_0^{n_0-n_a} \quad (5.33)$$

where $\rho_{ref,0}$ and $\rho_{ref,a}$ are the electrical resistivity of specimen at reference temperature before and after FTCs, respectively. $\sigma_{ref,0}$ is the electrical conductivity of specimen at reference temperature before FTCs.

In particular, for DI water case, there is no chemical phase change in the sample during the FTCs, the electrical conductivity of pore solution would be the same with before FTCs. So the normalized electrical resistivity at reference temperature is

$$\frac{\rho_{ref,a}}{\rho_{ref,0}} = \left(\frac{\sigma_{ref,pore,0}}{\sigma_{ref,pore,0}} \right) \cdot \phi_0^{n_0-n_a} = \phi_0^{n_0-n_a} \quad (5.34)$$

Obviously, $\phi_0 < 1$. If there is damage, ϕ and β would increase, so fitting parameter n would decrease. Since $n_0-n_a > 0$, the normalized electrical resistivity is less than 1.

With regard to Eq. (5.33), the ratio of formation parameter before and after FTCs can be

$$\frac{F_a}{F_0} = \frac{\phi_0^{n_0}}{\phi_a^{n_a}} = \frac{\phi_0^{n_0}}{\phi_0^{n_a}} \cdot \frac{\phi_0^{n_a}}{\phi_a^{n_a}} = \phi_0^{n_0-n_a} \cdot \left(\frac{\phi_0}{\phi_a} \right)^{n_a} = \frac{\sigma_{ref,pore,a}}{\sigma_{ref,pore,0}} \cdot \frac{\rho_{ref,a}}{\rho_{ref,0}} \cdot \left(\frac{\phi_0}{\phi_a} \right)^{n_a} \quad (5.35)$$

where F_0 and F_a are the electrical resistivity of specimen at reference temperature before and after FTCs, respectively.

5.5.1.2 Activation energy

From Chapter 2, the activation energy of partially saturated specimen can be calculated with the activation energy at full saturation, saturation degree and saturation coefficient, as below

$$E_{a,p} = E_{a,s} - R_g T_{ref} \ln(S^n) \quad (5.36)$$

where $E_{a,p}$ and $E_{a,s}$ are activation energy of partially and fully saturated specimen, respectively. n is the saturation coefficient. R_g is the universal gas constant (8.314J/mol/K) and the reference temperature T_{ref} is 296.14K in this study.

In Eq. (5.36), the activation energy at full saturation can be obtained from electrical measurements and calculated as below

$$E_{a,s} = - \frac{R_g \ln\left(\frac{\sigma_{T,s}}{\sigma_{ref,s}}\right)}{\frac{1}{T} - \frac{1}{T_{ref}}} \quad (5.37)$$

where $\sigma_{T,s}$ is the electrical conductivity of fully saturated mortar sample at the absolute temperature T , $\sigma_{ref,s}$ is the electrical conductivity of fully saturated mortar sample at the absolute reference temperature T_{ref} .

After frost damage, the degree of saturation would be changed, so the activation energy changes with the damage (Chapter 2)

$$E_{a,a} = E_{a,p,a} = E_{a,s,a} - R_g T_{ref} \ln(S^{n_a}) \quad (5.38)$$

where $E_{a,a}$ is the activation energy of specimen after frost damage, $E_{a,p,a}$ and $E_{a,s,a}$ are the activation energy of partially and fully saturation specimen after FTCs respectively. The activation energy at full saturation after FTCs is an assumed parameter, which is different from the original activation energy and the activation energy after FTCs. It could be calculated based the activation energy at full saturation before FTCs and the change of electrical conductivity at reference temperature.

The relationship between activation energy and electrical conductivity at reference temperature was clear in the study of Liu and Presuel-Moreno (2012). After frost damage, for fully saturated specimens, the activation energy change can be expressed as Eq. (5.39)

$$E_{a,s,a} - E_{a,s,0} = A \ln\left(\frac{\rho_{ref,s,a}}{\rho_{ref,s,0}}\right) = A \ln\left(\frac{\rho_{ref,p,a}}{\rho_{ref,s,0}} \cdot S^{n_a}\right) \quad (5.39)$$

where A is a fitting parameter. For OPC concrete, A was fitted as 6.0157 in Liu and Presuel-Moreno's study.

Substituting the Eq. (5.39) into Eq. (5.38), there is

$$E_{a,a} = E_{a,s,0} - A \ln\left(\frac{\rho_{ref,p,a}}{\rho_{ref,s,0}}\right) + A \ln(S^{n_a}) - R_g T_{ref} \ln(S^{n_a}) \quad (5.40)$$

So the saturation effect can be

$$S^{n_a} = e^{\left[\frac{E_{a,a} - E_{a,0} + A \ln \left(\frac{\rho_{ref,p,a}}{\rho_{ref,s,0}} \right)}{A - R_g T_{ref}} \right]} \quad (5.41)$$

5.5.1.3 Damage index

Since the water content was not changed during the FTCs, in Farnam et al.' (2015) study, the saturation was considered a constant. Assuming the electrical resistivity of pore solution was not changed during the FTCs, the damage index could be considered as the change of electrical resistivity at reference temperature

$$\text{Damage index (ER)} = 1 - \frac{F_a}{F_0} = 1 - \frac{\rho_a}{\rho_0} \quad (5.42)$$

where F_a , ρ_a and F_0 , ρ_0 are the formation parameter, electrical resistivity at reference temperature after and before FTCs, respectively. It is reasonable to interpret the change of formation parameter as the damage index, but it is not in linear relationship between formation parameter and electrical resistivity at reference temperature.

After salt crystallization, the movable ion in the pore solution would be lesser, so $\sigma_{ref,pore,0} > \sigma_{ref,pore,a}$. Due to salt frost damage, $\phi_0/\phi_a < 1$ for specimen with $w/c=0.5$ and 0.7 . But for specimen with $w/c=0.3$, because of its high strength and stiffness, there is almost no damage. Besides, because of salt crystallization fills part of the pores, ϕ_0/ϕ_a could be higher than 1. For specimens saturated with NaCl solutions with $w/c=0.3$, the normalized electrical resistivity increases with FTCs, while the others decreases. In this case, considering Eqs. (5.29), (5.35) and (5.41), the damage index could be

$$\begin{aligned} \text{Damage index (ER)} &= 1 - \frac{F_a}{F_0} = 1 - \frac{\phi_0^{n_0}}{\phi_a^{n_a}} = 1 - \left(\frac{\rho_{ref,a}}{\rho_{ref,0}} \right) \cdot \left(\frac{\sigma_{ref,pore,0}}{\sigma_{ref,pore,a}} \right) \cdot \left(\frac{\phi_0}{\phi_a} \right)^{n_a} \\ &= 1 - \left(\frac{\rho_{ref,a}}{\rho_{ref,0}} \right) \cdot \left(\frac{\sigma_{ref,pore,0}}{\sigma_{ref,pore,a}} \right) \cdot e^{\left[\frac{E_{a,a} - E_{a,0} + A \ln \left(\frac{\rho_{ref,p,a}}{\rho_{ref,s,0}} \right)}{A - R_g T_{ref}} \right]} \end{aligned} \quad (5.43)$$

For DI water case, the damage index reduced to

$$\text{Damage index (ER)} = 1 - \left(\frac{\rho_{ref,a}}{\rho_{ref,0}} \right) \cdot e^{\left[\frac{E_{a,a} - E_{a,0} + A \ln \left(\frac{\rho_{ref,p,a}}{\rho_{ref,s,0}} \right)}{A - R_g T_{ref}} \right]} \quad (5.44)$$

5.5.2 Comparison of damage index and elastic modulus change

For the DI water case, the damage index was calculated based on Eq. (5.44). The normalized electrical resistivity and activation energy changes with FTCs can be obtained from the electrical test results, as shown in sections 3.5.2 and 3.5.3. Besides, the activation energy changes with pore characteristics. For saturated specimens with different w/c , they have different pore characteristics. Therefore, with regard to the electrical results of specimens saturated with DI water, the parameter A was fitted (about 15.313). Then the

results of damage index were compared with the elastic modulus. As shown in Fig. 5.26, they have a good agreement. This verified the damage evaluation model based on electrical measurements.

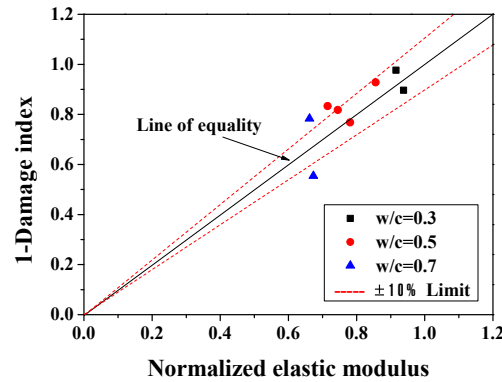


Fig. 5.26 Comparison of damage index from electrical measurements and elastic modulus change

5.6 CONCLUSIONS

In this chapter, the mortar specimens in meso scale were studied. After suffering from NaCl attack and FTCs, the mechanical properties of specimens were quantified by three point bending test and further studied by chemical analysis. The following conclusions can be reached.

- (1) In sealed condition, the specimens with $w/c=0.5$ and 0.7 suffered from NaCl attack and FTCs were severely damaged. The flexural strength and elastic modulus reduced with FTCs the most for specimens saturated with intermediate NaCl solution (5% NaCl), which implies that internal frost damage of mortar is also a serious problem in addition to surface scaling. In addition, the lower w/c of specimen, the higher salt frost resistance it had. For different concentration NaCl solution saturated specimens, the mechanical reduction with FTCs varied with solution concentration.
- (2) For 20% NaCl solution exposed specimens, the frost damage was also severe. This phenomenon confirmed the damage effect of salt since the amount of ice during freezing is supposed to be much smaller than the other cases in this study.
- (3) According to the chemical analysis, before FTCs, the mechanical degradation of specimens was mainly due to Portlandite leaching during the immersion of NaCl solution, while the salt damage during FTCs may be because of precipitation of NaCl instead of formation of Friedel's salt.
- (4) Prediction models for flexural strength and elastic modulus before and after FTCs were proposed, in which the fitting parameters were regressed from experimental data. According to the comparison, experimental and predicted values have an acceptable agreement.
- (5) A damage index model was proposed based on the normalized electrical resistivity. Normalized electrical conductivity of pore solution and activation energy change with FTCs. For DI water case, the damage index results were compared with the normalized elastic modulus with FTCs. Acceptable agreement was found, which verified the reliability of the damage evaluation model.

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Chapter 6

PREDICTION OF MECHANICAL PERFORMANCE UNDER COMBINED FREEZE-THAW CYCLES AND SODIUM CHLORIDE ATTACK

6.1 INTRODUCTION

Salt frost damage of concrete is a serious durability problem, which arises concern of researchers recently due to the increasing usage of deicing agents (Beddoe and Setzer, 1988; Chandra and Xu, 1992; Litvan, 1975, 1976; Penttala, 2006; Shi et al., 2010; Valenza and Scherer, 2007; Zeng et al., 2014a,b). According to the existing investigations (Liu and Hasen, 2015; Sun and Scherer, 2010), the mechanisms of both observed external and internal damage phenomenon (surface scaling and internal frost damage), relating to the formation of ice crystal. To predict the frost damage, plenty of efforts have been made to analyze the pore pressures induced by ice crystallization (Coussy and Fen-Chong, 2005; Coussy and Monteiro, 2008, 2009; Scherer, 1999; Scherer and Valenza, 2015; Gong et al., 2015a,b; Zuber and Marchand, 2004). Although there are reports shown that the salt crystallization also contributes to the frost damage (Farnam et al., 2014), most of experimental observations released that the ice formation dominants the salt frost damage (Sun and Scherer, 2010; Zeng et al., 2013, 2014a,b). It is the common understanding that concrete saturated with intermediate concentration NaCl solution can cause the most severe damage. In chapter 4, the results show that the ice content was the largest at intermediate concentration and the water absorption results from chapter 5 also corresponds to this phenomenon.

It is true salt crystallization can cause severe damage of mortar (Hoffmann, 1984; Lubelli et al., 2006; Thaulow and Sahu, 2004). However, the crystallization pressure depends on the degree of supersaturation (Correns, 1949; Scherer, 2004; Winkler and Singer, 1972), which was believed not be an issue for intermediate concentration solution saturated specimen because it cannot reach the saturation even half of the pore water transferred to ice. For concrete exposed to intermediate NaCl solutions, damage was also observed (Wang et al., 2006). In chapter 6, the chemical analysis reveals that the damage varies with the amount of calcium hydroxide, which means that the damage is mainly due to calcium leaching instead of salt crystallization. Furthermore, the chemical analysis of specimen with FTCs implies that the leaching was impeded with FTCs since the specimen was sealed, whereas the severe mechanical reduction was observed not only in intermediate concentration case, but also specimen saturated with high concentration NaCl solution. In this case, the possible reason could be ice formation and crystallization of NaCl. The eutectic point was observed by Litvan (1976) at temperature -25°C , and our theoretical analysis in Chapter 6, in which the eutectic temperature depends on pore size, predicts that the amount of crystal salt could be significant. However, according to the electrical test results and the ice formation estimation model in Chapter 3, no turning point was observed at temperature range from -21°C ~ -28°C during freezing. Therefore, only the supercooling effect in NaCl solution was considered in this study.

Upon freezing, with water phase transfer, hydraulic pressure (Powers and Willis, 1949; Coussy and Monteiro, 2008) crystallization pressure and cryosuction pressure (Sun and Scherer, 2010) will be induced. The destructive pressures could be calculated based on ice content and the damage can be predicted with the sum of these pore pressures (Gong et al., 2015a). However, the prediction model was merely applied to deionized (DI) water case. For NaCl solution cases, because of the ice formation difference, pressure induced by NaCl

crystallization, and chemical compound difference due to consumption of CH, the mechanical prediction model still needs further investigation.

Then, to predict the salt frost damage, the ice formation in sample with different NaCl concentration solution is supposed to be known. Based on the method with electrical resistivity measurements in Chapters 2 and 3, the ice content was estimated, which agrees acceptably with the theoretical results from thermodynamic analysis. With the estimated ice content, the mechanical model was extended to NaCl solution cases in this chapter.

6.2 MECHANICAL MODEL FOR MORTAR UNDER COMBINED FTCS AND NACL ATTACK

In open condition, it is the common sense that the DI water saturated concrete would be expansion under freezing. While for DI water saturated mortar specimen in sealed condition, the deformation of specimen develops from expansion to contraction with FTCs (Sicat et al., 2013). Based on these phenomena, by combing the poromechanical rules and Darcy's law, Gong et al. (2015a) proposed a comprehensive hydraulic model to calculate the pore pressures, which can account for all the mechanisms and predict the frost damage of mortar sample with FTCs satisfactorily. For NaCl solution case, the damage mechanism is similar to the DI water case. Therefore, the model was followed in this study. However, it is worthy to note that two important factors are changed due to the existence of NaCl solute. One is the change of ice formation with temperature. The other is the transport property of pore solution such as viscosity, which determines the solution flow under freezing.

Considering both water flow and self-compression, a comprehensive hydraulic pressure was proposed and the hydraulic pressure can be calculated as below (Gong et al., 2015a)

$$0.09\phi\dot{\psi}_c - \frac{A}{V} \cdot \frac{k}{\eta} \cdot \frac{2}{R_E - r_E} p_h = \left(\frac{b}{K_p} + \frac{\phi\psi_c}{K_C} + \frac{\phi\psi_L}{K_L} \right) \cdot \dot{p}_h \quad (6.1)$$

where ϕ is the porosity, $A=4\pi r_E^2$, $V=4\pi (R_E^3 - r_E^3)/3$. r_E and R_E are the equivalent radii of the entrained air (or the empty pores) and the influential volume. $b=2\phi/(1+\phi)$ is the boit coefficient, K_p , K_C , K_L are the bulk modulus of porous body, ice crystal and liquid water, respectively (GPa). In saturated case, ψ_c is the relative ice content and $\psi_L=1-\psi_c$ is the relative water content. p_h is the hydraulic pressure in pore, k is the permeability of porous body and η is the viscosity of liquid. The ice forming rate $\dot{\psi}_c = (d\psi_c / dT) \cdot (dT / dt)$ is determined by the cooling rate and the ice amount at certain temperature.

When subjected to freezing temperature, the water forms ice, which will block the pores and impede the flow of liquid, so the permeability change due to the ice formation should be considered. Based on existing test results, Gong et al. (2015a) proposed a practical equation to calculate the relative permeability by liquid saturation

$$k_r = \frac{k}{k_0} = S_L^{0.5} \left[1 - (1 - S_L^2)^{0.5} \right]^2 \quad (6.2)$$

where k_0 is the initial permeability, k is the permeability under freezing and S_L is remaining liquid saturation.

From Chapter 4, the viscosity of salt solutions with temperature and concentration change can be as follows

$$\eta = \eta_{\text{water}, T_0} \cdot \left(1 + a_1 c^{1/2} + a_2 c + a_3 c^2\right) \cdot \exp \left[\frac{E_a}{R_g} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (4.18)$$

where η_{water, T_0} is the viscosity of pure water at the reference temperature, c is the concentration of solution (% by mass). From the test results of Villani et al. (2014), E_a is the activation energy which is around 20.9kJ/mol for NaCl solution. From Wikipedia (viscosity), at 25°C, the viscosity of water is 8.94×10^{-4} Pa·s. a_1 , a_2 and a_3 are constant parameters fitting by testing results and $a_1=0.1134$, $a_2=-0.0551$, $a_3=0.0027$.

If assuming the pore gas pressure is zero (the same with ambient pressure), then the cryosuction pressure could be calculated based on liquid amounts, as below

$$p_l = \psi_L \cdot \Delta S_{fv} (T - T_0) \quad (6.3)$$

The crystallization pressure is always accompanied with cryosuction pressure, it depends on the shape factor, by regressing the data from Sun and Scherer (2010), the crystallization can be the function of temperature and ice amount.

$$p_c = -\psi_C \cdot (0.875 + 0.0095T) \Delta S_{fv} (T - T_0) \quad (6.4)$$

Then, the total pore pressure is

$$p = p_h + p_l + p_c \quad (6.5)$$

When the specimen suffered from FTCs with the presence of deicing agent, in addition to the three mentioned pore pressures, the osmotic pressure, thermal shock could also cause the damage. However, in this study, the specimen is in meso-scale, the pore solution is assumed to be uniform, so the tensile stress due to temperature difference in each layer is not likely to be an issue. Another, the osmotic pressure depends on the pore solution concentration difference. Since the specimen is meso-scale, there is no much difference for the concentration within one layer so that the osmotic pressure is negligible.

Because of the pore pressure, the specimen would have deformation. In one dimension, the strain caused by the total pore pressure is

$$\varepsilon_x = \frac{b \cdot p}{3K_p} \quad (6.6)$$

According to existing studies, the peak strain at each FTC is in linear relationship with the residual strain at the end of that FTC. Based on the experimental observations, the relationship was regressed by Gong et al. (2013) as below

$$\varepsilon_{pi} = 0.5375 \varepsilon_{ti} \quad (6.7)$$

where ε_{pi} is the residual strain at i freeze-thaw cycle and ε_{ti} is the peak strain at the end of i FTC.

The above model was developed based on the poroelastic properties of mortar, the residual deformation was not considered. The damage was occurred during the freezing, then the stiffness and strength of specimen decrease. To predict the mechanical performance under

FTCs, the plasticity of specimen is also necessary to be considered. The elasto-plastic model for stress-strain relationship will be studied in the future.

6.3 RESULTS AND DISCUSSIONS

In the pore pressure model, the ice forming rate and the solution viscosity at certain temperature are the inputs. However, due to the supercooling effect, there is slightly difference for the ice formation results from theoretically and experimentally. So the pore pressures including the hydraulic pressure, crystallization pressure (Eq. (6.4)) and cryosuction pressure (Eq. (6.4)) were calculated by the two methods individually. Before the calculation, several parameters should be known and they can be obtained by empirical estimation (see Table 6.1)

Table 6.1 Parameters for the model (Gong et al., 2015a)

Type (w/c)	Mortar (0.5)
Critical radius r_0	$2 \times 10^{-4} \text{m}$
Water saturated (vacuum saturated)	0.205 g/cc
Lowest temperature	-28°C
Cooling/heating rate	15°C/h
Elastic modulus (solution concentration)	19.9 GPa (0); 21.11Gpa (5%); 20.97 Gpa(15%)
Saturated permeability (undamaged) k_0	10^{-21}m^2
Poisson's ratio of mortar ν	0.2
Bulk modulus of porous body (solution concentration) $K_p = E / [3(1-2\nu)]$	11.06 GPa (0); 11.73GPa (5%); 11.65GPa (15%)
Bulk modulus of ice crystal K_C	8.8Gpa
Bulk modulus of liquid water K_L	2.2Gpa
Equivalent r_E	$6 \times 10^{-4} \text{m}$
Equivalent R_E	0.0028m

Besides, after freezing, the hydraulic pressure is caused by the liquid flow and it is closely related to the transport property of solution. According to Eq. (4.18), the viscosity of solution before freezing can be obtained by considering the solution concentration and temperature. However, due to the ice phase transformation, the remaining solutions concentration changes with the temperature. Once the water forms to ice, the solute dissolves into the remaining solution, increasing the remaining solution concentration. So the concentration change depends on the ice content. As a result, the viscosity equation can be extended with regard to ice content

$$\eta = \eta_{\text{water}, T_0} \cdot \left(1 + a_1 c_T^{1/2} + a_2 c_T + a_3 c_T^2\right) \cdot \exp \left[\frac{E_a}{R_g} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (6.8)$$

where c_T is the solution concentration at temperature T . It can be calculated as below

$$c_T = \left(\frac{c_0}{1 - c_0} \right) / \left(\frac{c_0}{1 - c_0} + \psi_L \right) \quad (6.9)$$

in which c_0 is the initial solution concentration at reference temperature.

6.3.1 Ice formation from theoretical analysis

In Chapter 3, the ice formation in cementitious was estimated based on thermodynamic analysis. The results were applied to predict the mechanical reduction with the mentioned mechanical model. First of all, the viscosity change was calculated based on the formation with temperature, the solution concentration was also analyzed. The change of pore solution concentration and viscosity with temperature were shown in Fig. 6.1. As can be seen in Fig. 6.2, based on Eq. (6.2), the relative permeability with temperature was also obtained. These information are essential for calculating hydraulic pressure of partially saturated specimen.

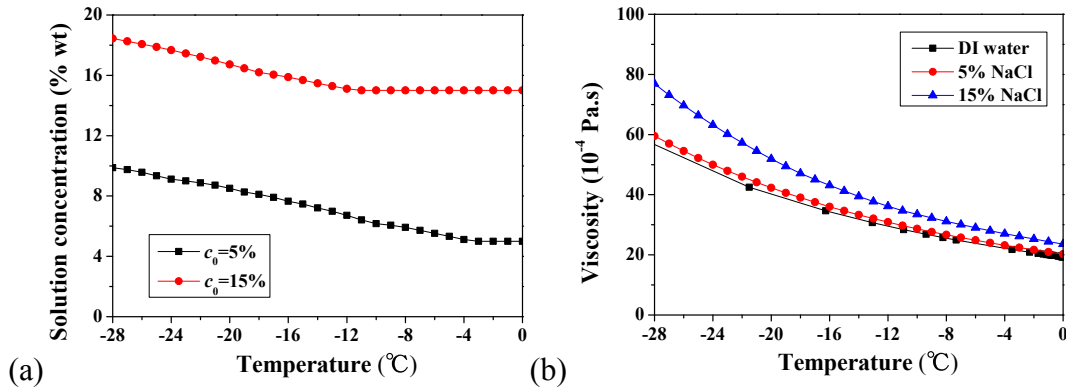


Fig. 6.1 Change with temperature (based on theoretical ice content) (a) pore solution concentration (b) viscosity of pore solution

However, in our study, the specimens were vacuum saturated. It is reasonable to assume that the specimens were fully saturated so that the hydraulic pressure release can be neglected. In this case, the hydraulic pressure could be calculated based on Coussy and Monteriro's model, as below

$$p_h = 0.09\phi\psi_c / \left(\frac{b}{K_p} + \frac{\phi\psi_c}{K_c} + \frac{\phi\psi_L}{K_L} \right) \quad (6.10)$$

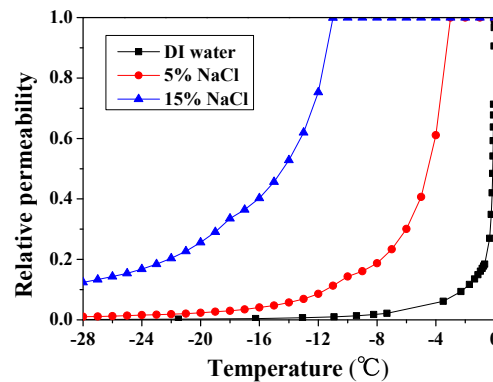


Fig.6.2 Relative permeability change with temperature during freezing (based on theoretical ice content)

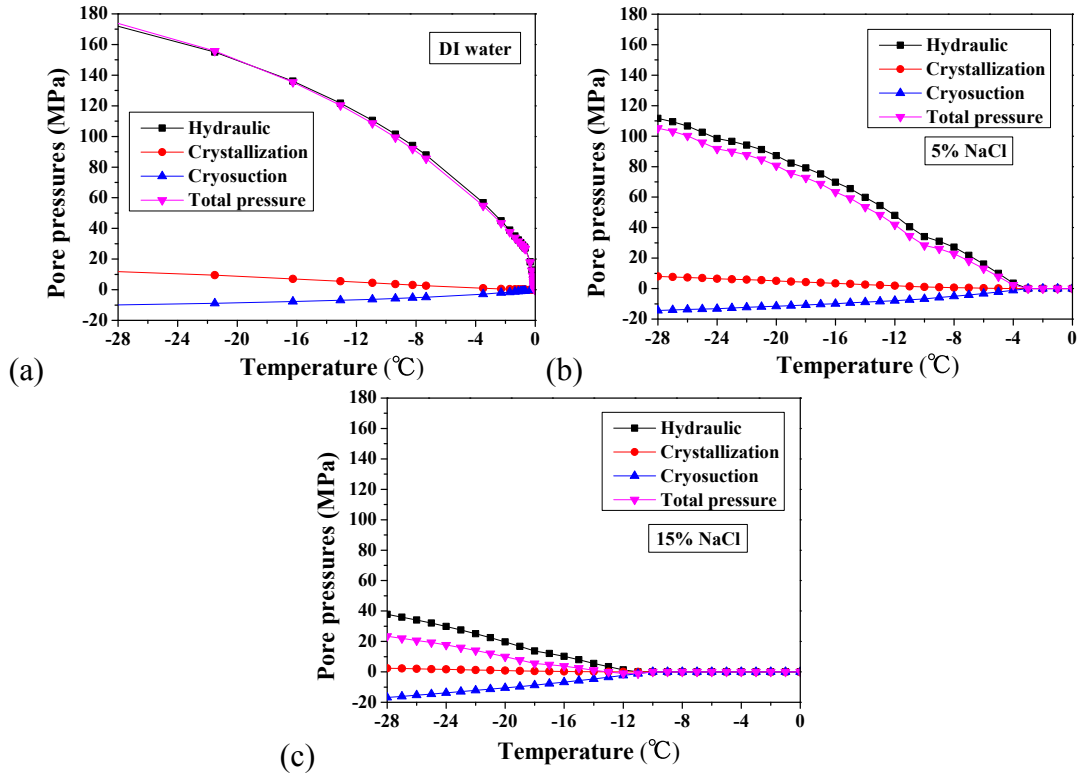


Fig. 6.3 Pore pressures change with temperature based on the theoretical ice information
(a) DI water (b) 5% NaCl (c) 15% NaCl

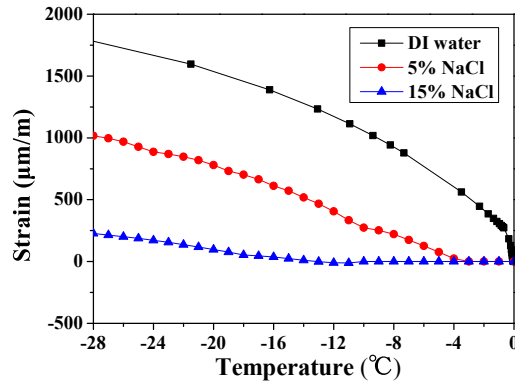


Fig. 6.4 Comparison of strain developments with temperature decrease for mortar specimen saturated with NaCl solutions (theoretical ice information)

After the pore pressures calculation, the comparison of each pore pressure was presented in Fig. 6.3. According to Eq. (6.6), the strain induced by pore pressures was further calculated and shown in Fig. 6.4. In the study of Zeng et al. (2014b), the strains of mortar specimen saturated with NaCl solutions were measured with FTCs. For mortar specimen ($w/c=0.5$), the strain during freezing of the first cycle was chosen for comparison. As shown in Fig. 6.5, the strain increased with lowering temperature and there was a big difference between the cases of DI water and 15% NaCl. While the DI water case develops large strain with ice formation, the strain for the case of 15% NaCl was minimal due to lesser ice content, which means the frost damage was more severe for the case of DI water theoretically. Comparing of our theoretical predictions and Zeng et al. (2014b)'s experimental results, acceptable agreement was observed although there was a gap for the DI water case. Because cement paste specimen

was used in Zeng et al. (2014b)'s study, there was smaller amount of ice compared with mortar specimen due to the pore size distribution difference. The ice formation difference was described in Chapter 3 in detail.

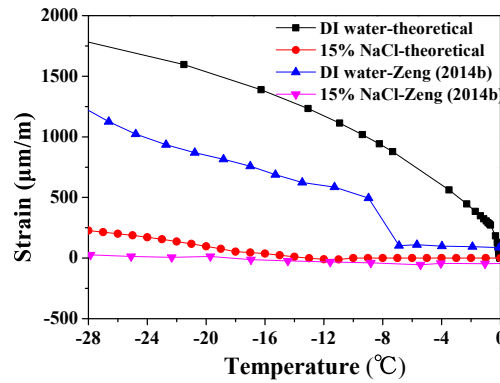


Fig. 6.5 Comparison of the strain develops with temperature for mortar specimen saturated with NaCl solutions exclusive of thermal strain (Our theoretical prediction and Zeng et al.'s (2014b) experimental results)

6.3.2 Ice formation from test results

From the electrical test results, the ice content was estimated by the proposed model in Chapter 3. The pore pressures developed with FTCs were calculated as described in section 6.3.1. The results were presented in Fig. 6.6. Then the strain was further calculated and presented in Fig. 6.7.

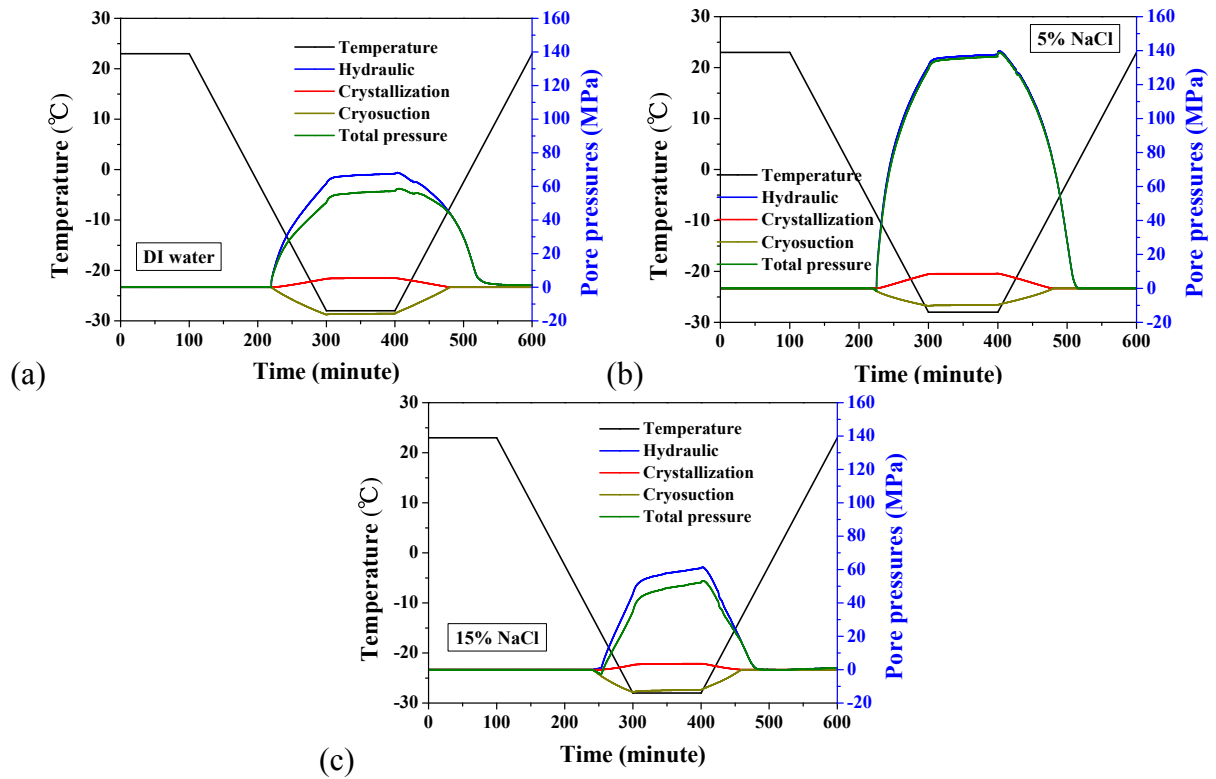


Fig. 6.6 Pore pressures change with time based on the experimental ice information (a) DI water (b) 5% NaCl (c) 15% NaCl

As shown in Fig.6.6, the hydraulic pressure is much higher than crystallization pressure and cryosuction pressure at the first freeze-thaw cycle. In particular, the overall pore pressure was positive and almost matched with the hydraulic pressure for the case of 5% NaCl, it implies the expansion occurs at freezing temperature and can be destructive. This is different from the theoretical results, in which DI water case had the largest pore pressure and strain. At lowest temperature, the reason of the maximum ice content for the case of 5% NaCl is still not clear. But this damage tendency can somehow match the flexural strength and static stiffness reduction with FTCs. Additionally, the strain of the case of 15% NaCl was just slightly less than the case of DI water, as the progressive mechanical property degradation with FTCs shown in Chapter 5. It implies that the damage in the case of high concentration NaCl solution saturated specimen was also due to the pore pressured induced by ice formation. The damage mechanism of NaCl solution case is same to the case of DI water.

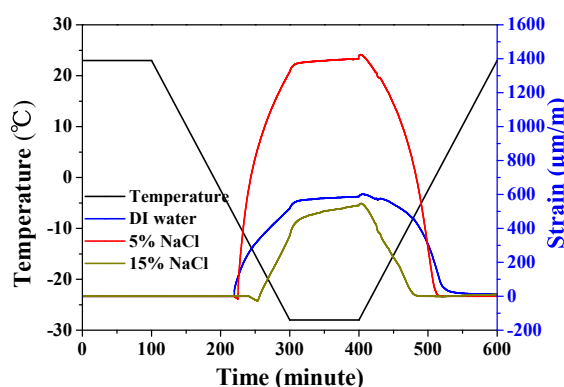


Fig. 6.7 Comparison of strain developments with time for mortar specimen saturated with NaCl solutions (experimental ice information)

6.4 CONCLUSIONS

In this chapter, the damage mechanism of salt frost damage was further discussed. The ice formation was regarded as the main reason to the damage. Based on the ice formation information from thermodynamic analysis and experimental results calculations, the mechanical property was predicted. The results can be concluded as following

(1) Upon freezing, pressure model was extended to samples with NaCl solutions. The pore solution concentration change with lowering temperature and the corresponding solution viscosity were presented. They are especially important for specimen partially saturated because the hydraulic pressure release is related to the solution property. Since the hydraulic pressure also depends on permeability of the sample, how the relative permeability change with temperature was discussed for DI water, 5% NaCl and 15% NaCl cases. All of them reduce with lowering temperature significantly, especially for the case of DI water.

(2) Similar to DI water case, three pore pressures (hydraulic pressure, crystallization pressure and cryosuction pressure) were calculated for 5% and 15% NaCl solution cases based on ice content calculated theoretically. The overall pore pressure was largely influenced by the hydraulic pressure in the first cycle. The strain development with FTCs was also understood based on the overall pore pressure. Among the three cases, DI water case reached the largest strain while the 15% NaCl case was the least. When the cases of DI water and 15% NaCl compared with the results from strain measurement by Zeng et al. (2014b), acceptable agreement was reached.

(3) The pore pressure of mortar specimen saturated with NaCl solutions was also calculated based on ice content from our electrical test results calculation. The largest deformation was observed in the case of 5% NaCl, and the strain of the case of 15% NaCl

was just slightly less than the case of DI water. The strain development is corresponding to the mechanical property change tendency with FTCs, which verifies that the damage of specimen with higher concentration NaCl solution is also due to ice formation.

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Chapter 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

The ice formation in mortar saturated with NaCl solutions was studied theoretically and experimentally. The mechanical performance of mortar suffered from NaCl attack and freeze-thaw cycles (FTCs) was evaluated and predicted based on ice and calcium hydroxide (CH) amounts. The main findings of this dissertation can be summarized as below.

- (1) The combined effect of temperature and moisture content on electrical conductivity of concrete was explained from a theoretical point of view. Under freezing conditions, the two effects both play significant roles in the electrical behavior of concrete and the interactive effect is more obvious under higher temperatures and higher degrees of saturation. The relationship between the activation energy and the degree of saturation was derived. A method to estimate the ice content based on electrical measurements was proposed considering the coupled effect of temperature and moisture content. Based on the proposed method, the relative ice content of mortar was estimated by conducting the electrical test. The test results during FTCs were consistent and the ice formation process was continuous with temperature variation. In addition, during FTCs, the relative ice content (the mass ratio of frozen water content to the total water content in mortar) during thawing was higher than that of freezing under the same temperature. The maximum value for the samples saturated with deionized (DI) water and $w/c=0.5$ was around 0.5 at temperature -28°C . The calculated ice content from the developed model was compared with theoretical result from thermodynamic analysis and found in acceptable agreement with each other. The calculated ice content was also compared with existing experimental results of other researchers', which were based on calorimetric test and electrical test data interpreted with this study's model. The shape of ice content and temperature curves looked similar. The difference in ice contents between our test and the existing tests can be explained by difference in material properties and curing condition. The effect of frost damage of mortar on electrical conductivity was also discussed and concluded that the damage effect may be ignored within one FTC for estimating ice formation because the frost damage is cumulative and it is not so significant for a cycle. These verified the reliability and applicability of the proposed model.
- (2) According to the solute mass conservation, ice content information for bulk NaCl solutions under freezing can be calculated. From thermodynamic analysis, the effect of salt and pore size on freezing point was found in a product relationship. As a result, the freezing point of solution in cementitious materials was calculated. Then the ice formation of NaCl solutions in cementitious materials was estimated as well. The ice content estimation model based on electrical measurements was extended to the NaCl cases by clarifying the combined effects of moisture, temperature and ion concentration to electrical properties of pore solution. For mortar specimen saturated with NaCl solutions, it is possible to have salt crystallization at temperature above freezing point. Based on this physical phenomenon, four stages ice content estimation model was proposed. 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 study was also 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 compared with the theoretical results and our test results. In addition, both of the electrical resistivity at highest and lowest temperatures changes with the damage development, while activation energy does not show apparent relationship with frost damage development. Freezing and thawing points was detected from the relationship between electrical resistivity and temperature. From the previous report, the freezing point increases with FTCs. But in our meso-scale test results, such tendency was not observed.

- (3) The solution transport depends on the pore characteristics of mortar. It varied with different w/c . The solution property change with solution concentration and temperature were analyzed and the relative sorptivity change with concentration was presented. The overall transport behavior difference with solute difference at 23°C can be explained by the difference in two phenomena, salt crystallization and calcium (Ca^{2+}) leaching. Exposure to intermediate concentration (3% by weight) solution, although the salt crystallization and Ca^{2+} leaching were co-existing, the sample absorbed almost the same amount of water as DI water case. When ice formation and salt crystallization occur at subzero temperature, the expansion due to ice and salt induce internal pressures. The pressure is more severe than the pressure in the DI water case, which is induced by ice formation alone, resulting in more destructive frost damage. Exposure to high concentration (20% by weight) solution, the salt crystallization had greater effect on transport properties of mortar than Ca^{2+} leaching. The salt filled the voids or blocked the gel pores with solution transport. Subsequently, it reduced the further water penetration, so that the specimen would have less degree of expansion when the water transforms to ice.
- (4) In sealed condition, the specimens with $w/c=0.5$ and 0.7 suffered from NaCl attack and FTCs were severely damaged. The flexural strength and elastic modulus reduced with FTCs the most for specimens saturated with intermediate NaCl solution (5% NaCl), which implies that internal frost damage of mortar is also a serious problem in addition to surface scaling. In addition, the lower w/c of specimen, the higher salt frost resistance it had. For different concentration NaCl solution saturated specimens, the mechanical reduction with FTCs varied with solution concentration. In particular, for 20% NaCl solution exposed specimens, the frost damage was also serious. This phenomenon confirmed the damage effect of salt since the amount of ice during freezing is supposed to be much smaller than the other cases in this study. According to the chemical analysis, before FTCs, the mechanical degradation of specimens was mainly due to Portlandite leaching during the immersing process, while the salt damage during FTCs may because of supercooling induced sudden expansion. Prediction models for flexural strength and elastic modulus before and after FTCs were proposed, the fitting parameters were regressed from experimental data. According to the comparison, experimental and predicted values had an acceptable agreement. A damage index model was proposed based on the normalized electrical resistivity. Normalized electrical conductivity of pore solution and activation energy change with FTCs. For DI water case, the damage index results were compared with the normalized elastic modulus with FTCs. Acceptable agreement was found, which verified the reliability of the damage evaluation model.
- (5) Since the ice formation was regarded as the main reason to the salt frost damage, the mechanical property was predicted based on the ice formation information from

thermodynamic analysis and electrical measurement results calculations. Similar to DI water case, three pore pressures (hydraulic pressure, crystallization pressure and cryosuction pressure) were calculated for 5% and 15% NaCl solution cases based on ice content calculated theoretically. The overall pore pressure was largely influenced by the hydraulic pressure in the first cycle. The strain development with FTCs was also understood based on the overall pore pressure. Among the three cases, DI water case reached the largest strain while the 15% NaCl case was the least. When the cases of DI water and 15% NaCl compared with the results from strain measurement by Zeng et al. (2014b), acceptable agreement was reached. The pore pressure of mortar specimen saturated with NaCl solutions was also calculated based on ice content from our electrical test results calculation. The largest deformation was observed in the case of 5% NaCl, and the strain of the case of 15% NaCl was just slightly less than the case of DI water. The strain development is corresponding to the mechanical property change tendency with FTCs, which verifies that the damage of specimen with higher concentration NaCl solution is also due to ice formation.

7.2 SUGGESTIONS FOR FUTURE STUDIES

This dissertation described the electro-chemo mechanical responses of meso-scale mortar specimen suffered from FTCs and NaCl attack. According to the results, the mechanism of salt frost damage of mortar could be clarified and the mechanical performance of concrete layer under the combined effects could be evaluated and predicted. However, how to intergrade the meso-scale information to predict the mechanical performance of real concrete structures has still not been achieved. To assess the life cycle of concrete structures exposed to FTCs and NaCl attack, the following further studies need to be done:

- a) In Chapter 6, for the pore pressures in meso-scale size specimen, only hydraulic pressure, crystallization pressure and cryosuction pressure were considered for mechanical behavior prediction with FTCs. Although the model can predict the strain development with FTCs based on ice formation, deformation experimentation of specimen in meso-scale is still needed for further verification. In addition, after the constitutive law has been obtained, meso-scale modeling of salt frost damage of mortar based on rigid body spring model (RBSM) could be developed. Also, the simulation of three-point bending test could be achieved based on the proposed model and the results could compare with our test results in Chapter 5. Another, for macro scale specimen, osmotic pressure and thermal shock are also worthy to paying attention. Based on the two factors, the bridge between meso-scale and macro scale modeling could be built.
- b) This study only concerned about mortar, for internal salt frost damage of concrete, the interfacial transition zone (ITZ) is more likely to be key point to determine the damage degree of concrete. As shown from our test results, with higher porous sample, the salt frost damage is more serious. This means that the salt frost damage in ITZ is probably much more severe than the mortar samples. Therefore, to predict the concrete damage by the combined effects accurately, the mechanical reduction due to ITZ deterioration should be understood in the future studies.
- c) In Chapter 4, the transport properties of mortar suffered from NaCl attack was studied from the meso-scale point of view. After salt or frost damage, the transport properties of mortar or concrete will be altered. This information is essential for understanding

the reinforcement corrosion due to aggressive ions ingress. From the absorption and reabsorption curve, the pore characteristics change can be understood. However, the quantitative analysis of pore structural change based on the curves has not been reached. The rate of absorption in each stage was related to the pore diameters of mortar. By developing the model connecting with pore diameter and absorption, the pore diameter change in each range may be understood accurately. It still needs further investigation. After exposed to FTCs, the pore characteristics could be further altered. How the transport properties change under the combined effect is also unknown. Generally, for onsite concrete structures, the diffusivity is important to evaluate the durability and life cycle. Therefore, it is necessary to make this point clear. Considering the condition of reinforcement, the mechanical performance of the concrete structure can then be predicted.

- d) In Chapter 5, the damage index for specimen saturated with NaCl solution not only needs the normalized electrical resistivity and activation energy change, but also the change ratio of electrical conductivity of pore solution. The DI water case was used to verify the damage evaluation model, but for the NaCl solution cases, further investigation is needed since there is no sufficient data for the electrical conductivity of pore solution.