Study on the variation of electric potential in reinforced concrete members during accelerated corrosion and electrochemical chloride extraction process

T Y Hao\(^1\), Y Q Su\(^2,3\), Y Li\(^2\) and H Lin\(^2\)

\(^1\) Central Research Institute of Building and Construction Co., Ltd, 100088, China
\(^2\) The Key Laboratory of Urban Security and Disaster Engineering, MOE. Beijing University of Technology, 100124, China
\(^3\) E-mail: 2293015145@qq.com

Abstract. This paper mainly studies the corrosion potential and current of reinforced concrete beams during accelerated corrosion and electrochemical chloride extraction. The results show that the corrosion potential and current of concrete beams increase with the corrosion time. In the process of electrochemical chloride extraction, the corrosion potential and current of concrete beams decrease with the prolongation of chlorine removal time. Electrochemical chloride extraction can effectively reduce the corrosion rate of reinforced concrete components and reduce the corrosion risk of steel bars.

1. Introduction

Corrosion of steel bars is the main factor affecting the durability of reinforced concrete structures. Improving the corrosion resistance of steel bars is an important aspect in the durability study of reinforced concrete structures \([1]\). Chloride salt corrosion is the main cause of steel corrosion \([2-4]\). Chloride ions can destroy the passive film on the surface of steel bars and cause steel corrosion. The reaction equation is shown in (a) ~ (d). Expansive corrosion products caused by corrosion of steel bars lead to cracking or spalling of concrete structures, resulting in failure of reinforced concrete structures.

\[
\begin{align*}
Fe & \rightarrow Fe^{2+} + 2e \quad (a) \\
Fe^{2+} + 2Cl^- + 4H_2O & \rightarrow FeCl_2 \cdot 4H_2O \quad (b) \\
FeCl_2 \cdot 4H_2O & \rightarrow Fe(OH)_2 + 2Cl^- + 2H^+ + 2H_2O \quad (c) \\
4Fe(OH)_2 + O_2 + 2H_2O & \rightarrow 4 Fe(OH)_3 \quad (d)
\end{align*}
\]

At present, the measures to prevent steel corrosion in new concrete structures mainly include cathodic protection, epoxy coating protection on steel bar surface, coating on steel bar surface, impregnation and use of corrosion inhibitors \([5-7]\). For corroded reinforced concrete structures, the traditional method is to determine the corroded area by potential detection technology, determine the chloride concentration in the area, and remove the chloride contaminated concrete and repair it \([8]\). However, after reinforcement, the residual chloride ions in concrete will continue to cause steel corrosion, weakening the reinforcement effect, and can not repair and protect the concrete structure from the root \([9]\).

Electrochemical chloride extraction (ECE) is a new non-destructive repair technology to prevent reinforcement corrosion in concrete \([10, 11]\). The method uses steel bar as cathode and external anode. Under the action of electric field force, Cl\(^-\) moves directionally away from the reinforced concrete.
until leaving reinforced concrete, thus greatly reducing the free Cl\(^-\) concentration around the steel bar and reducing the risk of corrosion of the steel bar. The schematic diagram of ECE is shown in Figure 1.

![Schematic diagram of ECE.](image)

In the process of ECE, the anode reaction is as follows:

\[
4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e} \tag{e}
\]

\[
2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e} \tag{f}
\]

\[
2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e} \tag{g}
\]

The cathodic reaction is as follows:

\[
2\text{H}_2\text{O} + \text{O}_2 + 4\text{e} \rightarrow 4\text{OH}^- \tag{h}
\]

\[
2\text{H}_2\text{O} + 2\text{e} \rightarrow 2\text{OH}^- + \text{H}_2 \tag{i}
\]

At present, titanium mesh, steel wire mesh and cement-based conductive materials are commonly used as external anode materials for ECE [12, 13]. However, the cost of titanium mesh is high, steel wire mesh is easy to rust and pollute concrete in the process of ECE, and the performance of cement-based materials will deteriorate in the process of ECE. Magnesium phosphate cement (MPC) is a new type of inorganic cementitious material. It has been widely used in the repair and reinforcement of building structures because of its excellent bonding properties, early strength, volume stability and good corrosion resistance in low concentration alkali solution [14, 15]. CFRP has the characteristics of high strength, corrosion resistance and field construction convenience, and is often used for the repair and reinforcement of building structures [16]. CFRP may also be a potential anode material in ECE system because of its good conductivity and electrochemical performance [17]. Therefore, MPC bonded CFRP (MPC-CFRP) can not only reinforce corroded reinforced concrete structures, but also be used as an external anode for ECE. The problem of chloride ion residue in traditional reinforcement methods is solved from the root, and the integration of reinforcement and ECE of corroded reinforced concrete structures is realized.

In this paper, the corrosion potential and corrosion current of reinforced concrete beams during electrochemical accelerated corrosion were studied. After accelerated corrosion, with MPC-CFRP as external anode, the corrosion potential and current of reinforced concrete beams in saturated calcium hydroxide solution with current density of 3A/m\(^2\) and 28 days of ECE were studied.
2. Test overview

2.1. Raw materials
Magnesium oxide used to prepare MPC is obtained directly from magnesite calcined at 1600°C. Its chemical composition and related physical properties are shown in Table 1. The cement used is PO42.5 cement, and its chemical composition and related physical properties are shown in Table 2.

The coarse aggregate used is 5~25mm continuous graded crushed stone, and fine aggregate is river sand with fineness modulus of 2.56. The water reducing agent is polycarboxylate superplasticizer with a water reducing rate of 31%. The chemical reagents involved in the experiment, such as KH₂PO₄, Na₂B₄O₇·10H₂O, NaCl and Ca(OH)₂, were all chemically pure with purity greater than 99%. The yield strength of two kinds of steel bars, HRB400 and HPB300, are 308 MPa and 367 MPa respectively, and the ultimate strength is 447 MPa and 535 MPa respectively. The thickness of CFRP is 0.19 mm and the area density is 300g/m². The ultimate tensile strength, elastic modulus and fracture strain of CFRP are 4200 MPa, 210 GPa and 0.02, respectively.

| 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                    |

| Chemical composition (wt%) | Physical properties | Specific surface area (m²/kg) |
|---------------------------|---------------------|-----------------------------|
| Loss | SiO₂ | Fe₂O₃ | Al₂O₃ | CaO | MgO | SO₃ | Specific gravity (g/cm³) | |
| 2.12 | 22.9 | 3.8 | 5.7 | 63.5 | 2.2 | 1.9 | 3.16 | 354 |

2.2. Material mix design

2.2.1. MPC. According to the existing research, the mix design of MPC and the related performance of MPC are shown in Table 3.

| P/M | B | W/C | Compressive strength (MPa) | Porosity (%) | Bonding strength with C30 concrete of 28days |
|-----|---|-----|--------------------------|--------------|---------------------------------------------|
| 1/4.5 | 5% | 0.14 | >22  | >32 | >41 | >65 | 17~22 | Broken in Concrete matrix |

2.2.2. Concrete. The water cement ratio of concrete is 0.57. The dosage of each material is shown in Table 4. The content of Cl⁻ is 1.82% of the cement quality.

| cement | sand | stone | water | water reducer | NaCl |
|--------|------|-------|-------|---------------|------|
| 325    | 662  | 1228  | 185   | 0.65          | 9.75 |
2.3. Sample making
Four reinforced concrete beams were fabricated. The length of the beams was 1200 mm, the section size was 120 mm *160 mm, the thickness of the protective layer was 30 mm, and two hot-rolled ribbed bars (HRB400) with 10 mm diameter were arranged at the bottom of the beams. The concrete was 150 mm at one end. Two hot-rolled ribbed bars (HRB400) with diameter of 10mm are arranged in the compression zone of the beam, and the stirrups are arranged with round bars (HPB300) with diameter of 8mm and spacing of 60mm. The details of the size of the test beam are shown in Figure 2. The specimens were released for 24 hours after curing and accelerated corrosion after natural curing of 28d. After the corrosion, the MPC paste was evenly coated on the bottom of the concrete beam near the accelerated corrosion reinforcement, and then CFRP was laid on the MPC paste. After curing for 7 days, the samples were dechlorinated by electrochemical method.

![Figure 2. Dimensions of beams.](image)

2.4. Accelerate corrosion
After 28 days of natural curing of reinforced concrete beams, the tensile longitudinal bars at the bottom of the beams were electrically accelerated to corrode by constant current method [18]. The current density was 680.15 μA/cm², and the electrification time was 18 days. The beam is immersed in water, and the stainless steel pipe immersed in water is used as cathode, and the longitudinal bar at the bottom of the beam is used as anode, which is connected with a voltage stabilized DC power supply. The test beam was padded with a 50 mm thick wooden support, and the water solution height was 60 mm, so that the 10 mm part of the bottom of the beam was immersed in water. After one week's immersion, the specimens were electrified to accelerate corrosion. According to Faraday's law, the time needed for the longitudinal reinforcement to reach the theoretical corrosion rate was calculated. The accelerated corrosion device is shown in Figure 3.

![Figure 3. Accelerated corrosion device.](image)

\[ t = \frac{n \cdot F \cdot r \cdot \eta_s}{2 \cdot A \cdot i} \]  

 Among them, \( n \) is the valence of anodization; \( F \) is Faraday constant, 96500C/mol; \( r \) is the radius of reinforcing bar; \( \rho \) is the density of iron, \( \eta_s \) is the mass corrosion rate; \( A \) is the molecular mass of iron; \( i \) is the corrosion current density, \( i = \frac{I}{n \cdot D \cdot l} \), \( I \) is the current, \( D \) is the diameter of reinforcing bar, \( l \) is the exposed length of reinforcing bar.

2.5. Electrochemical chloride extraction
MPC-CFRP composite material is made up of magnesium phosphate cement (MPC) paste and carbon fiber sheet (CFRP) as binder. The longitudinal bars at the bottom of the beam are used as cathode. The electrolyte is saturated with Ca(OH)₂ solution and powered by Longwei PS-305DM high precision DC voltage regulator with current density of 3A/m². The electrolyte was replaced every 7 days and the ECE time was 28 days. The ECE device is shown in Figure 4.
2.6. Polarization curve test

Corrosion potential and corrosion current of concrete beams during corrosion and ECE were measured by PAR2273 instrument of Ametek Company. In the experiment, a two-electrode system was used to connect the working electrode with the longitudinal bar at the bottom of the beam to be measured, and the auxiliary electrode and the reference electrode were connected with the external electrode: in the process of accelerated corrosion, the external electrode is stainless steel pipe immersed in water; in the process of ECE, the external electrode is MPC-CFRP composite material. The scanning speed of the instrument is 25 mV/s, and the scanning potential range is from -200mV to +200mV relative to the open circuit potential. The test schematic diagram is shown in Figure 5. The polarization curves of steel bars were measured and processed by PowerSuite software. In order to reduce the errors caused by environmental and human factors, the average values of four reinforced concrete specimens were obtained.

3. Results and analysis

3.1. Corrosion potential and corrosion current variation of steel bar during corrosion process

The polarization curves of the specimens were measured every three days during the accelerated corrosion process. The changes of corrosion potential and corrosion current during the corrosion process of reinforced concrete beams were obtained, as shown in Figure 6.
From the Figure 6, it can be seen that before accelerate corrosion, the corrosion potential of the steel bar is -89mV, the corrosion current is 2.177 μA/cm$^2$, the steel bar is in passive state, and the corrosion risk is small. During the accelerate corrosion process, the corrosion potential of the steel bar shifts negatively with the extension of the electrification time, and the corrosion current increases gradually. After 18 days of electrification, the corrosion potential of steel bar is -579.6 mV and the corrosion current is 9.484 μA/cm$^2$. The steel bar was corroded at a higher rate. The corrosion current increased slowly in the early stage, and increased significantly after the 12th day.

The corrosion potential of reinforcing steel bar in concrete can qualitatively judge the possibility of corrosion of reinforcing steel bar. The discrimination between reinforcement potential and corrosion of steel bar is shown in Table 5. Corrosion current, which reflects the corrosion rate of steel bars, is of great significance to the corrosion status of steel bars and the prediction of structural life. Corrosion current of steel bars, corrosion rate of steel bars and damage life of components are discriminated in Table 6. The corrosion potential of steel bars is lower than -200 mV and the corrosion probability is only 5% before accelerate corrosion, and the corrosion current is 2.177 μA/cm$^2$, which indicates that the corrosion rate of steel bars is high, but the corrosion amount is very small. With the prolongation of the electric time, the corrosion potential of steel bar keeps shifting and the corrosion current increases. The corrosion probability of steel bars reaches about 50% after 9-12 days of accelerate corrosion. There may be pitting corrosion on the surface of steel bars, and the corrosion rate will be further accelerated. After 12 days of electrifying, the corrosion of steel bar is obvious and the corrosion rate is greatly accelerated.

In the early stage of electrified corrosion, the passive film on the surface of steel bar was destroyed and began to corrode due to the addition of 3% NaCl into concrete and soaking in water for a week. With the deepening of the corrosion of reinforcing steel, the corrosion products on the surface of the reinforcing steel bar continue to accumulate and the volume increases. In the early stage of corrosion, the compactness and impermeability of concrete are improved by the volume expansion of steel bars, and the corrosion rate of steel bars increases slowly due to the lack of moisture and oxygen needed for corrosion. After 12 days of electrification, the pitting corrosion on the surface of the reinforcing bars further accelerated the reaction, and cracks began to appear on the surface of the reinforcing bars to the concrete, which provided enough chloride, water and oxygen for the corrosion of the reinforcing bars, and greatly increased the corrosion rate.
Table 5. Discrimination of reinforcement potential and steel corrosion.

| Serial number | Reinforcement potential (mV) | Judgement of steel corrosion |
|---------------|-----------------------------|-----------------------------|
| 1             | -350 ~ -500                 | The probability of steel corrosion is 95%. |
| 2             | -200 ~ -350                 | The probability of corrosion of reinforcing steel is 50%, and pit corrosion may occur. |
| 3             | -200 or higher than -200    | No rust activity or rust activity is uncertain. The probability of corrosion is 5%. |

Table 6. Corrosion current of steel bar and corrosion rate of steel bar and component age of damage.

| Serial number | Corrosion current (μA/cm²) | Corrosion rate | Damage period of protective layer |
|---------------|-----------------------------|----------------|----------------------------------|
| 1             | <0.2                        | Passivation state |                                   |
| 2             | 0.2 ~ 0.5                   | Low corrosion rate | >15 years                        |
| 3             | 0.5 ~ 1.0                   | Moderate corrosion rate | 10~15 years                     |
| 4             | 1.0 ~ 10                    | High corrosion rate | 2~10 years                       |
| 5             | >10                         | Extremely high corrosion rate | Less than 2 years                |

3.2. Variation of corrosion potential and corrosion current in ECE process

During the ECE process, the polarization curves of the specimens were tested every 7 days, and the changes of corrosion potential and corrosion current in ECE process of reinforced concrete beams were obtained, as shown in Figure 7.

![Figure 7](image-url)

**Figure 7.** Variation of corrosion potential and corrosion current of steel bar during ECE.

As can be seen from Figure 7, after 28 days of ECE, the corrosion potential of steel bar shifted from -655mV to -298mV; the corrosion current increased first and then decreased: in the initial stage of ECE, the corrosion current increased slowly, then decreased sharply, and in the middle and late stage of ECE, the corrosion current decreased slowly. After 28 days, the corrosion potential of reinforcing bars increased to -289 mV, and the corrosion risk of reinforcing bars decreased
significantly compared with that before ECE. The corrosion current of reinforcing bars decreased to 0.196 μA/cm², indicating that the reinforcing bars were in passivation state.

Previous studies have shown that the corrosion potential rises slowly or decreases slightly in the early stage of ECE. The corrosion potential rises sharply in the 10~20 days of ECE, and then the change of corrosion potential tends to be stable, higher than 200 mV [19, 20]. Using MPC-CFRP as the external anode of ECE system, the effect of ECE will not deteriorate while strengthening the concrete structure.

After the accelerated corrosion of reinforcing steel bar, a large amount of Cl⁻ are accumulated in the concrete around the reinforcing steel bar, and the corrosion cracks provide enough moisture and oxygen for the corrosion of reinforcing steel bar. The corrosion rate of reinforcing steel bar is high. In the initial stage of ECE, the Cl⁻ removal efficiency is high, but the Cl⁻ in the concrete around the reinforcement needs a certain time to migrate outward. At this point, the Cl⁻ content in the concrete around the steel bar is higher than the Cl⁻ corrosion threshold, and the corrosion rate is slightly increased. Therefore, the corrosion potential and corrosion current increase at the early stage of ECE. With the prolongation of chlorine removal time, a large number of free Cl⁻ in concrete migrate to the surface of concrete or electrolyte under the action of external electric field, the Cl⁻ content in concrete around the reinforcement decreases significantly, and the corrosion rate decreases significantly. In addition, in the process of ECE, the cathodic reaction produces a large number of OH⁻. The increase of alkalinity of concrete around the reinforcement restores the passive state of the reinforcement and reduces the risk of corrosion.

4. Conclusions
(1) The constant current method was used to accelerate the corrosion of steel bars in concrete. The polarization curves of steel bars in concrete were measured every three days for 18 days. The results showed that the corrosion potential of reinforcing bar shifts negatively and the corrosion rate of reinforcing bar increases gradually during the accelerated corrosion process.

(2) Using MPC-CFRP as reinforcement material and external anode of ECE system, the corroded reinforced concrete beams were strengthened and ECE treatment was carried out for 28 days. The polarization curves of steel bars in concrete were tested every 7 days and the data were processed. The results show that MPC-CFRP has dual functions of reinforcement and ECE. ECE can effectively reduce the corrosion rate of reinforced concrete members. After 28 days of ECE, the corrosion current of steel bars is less than 0.2 μA/cm², and the steel bars corroded by Cl⁻ are passivated again to prevent the steel bars from corrosion.

Acknowledgements
The author would like to acknowledge the financial support provided by Open Foundation of National accredited Enterprise Technology Center of China Jingye Engineering Technology Co., Ltd (No. JZA2017Kj02) and National Natural Science Foundation of China (No.51678011)

References
[1] J P Broomfield 1997 Corrosion of Steel in Concrete John Wiley & Sons, Inc.
[2] Castel A, Vidal T, François R, et al. 2003 Influence of steel - Concrete interface quality on reinforcement corrosion induced by chlorides Magazine of Concrete Research 55(2):151-159
[3] Ormellese M, Berra M, Bolzoni F, et al. 2006 Corrosion inhibitors for chlorides induced corrosion in reinforced concrete structures Cement & Concrete Research 36(3):535-547
[4] Shi X, Xie N, Fortune K, et al. 2012 Durability of steel reinforced concrete in chloride environments: An overview Construction & Building Materials 30(5):125-138
[5] Bertolini L, Pedeferri P 2002 Laboratory and field experience on the use of stainless steel to improve durability of reinforced concrete Corrosion Reviews 20(1-2):129-152
[6] Hassanein A M, Glass G K, Buenfeld N R 2002 Protection current distribution in reinforced concrete cathodic protection systems Cement & Concrete Composites 24(1):159-167
[7] Chess P, Jakobsen D, Lawrence R, et al. 2000 Cathodic protection of reinforced concrete swimming pools 42(1):29-33
[8] Orellan J C, Escadeillas G, Arliguie G 2004 Electrochemical chloride extraction: efficiency and side effects Cement & Concrete Research 34(2):227-234
[9] Azad A K, Ahmad S, Al-Gohi B H A 2010 Flexural strength of corroded reinforced concrete beams Magazine of Concrete Research 62(6):405-414
[10] Ect Team P 2007 Electrochemical Chloride Extraction
[11] Fajardo G, Escadeillas G, Arliguie G 2006 Electrochemical chloride extraction (ECE) from steel-reinforced concrete specimens contaminated by “artificial” sea-water Corrosion Science 48(1):110-125.
[12] Petersen M A, Sale T C, Reardon K F 2007 Electrolytic trichloroethene degradation using mixed metal oxide coated titanium mesh electrodes Chemosphere 67(8):1573
[13] Cramer S D, Jr B S C, Holcomb G R, et al. 1999 Thermal sprayed titanium anode for cathodic protection of reinforced concrete bridges Journal of Thermal Spray Technology 8(1):133-145
[14] Ms S S S, Gupta S, Kumar S 1993 Rapid setting magnesium phosphate cement for quick repair of concrete pavements — characterisation and durability aspects Cement & Concrete Research 23(2):254-266
[15] Wu F, Wei J, Guo H, et al. 2008 Self-setting bioactive calcium-magnesium phosphate cement with high strength and degradability for bone regeneration Acta Biomaterialia 4(6):1873-1884.
[16] Li Y, Liu X, Li J 2016 Experimental Study of Retrofitted Cracked Concrete with FRP and Nanomodified Epoxy Resin Journal of Materials in Civil Engineering 29(5):04016275
[17] Li Y, Liu X, Wu M, et al. 2017 Research of electrochemical chloride extraction and reinforcement of concrete column using MPC-bonded carbon fiber reinforced plastic sheet & mesh Construction & Building Materials 153:436-444
[18] Al-Saidy A H, Al-Harthy A S, Al-Jabri K S, et al. 2010 Structural performance of corroded RC beams repaired with CFRP sheets Composite Structures 92(8):1931-1938
[19] M Sánchez, M C Alonso 2010 Electrochemical chloride removal in reinforced concrete structures: Improvement of effectiveness by simultaneous migration of calcium nitrite Construction and Building Materials 25(2)
[20] Carmona J, Garces P, Climent M A 2015 Efficiency of a conductive cement-based anodic system for the application of cathodic protection, cathodic prevention and electrochemical chloride extraction to control corrosion in reinforced concrete structures Corrosion Science 96:102-111