MICROSTRUCTURE AND MECHANISM OF CRACKS REHABILITATION IN REINFORCED CONCRETE USING ELECTRODEPOSITION TECHNIQUE

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Abstract

This paper reports on the design of an experimental device for cracks rehabilitation in reinforced concrete, using an electrodeposition method, firstly. The composition and microstructure of the electrodeposits in cracks and the crack healing effectiveness were studied. The Effect of current density on the microstructure of crystals, deposited in the cracks was investigated and the electrodeposition mechanism of crack healing was discussed. The results indicate that the Composition of the electrodeposits differs depending on the used electrolytes. Current density plays an important role on healing effectiveness of concrete cracks. The Mg(OH)$_2$ crystals produced in high current density regimes are large, lamellar and arrange loosely. The crack healing mechanism lies in that electrodeposits produced by cell reaction induce into nucleation and form insoluble crystals in cracks, and consequently the electrodeposits fill and heal concrete cracks gradually.

1. INTRODUCTION

Reinforced concrete (RC) is a widely used construction material for buildings, bridges, hydraulic constructions and marine projects etc. in the world. However, RC structures will usually crack inevitably in their service life under the influence of the surrounding environment, due to erosion, which will significantly reduce load bearing and durability of RC structures [1]. So, it is necessary to rehabilitate or repair them. Depending on the causes for crack initiation and the environmental conditions, various repair methods such as: embedding reinforcement, anchoring, grouting, sealing and concrete replacement etc. are proposed [2-6]. However, these methods show certain limitations for repairing cracks in RC structures in water environment. It is of great practical significance to develop new non-destructive rehabilitation methods for underwater concrete structures. The electrodeposition method is one of the newly developed methods for rehabilitation of cracks in underwater RC [7-10]. It
takes advantage of the character of RC and water environment condition. A weak direct current is exerted between rebar in RC structures and an external electrode (an anode) and produce electrodeposits around rebar in RC, which will form a barrier coating of inorganic insoluble compounds such as ZnO, CaCO$_3$ and Mg(OH)$_2$ etc. in cracks and surfaces, fill up cracks and seal surfaces of RC. These barriers not only provide a physical layer protection, but can also effectively minimize the migration and transmission of the gas-liquid medium into the concrete matrix. In recent years, several literature studies [7, 10-14] reported on this topic, namely the feasibility, the mechanism and the experimental control of cracks rehabilitation in RC, using the electrodeposition method.

In this paper, an experimental device of electrodeposition method for rehabilitation of cracks in reinforced concrete was first proposed. Composition and microstructure of electrodeposits in cracks were studied. And electrodeposition mechanism of crack healing was discussed and proposed.

2. EXPERIMENTAL PROGRAM

2.1 Raw materials and Mix proportions of concrete

The cement used in the experiment was Ordinary Portland cement with strength grade 32.5 in accordance with Chinese standard. Coarse aggregate with maximum diameter size of 16 mm was used. Fine aggregate was river sand with the modulus of fineness of 2.5. The water reducing admixture used in this experiment is naphthalene-based superplasticizer. The concrete’s mix proportions are shown in Table 1; slump of fresh concrete is 150±10mm.

<table>
<thead>
<tr>
<th>Mix proportion(kg/m$^3$)</th>
<th>Compressive strength(MPa)</th>
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<tbody>
<tr>
<td></td>
<td>3d</td>
</tr>
<tr>
<td>Water</td>
<td>175</td>
</tr>
<tr>
<td>Cement</td>
<td>750</td>
</tr>
<tr>
<td>Sand</td>
<td>1125</td>
</tr>
<tr>
<td>Coarse aggregate</td>
<td>750</td>
</tr>
<tr>
<td>Water-reducing admixture</td>
<td>2.8</td>
</tr>
</tbody>
</table>

2.2 Specimen preparation

The dimensions of the RC specimens were 100×100×200 mm. The reinforcement cages were made with plain rebar with a diameter of 8 mm as vertical rebar, and 6mm as the hoop reinforcement part. The reinforcement cages were fixed in the middle of the specimens. The concrete cover depth was 20 mm. The schematic illustration of the reinforcement cage and its location in the specimens are shown in Fig.1. In order to simulate concrete cracks in the actual environment, splitting load-induced cracks of 0.3 ~ 1.5 mm in width through the concrete (deep into the reinforcement cage surface) were made in all specimens after curing in the standard conditions of: temperature of 20±3°C and relative humidity above 90% for 28 days. It is critically important for this experiment to guarantee cracks penetrate the surface of the rebar.
2.3 Design of an experimental device for electrodeposition method

The cracked RC specimens were placed in a container filled in with electrolyte solution. Based on previous experimental results \cite{12-14}, Mg(NO$_3$)$_2$ and ZnSO$_4$ were chosen as the electrolyte, and the concentration of the solution was controlled as 0.05mol/L. Flexible graphite plate was selected as external anode material and was placed on the bottom of the container. A regulated DC power supplier with voltage range from 3 to 36V was used as the power and its positive pole connected the anode of graphite plate, while the negative pole connected rebar in the specimen. The diagrammatic sketch of experimental device for crack rehabilitation using electrodeposition is shown in Fig. 3. The current density of the circuit was controlled in two series of 0.5A/m$^2$ and 1.0A/m$^2$ by adjusting the voltage of the supplier. The current density was calculated based on the total surface area of rebar. The experiment was kept in the constant environment conditions with the temperature of 20±3°C and lasted for 8 weeks. The electrolyte solution was replaced every two weeks.

2.4 Testing methods

The specimens were taken out after deposited for 8 weeks, and then the electrodeposits in the cracks were sampled. XRD analysis method is used to analyze crystal composition of electrodeposits. SEM and EDX methods are used to analysis microscopic pattern of the electrodeposits.
3. Results and discussion

3.1 Composition analysis of electrodeposits resulting from different electrolyte solutions

3.1.1 Mg(NO$_3$)$_2$ solution

Figure 3: XRD analysis of the electrodeposits in cracks of specimens immersed in Mg(NO$_3$)$_2$ solution

Figure 4: EDX spectrum of the electrodeposits of specimens immersed in Mg(NO$_3$)$_2$ solution

XRD analysis and EDX spectrum of electrodeposits of specimens immersed in Mg(NO$_3$)$_2$ solution are shown in Fig.3 and Fig.4. From the XRD analysis, it can be seen that Mg(OH)$_2$ is the essential composition of the electrodeposits. And the element analysis from EDX spectrum shown in Fig.5 supports the results of XRD.
3.1.2 ZnSO₄ solution

![XRD analysis of electrodeposits in cracks of specimens immersed in ZnSO₄ solution](image1)

**Figure 5 :** XRD analysis of electrodeposits in cracks of specimens immersed in ZnSO₄ solution

![EDX spectrum of electrodeposits in cracks of specimens immersed in ZnSO₄ solution](image2)

**Figure 6 :** EDX spectrum of electrodeposits in cracks of specimens immersed in ZnSO₄ solution

XRD analysis and EDX spectrum of electrodeposits in ZnSO₄ solution are shown in Fig.5 and Fig.6. From the XRD analysis in Fig.5, it can be seen that ZnO is the essential composition of the electrodeposits. As shown in Fig.6, the element composition of electrodeposits analyzed from EDX spectrum is in accordance with the results of XRD. It also
shows that Ca element exists in the electrodeposits. It mainly comes from the leaching of Ca(OH)$_2$ in the concrete.

3.2 Microstructure of electrodeposits

From the SEM micrographs of Fig.7, it can be seen that microstructure of most of Mg(OH)$_2$ crystals in cracks is lamellar or massive. Mg(OH)$_2$ crystal with a lamellar structure usually has high strength and inelasticity while the massive ones has low strength. A small amount of Ca(OH)$_2$ with hexagonal platy structure can also be found in the electrodeposits. From the SEM micrographs (after applying different current density), the dimensions of the electrodeposited crystals increase and their thickness decreases. Mg(OH)$_2$ crystals produced in high current density are large, lamellar sheet and arrange loosely. Mg(OH)$_2$ crystals produced in low current density are small, thick sheet and arrange tightly due to low electrodeposition rate. It indicates that rapid electrodeposition under high current density will result in low-strength precipitated electrodeposits, while slow electrodeposition under low current density will form compact precipitated electrodeposits with high strength.

![Example of SEM micrographs](image)

(a) 0.5A/m$^2$ current density   (b) 1.0A/m$^2$ current density

Figure 7: SEM micrographs of electrodeposits obtained under different current densities

The compressive strength of the electrodeposits ranges up to 80MPa, and most of them range from 37 to 55MPa which is higher than that of normal concrete [10]. The strength of electrodeposition layer decreases with electrodeposition rate. Any factor that influences the nucleation process of electrodeposit plays an important role in electrodeposition process. It shall be noted that some other factors such as concentration of electrolyte solution, voltage and ionic activity take a certain effect on electrodeposition as well as current density.

3.3 Microstructure of interface zone between concrete and electrodeposits crack interface zone
As shown in Fig.8, electrodeposits in the crack have a dense structure, and grow along the wall surface of cracks in concrete specimen. It means that electrodeposits adhere to the surface of concrete tightly and it is proved that the use of electrodeposition technique to repair concrete cracks is not only feasible, but also effective.

3.4 Electrochemical mechanism of electrodeposition

Crack healing with electrodeposition technique imitate the mineral deposition process of organisms under natural abiotic environment. The voltage between anode and cathode builds up an electric field. By the effect of this electric field, the cell reaction happens among the electrodes. Meanwhile, the ions with different electric charge move to the counter charged electrode i.e.: positive ions move to cathode, and negative ions move to anode. Then the products of cell reaction react with positive ions around the rebar, which results in deposition of insoluble crystals. These electrodeposits will form a barrier of inorganic insoluble compounds such as ZnO, CaCO$_3$ and Mg(OH)$_2$ etc. in cracks and surfaces, which will fill and block cracks and seal surfaces of RC. Consequently, it is significant important for electrodeposition process to select appropriate electrodeposits in cracks and on the surface of concrete structure. In the process of electrochemical deposition, factors such as concentration gradient, attraction of ions and electro-migration may influence the rate of deposition on the cathode. Mostly, concentration gradient plays the critical role, but it is indispensable that three factors interact. The fundamental theoretical model of ions migration and reactions in electrodeposition process is generalized and shown in Fig.9 [9, 14].

Electrochemical deposition usually includes many complex processes. The major processes are summarized as follows [16]:

1) Electrochemical reaction process: ions lost or get electrons in the interface of electrode/solution and the electrodeposits produce. It is also a charge transfer process.

2) Mass transfer process of reactant and resultant: reactants transfer from solution to the surface of electrode, and resultants transfer from the surface of electrode to the solution or the interior of electrode.

3) Charging and discharging process of electric double layer of electrode surface.

4) Electromigration process of ions in the solution.

5) Chemical reaction and new phase’s production process.
The main problem of electrochemical reaction process to occur is to overcome the contradiction between energy of reaction particles and their activation energy peak. And the important influencing factors are electric-field intensity (namely, electrode potential), activity of reactant and actual surface area of electrode. The electrode potential is the driving force of electrochemical deposition [16].

Reactions among the electrodes are different from different anode materials and electrolyte solution. In this experiment, inert graphite is choose as anode and Mg(NO₃)₂ and ZnSO₄ is chosen as electrolyte. The reactions occurred on the electrodes are shown below:

Anode: 2H₂O-2e→O₂↑+2H⁺
Cathode: H₂O+2e→2OH⁻+H₂↑
Solution: Mg²⁺+2OH⁻→Mg(OH)_2↓
Zn²⁺+2OH⁻→Zn(OH)_2↓→ZnO↓+H₂O

3.5 Mechanism of crack healing

Pore solution in concrete containing many electrolytes is a weak alkaline solution. With the effect of direct current, electro-migration of ions happens in pore solution. In some case, concurrent electrodeposition happens among these ions.

Based on the study about mechanism of electrodeposition, electrochemical reactions and crack healing above, the mechanism of crack healing can be drawn as follows: with the effect of current, electrolytic reactions happen on the surface of the electrode. Ions in electrolyte and pore solutions move to two electrodes respectively. The resultants of these reactions are induced to nucleation in cracks and form crystal cells gradually. With the process of
electrochemical deposition, the crystal unit cells grow up crystals. Finally, the crystals accumulate, fill and heal cracks in concrete.

4. Conclusions

Based on the obtained experiment results and analysis, the following conclusions are drawn:

- Current density is an important factor on electrodeposition. Mg(OH)$_2$ crystals produced under high current density are large, thin sheet-shaped and arrange loosely. And Mg(OH)$_2$ crystals produced under low current density are small, thick sheet-shaped and arrange tightly.

- Electric potential difference between two electrodes is the driving force of electrodeposition. Electrodeposition usually includes several main processes such as electrochemical reaction process, mass transport process of reactant and resultant, charging and discharging process, electromigration process of ions and chemical reaction process.

- The mechanism of crack healing lies in that electrodeposits produced by cell reaction induce into nucleation and form insoluble crystals in cracks, and consequently the electrodeposits fill, block and heal concrete cracks.

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