Meso-scale Study of Water Transport in Mortar Influenced by Sodium Chloride and Freeze-thaw Cycles

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ABSTRACT

Salt frost damage of concrete is an important durability issue to concern since it can threaten to the structural safety. The mechanical properties of concrete could be degraded while the corrosion of steel bar can be initiated because of the penetration of chloride ion. After freeze-thaw cycles (FTCs), due to the increase of connectivity, the water transport property could be changed which is the main reason of steel corrosion. However, because of the non-uniform salt frost damage of concrete in depth direction, how the water transport in mortar influenced by the combined effects of sodium chloride and FTCs is still not clear. In this study, the water transport behavior of meso-scale salt frost damaged mortar samples was studied. Different water-to-cement ratios (0.3 and 0.7) and salt solution concentrations (DI water, 5% NaCl, 15% NaCl and 20% NaCl) were adopted for comparisons. In total, 30 FTCs were tested. After three-point bending test, the central part was removed and the remaining specimens (30×30×5 mm) were immersed into deionized water for evaluation of the transport property. The results show that the porosity increased clearly with FTCs for pure frost damage case, whereas different tendency was observed in salt frost damage cases. Finally, the relationship between the mechanical degradation and water transport property change is discussed, which can promote the understanding of salt frost damage mechanism.

Keywords: meso-scale; salt frost damage, water transport, FTCs, sodium chloride.

1.0 INTRODUCTION

Frost damage of concrete structures can threaten to the structural safety and it is paid much attention recently due to the increasingly usage of deicing agents. With the existing of deicing agent such as sodium chloride (NaCl), the frost damage process can be accelerated (Farnam et al., 2014). While the salt scaling could spoil the appearance and increase the permeability of concrete, more importantly, the internal frost action can degrade the mechanical performance of concrete structures (Valenza and Scherer, 2007). Due to more porous nature of concrete after salt frost damage, the salt could move inside of the concrete and reaching the site of steel bar (Wang et al., 2013). The corrosion of the reinforcement could be initiated due to the existing of chloride ions and the concrete structure will be endanger after severe reinforcement corrosion. Therefore, after the salt frost damage, the water transport property is worthy of further investigation for accurate evaluation the safety of the concrete structures.

The water transport property of concrete is highly depending on its pore structures. In the case of salt frost damage of concrete, it is the understanding that the change of pore characteristics of specimen is due to the frost damage, calcium leaching and salt crystallization (Wang et al., 2017). From existing studies, after calcium leached, the specimen contains more small pores and denudation. Besides, with salt crystallization, the surface would be more smooth and with dense structure (Liu et al., 2016). After freeze-thaw cycles (FTCs) exposure, because of the frost damage, the microcracks could also be observed (Wu et al., 2014). Therefore, the pore size change due to salt attack and frost action is different. While the salt attack changes the fine pores, the frost action mainly cause the change of capillary pores. Based on the absorption test results, the pore size distribution difference can be revealed.

Water transport property was commonly considered as a durability index because the aggressive ions usually can transport with water (Kelham, 1988). However, the absorption test was usually conducted with bulk specimens. It is known that the pore...
solution concentration will be different in each depth when the NaCl solution penetrates into concrete. So the salt frost damage under FTCs is correspondingly different. Because of the non-uniform salt frost damage of concrete in depth direction, the water transport in mortar influenced by the combined effects of NaCl and FTCs remains unclear. To quantitatively analyze the transport property alteration with salt or salt frost damage, the meso-scale size of specimens should be adopted. In this study, the specimens subjected to NaCl attack and/or FTCs were investigated. Three-point bending test was conducted to understand the degree of salt frost damage, while the corresponding water absorption test was for the transport property.

2.0 TEST PROGRAM

To understand the water transport property alteration with salt frost damage, the three-point bending test and water absorption test were conducted for specimens suffered from the combined effects of NaCl attack and FTCs. Meso-scale size of specimens were prepared to ensure the salt frost damage is uniform and the quantitative analysis can be achieved with this regard. The specimens preparation, three-point bending test and water absorption test were described below, as shown in Fig. 1.

2.1 Preparation of Specimens

Mortar specimens were studied in this experimental program. Mix proportions were based on ACI Committee (1991), in which coarse aggregate was excluded, as shown in Table 1 with different water-to-cement ratios (W/C). Ordinary Portland cement was used and the physical properties and chemical compositions were shown in Table 2. The maximum size of fine aggregate was 1.2 mm and its density was 2.67 g/cm³. 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 ºC. With regard to the bleeding effect, the mortar surface was removed and the core part was cut into samples with size of 70×30×5 mm by using a wet saw. The meso-scale small size was chosen because the pore solution concentration in the specimen can be considered as uniform and the mechanical degradation mechanism of mortar due to different NaCl solution exposure can be clear.

To assure the pore solution having the same concentration as designed, specimens were initially dried by putting inside of oven for 24 hours at 105 ºC 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. 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 vacuumed condition for deaeration. After 15 minutes, the mortar samples were immersed into solution and continuously staying in the vacuumed 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 was assumed that the samples are full saturation and have the same solution concentration with the solution in container (Wang et al. 2016). Then 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). During the 7 days immersion, the NaCl may have reaction with hydrated products to form Friedel’s salt. To assure the chemical reaction is completed, the sealed saturated specimens for reference were placed at room temperature 23±2 ºC for one month, while the other specimens were placed into an environmental chamber to undergo FTCs. The freeze-thaw temperature history of the chamber can be seen in Fig. 1.

Table 1. Mix proportions and properties of mortar

<table>
<thead>
<tr>
<th>W/C</th>
<th>Water kg/m³</th>
<th>Cement kg/m³</th>
<th>Fine aggregate kg/m³</th>
<th>Bulk dry density kg/m³</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>207</td>
<td>690</td>
<td>755</td>
<td>2173</td>
<td>0.188</td>
</tr>
<tr>
<td>0.7</td>
<td>207</td>
<td>296</td>
<td>1090</td>
<td>2125</td>
<td>0.214</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Specific gravity</th>
<th>Specific surface (cm²/g)</th>
<th>Compressive strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.16</td>
<td>3350</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3d</td>
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<td></td>
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<td>7d</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>28d</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>31.3±1.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>47.1±1.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>63.5±1.88</td>
</tr>
<tr>
<td>Composition</td>
<td>CaO</td>
<td>SiO₂</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Content (%wt)</td>
<td>64.20</td>
<td>21.40</td>
<td>5.51</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.21</td>
</tr>
</tbody>
</table>
Fig. 1. Specimen preparation and test procedures

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 ºC for 100 minutes, then decreased by 0.25 ºC per minute until it reached -28 ºC and remained constant for 100 minutes, and then increased by 0.25 ºC per minute until the maximum temperature 23 ºC. The FTCs was up to 30 cycles because the mechanical deterioration for meso-scale size specimens was very severe compared with the bulk concrete specimens, which is enough to reflect the whole deterioration process.

2.2 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. 1, the bending span was set 50mm 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 crack propagation, a notch with 5mm depth was made in each of the two sides of specimen central cross-section (The specimen size is 70×30×5 mm,
after obtaining the notches, the width in the middle of specimen becomes 20mm. 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. (1)) and elastic modulus (Eq. (2)) were calculated based on JCI standard 001 (2003), as following equations

\[ \sigma = \frac{3Pl}{2bh^2} \]  \hspace{1cm} (1)

\[ E = \frac{P_{1/3}l^3}{4d_1/3bh^3} \]  \hspace{1cm} (2)

where \( \sigma \) is the flexural strength (MPa), \( E \) is the elastic modulus (GPa), \( P \) is the maximum load (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).

### 2.3 Water absorption test

After the three-point bending test, the remaining part of the specimen was recutted for the size of 30×30×5 mm specimens. Ethanol was applied for cutting to keep the pore characteristics unchanged. To avoid the further damage, the specimens were dried in over at 50 °C for 7 days. Then, the dried weights of specimens were measured with a scale while the accuracy was 0.1 mg. 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 in water can be exact as designed. 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 C1585, 2004), the interval time of measurement is not constant, but increasing with absorption period (3s, 6s, 10s, 15s, 30s, and 1 minute) since the water absorption rate is not constant. After taking the specimen out of water, the surface moisture of specimen was removed rapidly with paper towel and put on the scale to measure its weight immediately. To eliminate the effect of moisture evaporation, the whole measurement process took less than 30 seconds. Since the sample was in meso-scale, though the evaporated water amount was small, it may be sensitive to the initial absorption results. When the absorption period was 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 were tested in one container. The volume ratio of solution to samples was controlled over 40:1 (Wang et al., 2016).

Based on the water absorption capacity, with regard to the size of samples, the water uptake amount \( q \) (g/g) may be determined by the dried mass of the sample

\[ q = \frac{m - m_d}{m_d} \]  \hspace{1cm} (3)

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

### 3.0 RESULTS AND DISCUSSIONS

The experimental program includes mechanical and water absorption 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 understand the pore characteristics alteration, the subsequent water absorption test was adopted.

#### 3.1 Mechanical test results

After FTCs, the mechanical properties degradation was measured by three-point bending test. The nominal flexural stress-deflection curves are presented in Fig. 2 (W/C=0.3) and Fig. 3 (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.

To evaluate the effect of FTCs, the normalized flexural strength and elastic modulus with FTCs were presented in Fig. 4 (W/C=0.3) and Fig. 5 (W/C=0.7). For specimens exposed to each concentration NaCl solution, they were normalized to the values with Non-FTCs condition. 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=0.7, 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 (c) and (d), 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.

### 3.2 Water absorption test results

For a short period of immersion (1 hour), the test results of cumulative solution absorption characteristics are presented in Figs. 6-9 with the square root of time. The absorption amount is analyzed based on Eq. (3), normalized by the dried mass of sample. In Figs. 6 and 7, water transport in specimens under different FTCs was shown, while the comparison for different NaCl solution concentration was presented in Figs. 8 and 9. It is clear that the absorption amount of specimens varies with FTCs, especially for the cases of W/C=0.7. As found in Fig. 6, the absorption process may be divided into two stages, initial absorption and long time absorption. 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). For the long time absorption, it is also linear. 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.

![Fig. 2. Nominal flexural stress-deflection curve with FTCs (W/C=0.3) (a) DI water (b) 5% NaCl (c) 15% NaCl (d) 20% NaCl](image1)

![Fig. 3. Nominal flexural stress-deflection curve with FTCs (W/C=0.7) (a) DI water (b) 5% NaCl (c) 15% NaCl (d) 20% NaCl](image2)
Fig. 4. Normalized flexural strength and elastic modulus with FTCs (W/C=0.3) (a) DI water (b) 5% NaCl (c) 15% NaCl (d) 20% NaCl

Fig. 5. Normalized flexural strength and elastic modulus with FTCs (W/C=0.7) (a) DI water (b) 5% NaCl (c) 15% NaCl (d) 20% NaCl
Fig. 6. Water transport in specimen (W/C=0.3) under different FTCs (a) DI water (b) 5% NaCl (c) 15% NaCl (d) 20% NaCl

Fig. 7. Water transport in specimen (W/C=0.7) under different FTCs (a) DI water (b) 5% NaCl (c) 15% NaCl (d) 20% NaCl
Fig. 8. Water transport in specimen (W/C=0.3) under different NaCl concentration (a) Non-FTCs (b) 30 FTCs

In the case of W/C=0.3, although there was no obvious mechanical degradation can be observed, the difference of absorption in initial stage is large. As shown in Fig. 6(a), the slope of the curve increases with FTCs, which means that the connectivity increased significantly with the FTCs. Similar tendency was also noticed in the case of W/C=0.7 (see Fig. 7(a)). More importantly, in both figures, the period of initial stage becomes shorter with FTCs, which implies the volume of capillary pores increases. It seems that the pore size change due to 5% NaCl attack and FTCs exposure was minimal for the case of W/C=0.3, whereas obvious variation was noticed from the case of W/C=0.7. This phenomenon can agree with the mechanical degradation. For the cases of W/C=0.3 specimen attacked by 15% NaCl, both total absorption amount and absorption rate increased after 10 FTCs while there is insignificant alteration until 30 FTCs. However, for the cases with 20% NaCl, the results were contrast to the previous findings. Suffered from 10 FTCs, the total absorption amount had almost no change, but the absorption rate decreased. More importantly, after 30 FTCs exposure, the absorption curve almost agreed with the one without FTCs exposure. For the cases with W/C=0.7 exposed to NaCl solutions, there was slight variation for the total absorption amount, whereas the absorption rate varied dramatically in the case of 5% NaCl and minimally in the cases of 15% and 20% although the mechanical degradation was significant. Therefore, no clear tendency can be observed for the relationship between water transport property and salt frost damage. It seems that the porosity has no big change after FTCs but the connectivity changes significantly. How the microstructural change due to salt frost attack correlates to the mechanical performance still needs further investigation.

4.0 CONCLUSIONS

In this paper, 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 the transport properties were further studied by water absorption test. The following conclusions can be reached.

1) In sealed condition, the specimens with W/C=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. 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) The solution transport depends on the pore characteristics of mortar. As a result, it varies with different W/C. The overall transport behavior difference can be explained by the difference of frost damage, salt crystallization and Ca$^{2+}$ leaching.

(3) The transport property can be affected by the salt frost damage significantly. Although there was no significant change for the total absorption amount while the absorption rate changed clearly with FTCs. The porosity was not affected by the frost damage dramatically, but the connectivity was.

(4) No obvious relationship was observed between the water transport property and mechanical degradation due to the combined effects of FTCs and NaCl attack, which needs further investigation.

Acknowledgement

The authors would like to express their sincere thanks to the National Natural Science Foundation of China (No. 51708133), the Grant-in-Aid for Scientific Research (A) of Japan Society of Promotion of Science (No. 26249064), and by China Postdoctoral Science Foundation (No. 2017M622633).

References


