Effects of electrochemical chloride extraction on the bonding properties of corroded reinforced concrete by the anode of magnesium phosphate cement bonding carbon fiber-reinforced plastics (CFRP)

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Abstract. This paper studied the effects of electrochemical chloride extraction (ECE) on the bonding properties of corroded reinforced concrete with the anode of Magnesium phosphate cement (MPC) bond CFRP. The results indicated that ECE can efficiently remove the chloride ions in the concrete. The interfacial bonding properties of steel-concrete decreased with the increase of chloride removal current density. Proper corrosion ratio of steel bars can reduce the bonding strength loss caused by ECE treatment.

1. Introduction
The most commonly form of deterioration of reinforced concrete is corrosion of reinforcement. The greatest threat for the corrosion of reinforcement is corrosion due to chloride. The passivation film of the steel bar can be destroyed by chloride ions, resulting in the corrosion of steel bar. The expansive corrosion products leads the concrete structure cracking and peeling, thereby reducing its service life [1]. The conventional repair methods for the corroded reinforced concrete structure is to determine the corroding areas and then replace the chloride-contaminated concrete with the repair mortar [2]. However, after reinforcement, the residual chloride ions continue to cause the corrosion of steel bar and the reinforcement effects is weakened.

ECE is a newly developed nondestructive method for preventing the corrosion of steel bar in concrete [3]. During the ECE process, an electric field is applied between the steel bar (the cathode) and an external electrode (the anode) placed in an alkaline electrolyte around the surface of concrete.

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Under the driving force of electric field, the negatively charged chloride ions migrate from the steel bar to the exterior electrode through the pores of concrete. Meanwhile, the cation migrates to the cathode, as shown in figure 1.

![Figure 1 Schematic diagram of ECE](image)

Currently, the commonly used ECE anode materials are mainly titanium mesh, wire mesh and cement-based conductive materials [4, 5]. In addition, for the corroded concrete structures, the method is ECE treatment first and then reinforcement, which is very intricate. Therefore, the integration method of chloride removal and strengthening was proposed. However, to achieve this method, the selection of the anode material is particularly important.

Magnesium phosphate cement (MPC) is a new inorganic cementitious material with excellent bonding strength, high early compressive strength, favorable volume stability and good corrosion resistance in low concentration alkaline solution [6, 7], which has been widely used in the field of repairment and reinforcement of building structures. CFRP is a good corrosion resistance, high specific strength and conductive material. Previous studies has confirmed the feasibility of using CFRP as anode for ECE treatment [8]. Therefore, MPC bonding CFRP (MPC-CFRP) is a potential composite anode material for ECE treatment.

This paper adopted MPC-CFRP as an ECE anode and studied the effect of ECE on the bonding properties of reinforced concrete with different corrosion degree after 28 days treatment in the Ca(OH)$_2$ electrolyte with the pH value 10 at three different current densities of 1.0 A/m$^2$, 2.0 A/m$^2$ and 3.0 A/m$^2$.

2. Experimental details

2.1 Raw materials

The MgO for the preparation of MPC directly calcined from magnesite at 1600°C, the used cement was P.O42.5, and their chemical compositions and physical properties are shown in table 1 and table 2, respectively. The coarse aggregates was continuous grading crushed stone with the particle size of 5~25mm. The fine aggregate was the siliceous sea sand with the chloride ions content of 0.113%. The superplasticizer was polycarboxylate superplasticizer with the water reduction rate of 31%. Tap water was used in concrete specimen and the deionized water was utilized to prepare the electrolytic solution. The involved chemical reagents, such as KH$_2$PO$_4$, Na$_2$B$_4$O$_7$·10H$_2$O, NaCl and Ca(OH)$_2$ were all chemically pure and the purity was larger than 99%. The round steel bar was plain carbon steel (Q235) with a diameter of 10mm. The morphology of the used CFRP is shown in figure 2. The thickness and surface density of CFRP are 0.19mm and 300g/m$^2$, respectively. Its ultimate tensile strength, elastic modulus and fracture strain are 4200 MPa, 210GPa and 0.02, respectively.

Table 1 Chemical composition and physical properties of calcined MgO
Table 2 Chemical composition and physical properties of cement

| Sample | MgO (%) | CaO (%) | SiO₂ (%) | Al₂O₃ (%) | Fe₂O₃ (%) | Density (g/cm³) | Bulk density (g/cm³) | Specific surface area (cm²/g) |
|--------|---------|---------|----------|-----------|-----------|----------------|----------------------|-----------------------------|
| MgO    | 91.7    | 1.4     | 1.6      | 4.0       | 1.3       | 3.46           | 1.67                 | 805.9                      |

Table 3 Materials proportions and physical properties of MPC

| P/M    | B (%) | W/C | Compressive strength (MPa) | Porosity (%) | Bond strength with C30 concrete at 28days |
|--------|-------|-----|---------------------------|--------------|----------------------------------------|
| 1/4.5  | 5%    | 0.14| ≥20                       | >30          | 15~18 Broken in Concrete matrix        |

Table 4 Proportions and properties of concrete

| Cement (kg/m³) | Aggregate (kg/m³) | Sand (kg/m³) | W/C ratio | Water Reduce (kg/m³) |
|----------------|-------------------|--------------|------------|----------------------|
| 325            | 1228              | 662          | 0.57       | 0.65                 |

2.2. Mix proportion design

2.2.1. MPC. The existing indicated that the properties of MPC with the molar ratio of KH₂PO₄/MgO (P/M), borax (B) and water binder ratio of W/C were 1/4~1/5, 4~8% and 0.14~0.16 were relatively good [9]. The proportions and physical properties of MPC in this paper are shown in table 3.

2.2.2. Concrete. The water-cement (W/C) ratio of the concrete is 0.57 and the materials proportions are presented in table 4. The chloride ions in sea sand, corresponds to 0.23% by weight of cement.

2.3. Laboratory studies

2.3.1. Preparation of concrete samples. The concrete was cast in a PVC mold with the size Ø100×200mm. A length of 250mm steel bar with the diameter of 10mm was centrally embedded in each sample and the embedded depth was 150mm. After demolding, the samples were cured 28 days at room temperature. Then, accelerated corrosion of the samples was conducted by the method of electrochemical technology, as shown in figure 3. The degrees of corrosion were set at 5%, 15% and
30% using Faraday's law. The corroded samples are shown in figure 4. Subsequently, MPC paste was spread evenly on the CFRP. Then the concrete sample was put on the MPC paste and rolled gently until completely wrapped, as shown in figure 5. After curing at room temperature for 7 days, all the samples were used to ECE treatment.

Figure 3 Electrochemical accelerated corrosion

Figure 4 The corroded concrete samples

Figure 5 Concrete sample

2.3.2 ECE treatment. The ECE device is shown in figure 6. Steel bar is the cathode, MPC-CFRP is the anode. To prevent the chlorine overflow from the Ca(OH)₂ electrolyte, the electrolyte is renewed every two days and the chloride ions concentration re-confirmed. In order to eliminate the influence of temperature change, the temperature of electrolyte was kept at 25°C by a heating rod. In addition, to prevent the evaporation of electrolyte, cling film covered the opening of the container. The current density ($i$) was applied by a DC regulated power supply.

Figure 6 Schematic diagram of ECE device

Figure 7 Experimental setup for pull-out tests

2.3.3 Pull-out test of steel bar. Interfacial bond properties were tested by pull-out test. Universal testing machine and reaction frame were used to induce tension on both ends of the column with the loading speed of 0.05MPa/min, as shown in figure 7.

3. Results and discussion
3.1 Chloride removal efficiency
After ECE treatment, the cumulative chloride removal efficiency of reinforced concrete calculated by equation (1) & (2) and the results are presented in Fig. 8.

\[
M = V_s \times M_L \times W \\
CT\% = \frac{M_C}{M} \times \sum C_i \times V_i \times 100\%
\]

Where, \(M\) is the initial chloride ions content of the reinforced concrete. \(V_s\) is the volume of each sample. \(M_L\) is the cement content ratio of each sample. \(W\) is the mass ratio of chloride ions and cement. \(M_C\) is the molar mass of chloride ions. \(C_i\) is the chloride ions concentration of electrolyte at two-day intervals. \(V_i\) is the volume of the renewed electrolyte.

![Figure 8 Chloride removal efficiency](image)

Figure 8 indicated that the chloride removal efficiency of concrete with different corrosion degree increased with the increase of current density. The chloride removal efficiency of concrete with the corrosion rate of 15% was relatively good at all current densities. When the current density was 3A/m\(^2\), the chloride removal efficiency was up to 58.62%.

3.2 Pull-out test of steel bar
After ECE treatment, the pull-out test of steel bar in different corrosion degree concrete is shown in figure 9. The bond strength loss of steel-concrete was calculated using equation (3) and the results are shown in table 5.

\[
\delta_{loss} = \frac{f_{max}}{f_{max}} \times \frac{f_0}{f_{max}} \times 100\%
\]

Where, \(\delta_{loss}\) is the bond strength loss. \(f_{max}\) is the maximum bond load of the natural corrosion. \(f_0\) is the maximum bond load of the concrete with the degree of corrosion of 5%, 15% and 30%.
Figure 9 Load-displacement curves of pull-out test of steel bar: (a) Natural corrosion, (b) The corrosion degree of 5%, (c) The corrosion degree of 15%, (d) The corrosion degree of 30%.

Table 5 The maximum bond load and bond strength loss of steel-concrete

| Corrosion degree | i (A/m²) | f_{max} (KN) | \delta_{loss} (%) |
|------------------|---------|-------------|-----------------|
| Nature corrosion |         |             |                 |
| 0                | 30.2    | —           |                 |
| 1                | 28.6    | 5.2         |                 |
| 2                | 26.5    | 12.1        |                 |
| 3                | 26.2    | 13.3        |                 |
| 0                | 25.6    | —           |                 |
| 1                | 24.8    | 1.6         |                 |
| 2                | 24.2    | 5.5         |                 |
| 3                | 22.2    | 13.1        |                 |
| 0                | 17.5    | —           |                 |
| 1                | 15.6    | 10.4        |                 |
| 2                | 16.2    | 7.1         |                 |
| 3                | 17.0    | 2.8         |                 |
| 0                | 12.9    | —           |                 |
| 1                | 11.9    | 7.7         |                 |
| 2                | 11.1    | 13.9        |                 |
| 3                | 7.1     | 44.8        |                 |
The pull-out curves and bond strength loss of the concrete with different corrosion degree are presented in figure 9 and table 5. The results indicated that the maximum bond load of steel-concrete without ECE treatment decreased with the increase of corrosion. After ECE treated, the bonding strength losses of the samples increased significantly with the increase of current density. When the current density was 3A/m², the bond strength losses of the concrete with natural corrosion, 5% corrosion degree and 30% corrosion degree were 13.31%, 13.11% and 44.8%, respectively. However, when the corrosion ratio of the sample was 15%, the bonding strength loss decreased with the increase of current density. The bond strength loss was decreased from 10.4% to 2.8% when the current density increased from 1A/m² to 3A/m². The results indicated that proper corrosion degree of 15% could reduce the interfacial bonding strength loss caused by ECE treatment.

4. Conclusion
(1) ECE treatment can efficiently remove the chloride ions in the reinforced concrete and achieve the wide application of sea sand by proper ECE parameters.
(2) ECE treatment has negative effects on the interfacial bond properties of steel-concrete. Proper corrosion degree of 15% can reduce the bonding strength loss caused by ECE treatment.

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