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STUDY ON THE CHLORIDE DIFFUSION COEFFICIENT CALCULATED FROM A SIMPLE ACCELERATED CHLORIDE PENETRATION TEST USING ELECTRICITY

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ABSTRACT

There are many reports on the durability of concrete structures affected by chloride-induced reinforcement corrosion in Japan. The penetration speed for chloride damage is evaluated using the chloride diffusion coefficient, which varies depending on mix proportion, cement type and admixture type. In general, the diffusion coefficient has been given as a function of the water-cement ratio or by experiment. An immersion experiment is usually carried out by soaking a specimen in salt water, but this method requires a long immersion period. On the other hand, electrophoresis examination can be carried out in a short period of time, but as this method is performed in the steady state the results may differ from the actual phenomenon.

In this research, an evaluation method is proposed for the unsteady state by inducing chloride ion movement with electricity. This method calculates the diffusion coefficient in the unsteady state by measuring the penetration depth of the chloride ions up to the time when electricity supply was stopped, and various cement types were examined such as normal (N), early strength (H), low heat (L), blast-furnace slag cement type A (BA), type B (BB), type C (BC) and fly-ash cement type B (FB). Not only could the diffusion coefficient be calculated from the chloride ion depth, but this calculation could be carried out for periods as short as 24 hours. The variation in diffusion coefficient by cement type was also verified. Overall, it is believed that this method can calculate the chloride ion coefficient in the unsteady state in a short period of time.

Keywords: chloride diffusion coefficient, electrophoresis examination, cement type, accelerated chloride penetration test, depth of chloride ion.

1. INTRODUCTION

Concrete structures may deteriorate due to chloride damage, so it is important to predict the progress of chloride penetration in concrete. However, in order to predict the chloride penetration...
depth, the chloride ion diffusion coefficient in concrete must be clarified. According to the JSCE Standard Specification for Concrete Structures 2012: DESIGN, there are three methods for determining the chloride ion diffusion coefficient. The first method uses a prediction equation based on the water-cement ratio and type of cement. The second is based on an experiment, such as the penetration test or the accelerated penetration test using electricity. The third method is from the measurement of penetration in actual structures. However, there are problems with each method: the predication equation is limited to the cement types calculated in the equation; the penetration test requires a long experimental period; and data from the accelerated penetration test with electricity are for the steady state, but it is unclear the difference in the mechanism between penetrating chloride ions measured in the steady state and the non-steady state of real concrete structures. However, a non-steady state electrophoretic test, NT BILUD 492 of NORDTEST, has been proposed. This test takes less time and is less complicated than the steady state electrophoretic test, and the Public Works Research Institute (PWRI) in Japan suggest applying the non-steady state electrophoretic test for determining the chloride ion diffusion coefficient from the penetration depth of the chloride ions.

In this study, the chloride ion diffusion coefficient over time was calculated using the calculation formulas of NT BILUD 492 and the PWRI method for a variety of different cement types, and the proper electricity supply time for calculating the chloride ion diffusion coefficient was determined.

2. OUTLINE OF EXPERIMENT

2.1. Concrete mix proportion and specimens

Table 1 shows the concrete mix proportions used in this experiment. Only the type of cement was varied, with the investigated types being N (ordinary Portland cement), BA, BB, BC (blast furnace slag cement type A, B, C), H (early strength Portland cement), L (low heat Portland cement) and FB (fly-ash cement type B). The water-cement ratio and unit water weight were kept constant. Cylinder specimens of the size φ100x200 mm were cast and and de-molded the day after casting. After 28 days of water curing, specimens were cut into four φ100x50 mm sections and the two sections from the center of the specimen were used for the experiment. Pre-treatment was then carried out by saturating the test pieces in a vacuum with a calcium hydroxide solution.

2.2. Non-steady state electrophoretic test

Figure 1 shows the outline of the experimental apparatus for the non-steady state electrophoretic test. 0.3N of the NaOH solution was placed on the anode side and 3% NaCl solution on the cathode side. A 30V direct electrical current was applied for 3, 6, 12, 18, 24, and 36 hours. After each electricity supply time, test specimens were removed from the electrophoretic test apparatus, then cut in half and sprayed with a 0.1N silver nitrate solution on the splitting surface area. The depth of the chloride ion penetration was then measured from the white area.
Table 1: Mix proportion

<table>
<thead>
<tr>
<th>Cement Type</th>
<th>W/C (%)</th>
<th>s/a (%)</th>
<th>Unit weight (kg/m³)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>W</td>
<td>C</td>
<td>BFS</td>
</tr>
<tr>
<td>N</td>
<td>313</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H</td>
<td>313</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>L</td>
<td>313</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BA</td>
<td>219</td>
<td>94</td>
<td>-</td>
</tr>
<tr>
<td>BB</td>
<td>188</td>
<td>125</td>
<td>-</td>
</tr>
<tr>
<td>BC</td>
<td>92</td>
<td>219</td>
<td>-</td>
</tr>
<tr>
<td>FB</td>
<td>250</td>
<td>-</td>
<td>63</td>
</tr>
</tbody>
</table>

Figure 1: Schematic of the electrophoretic test

3. RESULTS AND DISCUSSION

3.1. Experimental results

Figure 2 shows the relationship between the electricity supply duration and penetration depth of chloride ion for the different cement types. As the duration become longer, the penetration depth of chloride ion increased regardless of cement types. The final penetration depth increased in the order of L, FB, H, N, BA, BB and BC. The depth was the same for N and H cements regardless of the electricity supply time. For L and FB cements, the splitting face was completely white after 18 and 36 hours, respectively, which indicates that the chloride ion has penetrated the entire surface (depth of 50 mm). Therefore, the measurement results at 12 and 24 hours were used. For the other cements, the penetration depth of chloride ion did not reach 50 mm even after 36 hours, but could be seen to increase almost linearly over the experiment duration. When focusing on the replacement ratio of blast furnace slag, it can be seen that the penetration depth of chloride ion over the same duration is reduced with an increase in the replacement ratio.
3.2. Comparison of diffusion coefficient calculation methods

3.2.1. Calculation methods

The chloride ion diffusion coefficients calculated using the NT BUILD 492 and PAWI methods were compared for the different cement types. Equations (1) to (3) show the calculation formula for NT BUILD 492, and Equation (4) shows the PWRI calculation method.

\[ D_{\text{nsmm}} = \frac{RT}{zFE} \cdot \frac{X_d - \alpha \sqrt{X_d}}{t} \]  

\[ E = \frac{U - 2}{L} \]  

\[ \alpha = 2 \cdot \frac{RT}{zFE} \cdot \text{erf}^{-1}\left(1 - \frac{2C_d}{C_0}\right) \]

Where, \( D_{\text{nsmm}} \): non-steady-state migration coefficient, m\(^2\)/s; \( z \): absolute value of ion valence, for chloride, \( z = 1 \); \( F \): Faraday constant, \( F = 9.648 \times 10^4 \text{ J/(V·mol)} \); \( U \): absolute value of the applied voltage, V; \( R \): gas constant, \( R = 8.314 \text{ J/(K·mol)} \); \( T \): average value of the initial and final temperatures in the anolyte solution, K; \( L \): thickness of the specimen, m; \( x_d \): average value of the penetration depths, m; \( t \): test duration, seconds; \( \text{erf}^{-1} \): inverse of error function; \( C_d \): chloride concentration at which the colour changes, \( C_d \approx 0.07 \text{ N} \) for OPC concrete; \( C_0 \): chloride concentration in the catholyte solution, \( C_0 \approx 2 \text{ N} \).
\[
D = k \cdot \frac{RT}{zF} \cdot \frac{L}{\Delta \Phi}
\]

(4)

Where, \( D \): Diffusion coefficient, \( m^2/s \); \( k \): ratio of penetration depth on chloride ion, \( m/s \), \( \Delta \Phi \): absolute value of the applied voltage, \( V \)

3.2.2. Effect of cement types

Figure 3 compares the chloride ion diffusion coefficients calculated by both methods. For the NT BUILD 492, the diffusion coefficient was calculated from the 24-hour penetration depth. On the other hand, when using the PWRI method, the diffusion coefficient was calculated based on the 3 to 24 hour period. Normally, the chloride ion concentration \( (C_d = 0.07N) \) of the white area can only be applied to concrete using Ordinary Portland cement for NT BUILD 492. However, in this study the same \( C_d \) was applied to all cement types to examine whether NT BUILD 492 can be applied to various cement types.

For all cements excluding L, the calculated diffusion coefficient was nearly the same for both methods. From these results, the difference between the diffusion coefficient calculated using NT BUILD 492, based on only a single penetration depth point, and the coefficient calculated from the PWRI method, which uses a penetration rate based on two points, appears to be small.

Furthermore, the diffusion coefficient for BA, BB, and BC (concrete with blast furnace slag cement) may be smaller than the diffusion coefficient for N due to the dense void structure and immobilization of chloride in the cement hydrate. Overall, the non-steady state electrophoretic method appeared to be a superior means for evaluating the diffusion coefficient for different blast
furnace slag cement content ratios as compared with the previous methods such as chloride penetration test and steady state electrophoretic method.

3.2.3. Change in diffusion coefficient over time

Figure 4 shows the change over time of the diffusion coefficient calculated using NT BUILD 492. For this calculation, the results of L and FB were excluded because the chloride ion appeared to reach a depth of 50 mm in the specimen. As time increased the diffusion coefficient grew smaller for each cement type. The results in Figure 3 showed the diffusion coefficient as a constant rate, but the diffusion coefficient calculated from the penetration depth was actually not constant. Further research work is necessary to understand this phenomenon.

![Figure 4: Change in diffusion coefficient over time](image)

4. CONCLUSION

The results of this research are summarized as follows:

1) For each cement type, the diffusion coefficients calculated using the NT BUILD 492 and the PWRI method were found to be similar.

2) The diffusion coefficient calculated using the NT BUILD 492 became smaller over time.

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