INFLUENCE OF FREEZE-THAW CYCLE ON CONCRETE CHLORIDE ION MIGRATION

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Abstract

Many concrete structures locate in northern marine environment. Chloride corrosion is an important factor causing the concrete durability deterioration. The effect of freeze-thaw damage on concrete durability deterioration should also not be ignored. Many chloride ion migration models have been established in order to provide assistance for concrete structure life prediction and to give some basis for concrete durability design. But those chloride ion migration models and chloride ion migration coefficient of durability design indicators are almost obtained on the basis of the concrete matrix without any damage, while the influence of freeze-thaw cycle on the chloride ion migration of concrete have been neglected. Study on the time-dependent law of concrete chloride ion migration in freeze-thaw cycle is of great significance in area of concrete durability scientific prediction and design. In this work, the changes of concrete chloride ion migration under different freeze-thaw cycles have been investigated. Then the developments of relative dynamic elastic modulus and mass loss of concrete samples were recorded. The time-dependent migration law of chloride ion in concrete subjected to freeze-thaw process was summarized. Furthermore, the mechanism of chloride ion migration of concrete in the freeze-thaw process was systematically analyzed through capillary water absorption and pore structure development.

1. INTRODUCTION

The chloride ion migration coefficient is a particularly important concrete durability indicator which reflects the ability of concrete structure to resist the corrosion of harmful media and to ensure the structure service normally. In the literature, many scholars had predicted the chloride ion migration in concrete based on Fick’s second law. Shina, etc. [1] described the migration of chloride ion in concrete through a complete mathematical calculation which considered the influences of various parameters, such as the ambient temperature, moisture migration, chemical effect of chloride ion and concrete matrix pore structure. However, most of those studies conducted on the nondestructive concrete matrix, and the deterioration of structural concrete caused by environmental or other effects in the
service process were neglected. Freeze-thaw damage is the main form of concrete matrix degradation in cold environment. There may be some different performances between detrimental and nondestructive concrete matrixes because the effects of internal hydrostatic pressure, osmotic pressure and ice pressure during freeze-thaw process [2]. It is necessary to consider the influence of freeze-thaw cycle on chloride ion migration process when analyzed the chloride ion transport properties of structure concrete under a freeze-thaw environment.

In this paper, four concrete mix proportions were designed, in order to consider more comprehensive factors of concrete matrix changes and to obtain more typical test results during analyzing the influence of freeze-thaw cycle on concrete chloride ion migration. Firstly, the chloride ion migration coefficient changes of concrete (with different air content, water-cement ratio and mineral admixture) during different freeze-thaw cycles were measured. Secondly, the relative dynamic elastic modulus and mass loss of concrete were recorded and the correlations between chloride ion migration and freeze-thaw cycle parameters were summarized. Thirdly, the changes of capillary absorption during freeze-thaw process were analyzed via water absorption test and the concrete pore structure developments were tested using an automatic mercury analyzer. Finally, the mechanism of freeze-thaw cycle on the chloride ion migration was analyzed and decrypted.

2. RAW MATERIALS AND EXPERIMENTS

2.1 Raw materials and experiment design

The cement used in this study is type P. II 52.5 cement. The sand fineness modulus is 2.6, and the density of sand is 2650 kg/m³. The size of crushed basalt coarse aggregate used in this study is between 5mm and 25mm. Superplasticizer (PCA) and antifoaming agent (XP) are used in this study.

Table 1: Concrete mix proportion / kg·m⁻³

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Cement</th>
<th>Fly ash</th>
<th>Sand</th>
<th>Gravel</th>
<th>Water</th>
<th>PCA</th>
<th>XP</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>320</td>
<td>-</td>
<td>730</td>
<td>1118</td>
<td>160</td>
<td>2.56</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>320</td>
<td>-</td>
<td>730</td>
<td>1118</td>
<td>160</td>
<td>3.20</td>
<td>0.64</td>
</tr>
<tr>
<td>C</td>
<td>320</td>
<td>-</td>
<td>730</td>
<td>1118</td>
<td>112</td>
<td>3.20</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>224</td>
<td>96</td>
<td>730</td>
<td>1118</td>
<td>160</td>
<td>2.24</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2: Concrete basic physical properties

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Air content / %</th>
<th>Slump / mm</th>
<th>Compressive strength at 28 days / MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>7.0</td>
<td>160</td>
<td>56</td>
</tr>
<tr>
<td>B</td>
<td>3.1</td>
<td>145</td>
<td>62</td>
</tr>
<tr>
<td>C</td>
<td>6.8</td>
<td>140</td>
<td>81</td>
</tr>
<tr>
<td>D</td>
<td>6.5</td>
<td>165</td>
<td>47</td>
</tr>
</tbody>
</table>
Mix proportions of concrete used in this study and their basic physical properties are shown in Table 1 and Table 2 respectively. Several air content, water-cement ratio (W/C) and mineral admixture were considered in concrete mix proportion design. Chemical admixtures were used to adjust the concrete workability and to make sure all the changes in experiment design were single factor effect, rather than coupling effect of multiple factors. All the concrete specimens were casted at a temperature of 20°C and demoulded after (24±2) h. Then, they were put into a standard curing room (temperature of (20±2) °C and relative humidity of 95%), and cured28 days for test. All the test data were obtained from concrete specimen, instead of simulated mortar or cement paste, to ensure the authenticity of the data.

2.2 Test method

A. freeze-thaw cycle
The frost resistance of concrete specimen was tested according to Chinese standard (GB/T 50082-2009). The relative dynamic elastic modulus (RDEM) of specimens was tested after each 25 freezing-thawing cycles. Also, the external damage and mass loss of specimens were checked and recorded.

B. Chloride ion migration
The sample for chloride ion migration test is a cylinder with 100mm diameter and 300mm length. The specimens were cut to (50±2) mm thick disk specimens after cured for 28 days. Each group of sample (A, B, C and D) had 39 concrete disk specimens. All the specimens were put into automatic freeze-thaw cycle machine to subject to freezing and thawing and the chloride ion migration of specimens was tested every 25 cycles (from 0 to 300 cycles). The chloride ion migration coefficient (D_{RCM}) of concrete was tested and calculated according to NT BUILD 492.

C. Capillary water absorption
The concrete specimen size is Φ100mm×50mm, and each group has 3 pieces. Since the capillary water absorption was a non-destructive test. All the specimens were put into automatic freeze-thaw cycle machine to subject to freezing and thawing and the capillary absorption of specimens was tested every 25 cycles (from 0 to 300 cycles). Before the absorption test starting, the side of specimen needed to be sealed up completely with a sealing material. Then the specimen was put into an oven at 50°C for 24 hours to obtain a consistent weight and the initial weight was recorded. Keeping the testing surface of specimen immersing into water for 60min and then the specimen weight change (\(\Delta M\)) was recorded. The absorption test was carried out at temperature of (20±1) °C. The capillary absorption (I) of concrete was calculated by Eq. (1) where A was testing surface area and D was water density.

\[ I = \frac{\Delta M}{A \cdot D} \]  

(1)

The change of concrete capillary absorption rate during freeze-thaw cycle was obtained by analyzing the change in the slope of the tangent line of absorption curve.

D. Pore structure analysis
The concrete specimens (70mm×70mm×70mm) were cured at 20±2°C and RH= 95% for 28 days and then the specimens were subjected to freeze-thaw cycle. The samples amount was the same as chloride ion migration. The pore structure test was carried on after 50 freeze-thaw cycles. All pore structure test samples were taken at 0~15mm and 15~30mm separately from
the surface of specimens. The average pore size and pore size distribution of the cement paste samples were analyzed via mercury intrusion porosimeter (MIP).

3. RESULTS AND DISCUSSIONS

3.1 Change of chloride ion migration coefficient during freeze-thaw cycle

The macroscopic variation of chloride ion migration coefficient ($D_{RCM}$) during the whole freeze-thaw process needed to be understood before studying the influence of freeze-thaw cycle on chloride ion migration. Table 4 shows the concrete chloride migration coefficient variation in freeze-thaw process. The $D_{RCM}$ of concrete (Sample A, B, C and D) increased with the increasing freeze-thaw cycles. This proved that the $D_{RCM}$ varies during freeze-thaw cycle, rather than a constant value, and it was incorrect to use a constant $D_{RCM}$ in concrete durability design. However, macro-laws could only give a qualitative description of the freeze-thaw cycle affecting concrete chloride migration but it could not achieve the quantitative characterization. As we known, the concrete RDEM and mass loss during freeze-thaw cycle could be tested. It had a great significance for realizing the scientifically evaluation of structural concrete durability if the variation relationships between freeze-thaw process parameters and the development of $D_{RCM}$ were set up. Therefore, it is necessary to study the relationships between freeze-thaw parameters and $D_{RCM}$ during freeze-thaw process.

Table 4: chloride migration coefficient ($D_{RCM}$) of concrete subjected to freezing-thaw cycles / $\times 10^{-12}$ m$^2$/s

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Freezing and thawing cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>A</td>
<td>11.4</td>
</tr>
<tr>
<td>B</td>
<td>12.1</td>
</tr>
<tr>
<td>C</td>
<td>7.1</td>
</tr>
<tr>
<td>D</td>
<td>13.0</td>
</tr>
</tbody>
</table>

3.2 Relationships between freeze-thaw parameters and $D_{RCM}$

In this section, the concrete $D_{RCM}$ VS RDEM and $D_{RCM}$ VS mass loss during 0-300 freeze-thaw cycles were analyzed (Figure 1) in order to intuitively expressed the relationships between freeze-thaw parameters and $D_{RCM}$. The chloride ion migration coefficients of concrete (four different mix proportions) had some relative clear relationships with freeze-thaw parameters although the variation range of $D_{RCM}$ and freeze-thaw parameters were different. The $D_{RCM}$ changes of concrete (Sample A, B, C and D) were positive to the changes of mass loss, while the $D_{RCM}$ changes and RDEM changes were inversely proportional relationships. There was a decreasing trend of $D_{RCM}$ (Sample C) before 50 freeze-thaw cycles with the RDEM increasing and mass loss decreasing. After 50 freeze-thaw cycles, the development laws between $D_{RCM}$ and freeze-thaw parameters were the same as other Samples. The above study only gave the correspondence between $D_{RCM}$ and freeze-thaw parameters but the $D_{RCM}$ changes mechanism was still a theory without the test verification. There was water...
transportation in concrete during freeze-thaw process [3], and the chloride ion needed to migrate in water medium. It would provide the data and theoretical support to reveal the chloride ion migration time-dependent features if the influence of freeze-thaw cycle on chloride ion migration driving force was analyzed.

Figure 1: Relationships between freeze-thaw parameters and $D_{RCM}$

Notes: Solid line with spherical dot means time-dependent features of $D_{RCM}$ during freeze-thaw cycles in (x-RDEM, y-Mass loss, z-$D_{RCM}$) coordinate system. 2D dotted lines with spherical and triangle dot are projections of solid line in (x, y) and (x, z) coordinate systems respectively. 2D dotted lines mean relationships of $D_{RCM}$ VS RDEM and $D_{RCM}$ VS mass loss during 0-300 freeze-thaw cycles.

3.3 Influence of freeze-thaw cycle on driving force of chloride ion migration

There are two kinds of chloride ion in concrete, one is free chloride ion ($F_{Cl}^-$) and the other is bound chloride ion ($C_{Cl}^-$) [4]. In this section, $F_{Cl}^-$ was more important because the amount of cementitious material remained the same in concrete mix proportions and $C_{Cl}^-$ had been considered during $D_{RCM}$ calculation. Water has played an important role during freeze-thaw process. $F_{Cl}^-$ migrates into concrete in water medium, thus it is feasible to analyze the $F_{Cl}^-$ changes from the water transmission perspective. Capillary water absorption is an important parameter for water transmission which directly reflects the driving force of chloride ion
migration in concrete. Figure 2 (a) shows a concrete specimen used for testing the capillary water absorption and Figure 2 (b) shows the concrete capillary water absorption changes during the whole freeze-thaw cycle (height of capillary absorption at 1 hour is used as the testing indicator). The capillary absorption amount increased with freezing-thawing cycles increased. The absorption rate could be obtained by doing tangent line on capillary absorption curve (approximate representation with the tangent angle $\theta$). From Sample A to D, the capillary absorption rate increased with the freeze-thaw cycles increasing, this proved that the chloride ion migration driving force was growing. This test results were consistent with D$_{RCM}$ development during freeze-thaw cycle. But it was still macroscopic to analyze the influence of freeze-thaw cycle on chloride ion migration only from water transmission. Some scholars pointed that concrete microstructure could change during freeze-thaw cycle and analyzing the microstructure time-dependent characteristics was necessary for essentially revealing the influence of freeze-thaw cycle on chloride ion migration.

![Figure 2: Concrete capillary water absorption](image)

### 3.4 Concrete microstructure time-dependent characteristics during freeze-thaw cycle

In this section, concrete microstructure was tested after 50 freeze-thaw cycles because previous studies had found that concrete D$_{RCM}$ and capillary absorption properties appeared complicate at this time. Figure 3 shows the differential porosity changes of concrete (four mix proportions) during freeze-thaw cycle. Except Sample C, the porosity of Sample A, B and D increased after freezing-thawing cycles. The porosity increase of Sample A was the smallest. The capillary pore size (smaller than 100nm) had a creasing trend, while the big capillary pore (larger than 1000nm) number increased after 50 freeze-thaw cycles. S. Chatterji pointed that the hydrostatic pressure was released by air bubbles in concrete during freeze-thaw cycle, thus concrete deterioration degree was mitigated and porosity increase range decreased. A low W/C created more cement particles without hydration and they could continue hydration in water-saturated area during freeze-thaw cycle, thus the sample porosity decreased. After 50 freeze-thaw cycles, some hydration products could fill the capillaries (range of 100nm diameter) because of hydration reaction and the small capillary pore size decreased. The big capillary pore constantly filled with water during freeze-thaw process and they could continue grow under hydrostatic pressure effect, thereby the big capillary amount increased. The
reason of concrete microstructure changes during freeze-thaw cycle, the differences of capillary water absorption and chloride ion migration needed more in-depth analysis from mechanism.

Figure 3: Changes of concrete microstructure during freeze-thaw cycle

3.5 Influence mechanism of freeze-thaw cycle on concrete chloride ion migration

Figure 4 shows the schematic diagram of influence of freeze-thaw cycle on concrete microstructure and chloride ion migration. Before freeze-thaw cycle, there were some capillary pores and micro-cracks filled with water, while some closed bubble did not have water-filled due to the internal air pressure. $F_{Cl^{-}}$ migrated in those Unicom capillary pores and micro-cracks of cement paste. With the freeze-thaw cycle carried on, some cement paste capillary pores continued grow and the micro-cracks expanded due to the hydrostatic pressure, thus some closed bubbles became connection and chloride ion could migrate into bubbles or other microstructure using water as the transmission medium. At the same time, some small capillary pores and minor cracks were blocked by hydration products to make part of cement paste become dense, while the whole porosity of cement paste was increased. The analysis of microstructure changes mechanism here was consistent with test results in section 3.4. During freeze-thaw cycle, the porosity and Unicom degree of cement paste increased, the internal channels of chloride ion migration of cement paste increased, the capillary water transmission property enhanced and the chloride ion migration driving force enhanced. All these mechanism analysis above confirmed the view in section 3.3 and some macro-laws (such as test results in section 3.1 and section 3.2) were also explained.
4. CONCLUSIONS

- Freeze-thaw cycle affects the concrete chloride ion migration coefficient and the migration coefficient increases with the freeze-thaw cycle increasing.
- There are some relationships between chloride ion migration coefficient and freeze-thaw parameters. The development of migration coefficient and relative dynamic elastic modules is inversely proportional relationship and there is a positive relationship existence between chloride ion migration coefficient and mass loss.
- The concrete capillary absorption property and microstructure have changed during freeze-thaw cycle. Cement paste porosity increases and concrete capillary absorption property enhances during freeze-thaw process.
- The enhancement of water transmission driving force caused by capillary pore structure variation is the main reason for concrete chloride ion migration changes during freeze-thaw cycle.

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