Experimental Research on the Distribution of Chloride Ion Migration in Concrete Cover during Electrochemical Chloride Extraction Treatment

Jianghong Mao¹, Kaiqi Yu¹, Yidong Xu¹,*, Xixi Wu², Weiliang Jin¹,², Chen Xu², Chonggen Pan¹

¹Ningbo institute of Technology, Zhejiang University, Ningbo 315100, China; ²Institute of Structural Engineering, Zhejiang University, Hangzhou 310058, China

*E-mail: xyd@nit.zju.edu.cn

Received: 14 February 2016 / Accepted: 18 March 2016 / Published: 1 April 2016

Electrochemical chloride extraction (ECE) technology can effectively remove chloride ions inside concrete cover and can improve the durability of reinforced concrete (RC) structures. The distribution of chloride ion migration during ECE treatment should be studied further. This paper focused on two research topics. The first topic was how chloride ions became distributed from the electro migration over time, especially during short term ECE treatments. The second topic was how the chloride ions distributed along the depth of the concrete cover. A special ECE treatment device was designed to establish electric field of chloride removal in order to obtain desirable effects. It was found that the most efficient period of treatment occurred in the first few days. Thus, indoor experiments could be useful for determining the end time of ECE treatment. Also, relatively higher amounts of chloride ions in surface concrete were observed, and therefore, the long-term durability of concrete after ECE treatment should be examined.

Keywords: reinforced concrete structures; concrete durability; electrochemical chloride extraction; spatial characteristics

1. INTRODUCTION

Chloride from seawater or de-icing salts can penetrate into concrete and induce corrosion. In many countries, chloride-induced rebar corrosion is regarded as the most common type of reinforced concrete structure degradation [1-4]. Transportation agencies annually spend billions of dollars on the construction and maintenance of concrete bridges, and the US national bridge inventory includes numerous reinforced concrete structures that are exposed to either corrosive salt conditions of marine environments or cold-climates [5]. Consequently, improving the durability of reinforced concrete (RC)
structures during service life is important. Electrochemical rehabilitation is an effective method for enhancing the durability of RC structures. Types of this method include cathodic protection (CP), electrochemical re-alkalization (ER), electro deposition technique, electrochemical chloride extraction (ECE), inhibitor electro migration anticorrosion technology[6-9].

Of the above electrochemical rehabilitation methods, ECE is the widely used. Many researchers have found that there were spatial variations in the chloride distribution of concrete during ECE treatment. Pérez [10] used a 20mm thick conductive cement paste anode for ECE treatment and discovered that a high proportion of the chloride ions accumulated around the anode. Wang [11] found that the chloride content in the area close to concrete surface was lower than in the area around the first steel-bar layer. Garces [12] found that the extraction efficiency depended on the reinforcing bar arrangement; a uniform layer set-up could benefit chloride extraction. Cañón [13] discovered that the efficiency of chloride extraction in the area around the steel-bar (close to 100%) was higher than that in the area close to concrete surface (about 79%).

As well, some scholars have suggested that the efficiency of chloride extraction is related to time. Using a conductive cement paste with carbon fibers, Pellegrini found chloride contents of 0.22% (1.0 cm from the steel-bar) after 21 days of ECE and free extractions of chlorides up to 90.4% [14]. Swamy [15] discovered that a large amount of chlorides was removed in the first 15 to 20 days during the ECE treatment and after, the chloride extraction remained relatively steady. Orellan [16] demonstrated that chloride was reduced by 40-45% within 7 weeks of ECE treatment. After applying 1 A/m² for 90 days, Fajardo[17] found that the chloride content was decreased by 30% (5 cm concrete cover depth) to 75% (2 cm concrete cover depth). Sánchez [18] found that 3 months of ECE treatment resulted in an efficiency of the chloride removal of 55%. Carmona [19] discovered that the average reduction in chloride was 51% of the initial content, for a relatively low charge density of 1.5 × 10⁶ C/m² relative to concrete surface during ECE treatment. They also found that extending the time of ECE treatment time did not significantly increase chloride extraction.

These above studies highlight the effectiveness of ECE treatment in reducing the chloride content in concrete and promoting the durability of RC structures. However, the relationship between chloride extraction content and time during short term ECE treatment has not been studied. In this paper, an experimental method was designed in order to study the spatial distribution of chloride through the concrete and how time of the ECE treatment influenced the efficiency of chloride removal. The efficiency of extracting chloride ions remained at a high level for the first four days, and then, the mobile chloride content decreased. Meanwhile, a non-uniform distribution of residual chloride inside the concrete cover was also found.

2. EXPERIMENT DESIGN

2.1. Design of ECE treatment device

In order to establish electric field for chloride removal, the width of the ECE treatment device was designed to be as small as the diameter of the steel bar with the hope of reducing the influence of
chloride ions around the steel bar on the experimental results. The steel bar inside the concrete was connected to the cathode of direct current (DC) power; meanwhile, the stainless steel net set-up on the outer surface of concrete was connected to the anode. Finally, an electric field was generated between the steel bar and the stainless steel net. With the drive of the electric field force, chloride ions inside the concrete migrated towards anode. A schematic of the device for ECE treatment is shown in Fig.1:

![Figure 1. A schematic of the device for ECE treatment](image)

The pH value influences the efficiency of ECE treatment, and therefore, the pH should be greater than 9 during the whole process of ECE treatment. In these experiments, the pH was periodically checked. Once the pH value dropped below 9, the solution was changed. The direct current density was 1 A/m², and thus, the direct current was kept constant at 0.023A.

2.2. Design of concrete specimen

The size of the concrete specimen was 150mm×150mm×150mm (length×width×height). The 20 mm diameter steel bar was embedded into the concrete. The concrete cover was 20 mm. The length of steel bar was 250 mm, and thus, 50 mm of the steel bar were available for connection to the cathode. The chloride ions were added to the concrete during casting by mixing in NaCl powder at 3% of the Portland cement. The ratio of water: cement: sand: stone was 1:0.52:1.94:3.19.

This paper focused on two research topics. The first topic was how chloride ions became distributed from the electro migration over time, especially during short term ECE treatments. The second topic was how the chloride ions distributed along the depth of the concrete cover. In order to analyze the chloride ions along the depth, concrete specimens needed to be drilled for Rapid Chloride Testing (RCT) at different time points of ECE treatment. Thus, 24 reinforcement concrete specimens were cast for this experiment. All specimens were divided into 8 groups, and three specimens were set as parallel samples for each group. After a designated ECE treatment time, the three specimens in each group were taken away for RCT. The initial chloride ion concentrations of each group are listed in Table 1:
Table 1. Initial chloride ion concentrations

<table>
<thead>
<tr>
<th>Group number</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl (%)</td>
<td>0.1535</td>
<td>0.1951</td>
<td>0.1903</td>
<td>0.1782</td>
<td>0.1785</td>
<td>0.1506</td>
<td>0.1583</td>
<td>0.1872</td>
</tr>
</tbody>
</table>

Note: % is the mass percent of chloride ions to cementing materials

After curing for 28 days, ECE treatment was applied to each group. The numbers of days of ECE treatment for specimens in group A through group H are as follows: one, two, three, four, five, six, seven, and eight days, respectively.

2.3. Design of chloride ion concentration testing

In order to determine the chloride ion distribution along the depth of the concrete cover, concrete powders were precisely extracted at different depths. A machine with a 10mm diameter bit was used for drilling. A vernier caliper was applied to measure the drilling depth, and the drilling was performed in 5 mm increments. In order to avoid mixing of powder from different depths, the bit was cleaned and the drilled hole was cleaned with a blowing ball before extracting the next sample. Two grams of the powder were accurately weighed and were added to 20.0 g of deionized water in bottles. The bottles were sufficiently oscillated. Finally, after 24 hours, the chloride ion concentration was measured by a Chloride-Meter DY-2501 machine.

3. RESULTS AND DISCUSSION

3.1. Chloride ion extraction range

The main purpose of this study was to determine the distribution of chloride migration during the ECE treatment. A small size ECE treatment device was designed. In order to investigate the validity of the ECE treatment device for establishing electric field, the chloride ion concentration around steel bar was measured. The positions of the sampling points are shown in Figure 2.

Figure 2. Distribution of sampling points: I, II, III, and IV.
Sampling points I were located far away from the steel bar, and hence, the chloride ions of sampling points I were considered the initial values of each sample. Sampling points II were located just below the ECE treatment device and determining the chloride ions at this point was the main research objective of this paper. Sampling points III and IV were located 2.0 cm and 4.0 cm, respectively, away from the surface of the steel bar. The powders collected from the three drilled holes were mixed together and marked as a sampling point. The chloride ions were measured by RCT, and the results are shown in Figure 3.

The results from sampling points I are listed in Table 1. As observed in Figure 3, the residual chloride ion concentrations of sampling points II were obviously lower than those of sampling points III and IV. The residual chloride ion concentrations of sampling points III and IV were very similar and were also close to the values of sampling points I. These results indicated that the chloride ions in the concrete that were far away from the ECE device did not migrate into the device. Alternatively, the affected area of the electric field in this paper was only distributed between the device and the steel bar. Furthermore, the conclusion that the ECE efficiency of sampling points II was higher than those of sampling points III and IV could be arrived. Chloride extraction decreased as the increasing of the distance from the steel-bar. It agreed with the results in paper [20] which explained that the decrease of ECE efficiency was attributed to the loss of electric potential.

3.2. Relationship between Cl\textsuperscript{-} extraction and ECE time

During ECE treatment, the chloride ions between the steel-bar and the electrochemical device had migrated to different degrees in the solution. In order to conveniently analyze the distribution of chloride ion migration, the concrete cover was divided into four layers along its depth. The depth for each layer was 5.0 mm. The residual chloride ion concentration was measured by the RCT test for each layer. The mass of residual and initial chloride ions was calculated by equations (1) and (2):

\[
G = m \cdot c \quad \text{and} \quad G_0 = m \cdot c_0
\]
$G$ is the mass of residual chloride ions in each concrete layer after ECE treatment (g); $c$ is the residual chloride ion concentration (%); $G_0$ is the mass of initial chloride ions in each concrete layer before ECE treatment (g); $c_0$ is the initial chloride ion concentration (%); $m$ is the mass of each concrete layer (g).

Thus, the percentage of chloride ions ($x_i$) migrating out of each concrete layer was calculated by equation (3):

$$x_i = \frac{G_0 - G}{G_0} = \frac{C_0 - C}{C_0}$$

(3)

With these formulas, the variation of the removal of chloride ions with time and depth was uncovered. The results are shown in Fig.4:

**Figure 4.** The relationship between the concentration of extracted Cl$^-$ and ECE time

As shown in Fig.4, most of the chloride ions in the concrete cover below the device migrated out within the first four days. The percentages of chloride ion extraction were 67.89%, 75.81%, 78.23% and 83.78% for 0.5cm, 1.0cm, 1.5cm and 2.0 cm, respectively. After four days, the extraction percentage did not increase with time. It was similar with the results in paper [15]. The paper discovered that a large amount of chlorides was removed in the first 15 to 20 days during the ECE treatment and after, the chloride extraction remained relatively steady. The peak value for removal of chlorides was day 3. Thus, long-term ECE operation was not necessary for this kind of experiment. However, this high efficiency ECE treatment period could be different for individual specimens since the ECE efficiency is dependent on variables such as concrete cover thickness, concrete density, and permeability. The results led us to then determining the end time of ECE treatment by conducting similar indoor experiments.
3.3. Variation of Cl⁻ extraction with depth

As shown in Fig. 4, the extraction percentages of chloride ions in each layer were distinct. The ECE efficiency statistics of each layer for the first four days are listed in Table 2:

<table>
<thead>
<tr>
<th>Region</th>
<th>ECE Time</th>
<th>Percentage of Cl⁻ extraction / %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 d</td>
<td>2 d</td>
</tr>
<tr>
<td>0.0 cm - 0.5 cm</td>
<td>29.25</td>
<td>48.25</td>
</tr>
<tr>
<td>0.5 cm - 1.0 cm</td>
<td>46.64</td>
<td>56.09</td>
</tr>
<tr>
<td>1.0 cm - 1.5 cm</td>
<td>49.32</td>
<td>62.49</td>
</tr>
<tr>
<td>1.5 cm - 2.0 cm</td>
<td>54.53</td>
<td>65.92</td>
</tr>
</tbody>
</table>

There was a negative correlation between the ECE efficiency and depth from concrete surface for each ECE period. Alternatively, the ECE efficiency was higher in the regions that were closer to the steel bars. The chloride ion extraction percentage at 2.0 cm depth was significantly higher than that at 0.5 cm depth. The authors of paper [13] also found that the ECE efficiency in the area around the steel-bar (the efficiency closed to 100%) was higher than that in the area close to concrete surface (the efficiency closed about 79%) in four interrelated studies.

4. CONCLUSIONS

At present, ECE treatment is the main method for improving the durability of RC. However, there are few experimental studies that focus on the relationship between ECE treatment efficiency and time as well as between ECE treatment efficiency and depth from the concrete surface. In this paper, an ECE treatment device was designed for ECE experiments, and the main conclusions were as follows:

1) A special ECE treatment device was designed to establish electric field for chloride removal. It was found that chloride ions that were far away from the ECE device could not migrate into the device. The device was found to be an effective tool for ECE research.

2) The most efficient period of ECE treatment was during the first few days, and thus, long-term ECE operation may not be necessary in some cases. Conducting similar indoor experiments, as in this paper, could be useful for determining the end time of ECE treatment.

3) A non-uniform distribution of chloride extraction was observed. The ECE efficiency was higher for the regions that were closer to the steel bars. Although it is good for concrete durability due to the low chloride ion concentration next to the steel bar, the relatively higher amounts of chloride ions in the other layers can permeate and diffuse to the regions around steel bar. Therefore, the long-term durability of concrete after ECE treatment should be examined.

4) The results of this paper could also guide the design of a novel concrete durability detecting sensor for chloride ions. The relationship between the chloride ions transferred to solution in ECE device with chloride concentration in concrete could be established by conducting the experiment...
proposed in this paper. Comparing with traditional Rapid Chloride Testing (RCT), no drilled holes were required, thus it could be a kind of non-destructive testing. The results in this paper demonstrated that the small size ECE device could control the chloride moving range and also short ECE period could be enough for chloride ions detecting.

ACKNOWLEDGMENTS
This study was supported by the National Natural Science Foundation of China (Grant No. 51408544, 51408534, 51578490, 51541904), the Natural Science Foundation of Zhejiang Province (Grant No. LQ14E080007, LY15E080025) and the Ningbo Scientific and Technological Innovation Team (Grant No. 2011B81005).

References


© 2016 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).