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Short Communication

Effective Chloride Removal in Reinforced Concrete Using Electrochemical Method in the Presence of Calcium Nitrite

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Repairing reinforced concrete is an important issue in the construction industry. Electrochemical chloride extraction is an effective method for repairing reinforced structures. On the other hand, the widely use of corrosion inhibitors becomes another approach, which as a protective strategy for reinforcement against corrosion. The corrosion inhibitor can penetrate and migrate in an electric field, which could potentially enhance the inhibition performance. In this work, we proposed a simple electrochemical chloride extraction method that simultaneously can enhance the corrosion inhibitor molecule penetration. Several electrochemical methods were used for analyzing the performance of the proposed method, including corrosion potential measurement and polarization resistance measurement. Moreover, visual inspection was also used for confirming the effectiveness of the proposed method.

Keywords: Electrochemical chloride extraction; Corrosion; Concrete; Polarization resistance; Corrosion potential

1. INTRODUCTION

The durability of reinforced concrete is an important factor in the construction industry. Chlorides (Cl^-) penetration has been noticed as a very bad issue for steel reinforcement corrosion. Conventionally, repair mortar or clean the oxides of the rebar after removal of the concrete is two method for repairing a reinforced concrete structure. However, these conventional ways usually require high cost and large restoration work, which cannot be used in most case, especially when the corrosion behaviour still in a mild degree. Therefore, development of non-conventional repairing method is essential for this field. Electrochemical maintenance methods such as cathodic protection, electrochemical chloride extraction and electrochemical realkalisation were commonly used for removing the aggressive agent and passivation of the reinforcement. Among them, electrochemical chloride extraction approach was used for the restoration of the chloride-induced corrosion of the reinforcement. Specifically, the reinforcement was subjected as a cathode and an external anode was connected to the concrete surface. Hydroxyl ions at the level of the rebar when the high voltage direct current was applied between the reinforcement and anode, which provide an alkaline environment surrounding the rebar. If the carbonated concrete was used, the diffusion process of the hydroxyl ions could reach to the rebar through the pores. This process can be used for removing chloride ions. In most time, the current density used for electrochemical chloride extraction is more than 2 A/m^2. The time for electrochemical chloride extraction is typically between 5 to 10 weeks. For example, Marcotte and co-workers demonstrated an electrochemical chloride extraction method using a current of 8.37A/m^2 with 8 weeks treatment for reinforcement [1, 2]. Results showed the successful removal of chloride ions at the steel–concrete interface. Orellan and co-workers demonstrated an electrochemical chloride extraction approach which could remove more than 50% chloride ions at the steel–concrete interface after 7 weeks treatment [3-8].

However, the electrochemical chloride extraction also could lead to some problems after the treatment. For example, the high voltage of the direct current could decline the bond strength between the concrete and rebar [9-13]. In addition, the high voltage polarised the rebar to extreme cathodic potentials, which let the passivation reformation after the voltage ceased. The passivation process of the rebar usually could achieve several days after the electrochemical chloride extraction treatment. High corrosion rate was usually observed during this process [14-17]2. Moreover, previous study also showed this passivation process is temporary because the new passivation state could lost with time. The electrochemical chloride extraction treatment effectively moves the hydroxyl ions away from the rebar. However, the hydroxyl ions could re-penetrate back to the area near the rebar and lower the surrounding pH condition, thus further cause corrosion of the steel [18, 19].

In order to overcome this problem, corrosion inhibitor addition along with the electrochemical chloride extraction treatment has been considered to enhance the service life of the reinforcement [20, 21]. Generally, corrosion inhibitor could add into the concrete by mixing the inhibitor with the cement or directly used on the surface of the hard concrete. Mover, the inhibitor also can be applied in a solution form and penetrate into the concrete through the pores. In this case, the transportation of the inhibitor molecules inside of concrete usually takes a very long time period. Electrochemical based methods have been found could accelerate of the penetration process. Several studies showed that some inhibitor molecules could accelerate their penetration process in an electric field which the rebar acted as a cathode and an external anode was applied [22-26]. On the other hand, the penetration process also can be applied using two external electrodes without connection of the rebar. However, this process cannot apply for the condition contains the chloride ions by the influence of the generated stray currents [27, 28].

During the electrochemical chloride extraction treatment, the penetration of cationic inhibitors becomes possible because the rebar was used as a cathode. Study showed nitrites had an excellent inhibition performance towards corrosion inhibition. In this contribution, we proposed an electrochemical chloride extraction method in the presence of nitrites. This modified electrochemical chloride extraction process could achieve the removal of chloride ions and penetration of inhibitor molecules simultaneously. After treatment, several electrochemical based analysis method was used for investigating the corrosion process of the reinforcement. Result showed our proposed advanced electrochemical chloride extraction method effectively lowers the corrosion rate of the reinforcement.

2. EXPERIMENTS

2.1. Mortar sample preparation

The mortar sample was prepared using Qinghua cement (Qinghua Co., Ltd, China).

Table 1. Chemical compositions of the general use cement (wt/%).

Name	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	K_2O	Alkali	Free lime	Loss on ignition
Qinghua cement	25.88	49.65	9.66	0.65	0.74	11.12	0.52	0.15	0.08	1.55

Table 2. Chemical compositions of steel rebar (wt/%).

C	Si	Mn	Cr	Mo	Ni	Cu	P	S
0.35	0.05	0.36	0.65	0.14	0.02	0.12	0.02	0.08

Table 1 shows the chemical compositions of the Qinghua cement. Standardise sand and tap water were used for mixing. The water/cement and sand/cement ratios were in 1:2 and 3:1, respectively. In order to evaluate the corrosion behavior of the sample, NaCl with 1% mass of cement was added into the mixing tap water. The mortar samples were prepared in size of 20 × 40 × 50 mm. The steel rebars (HRB 335) with diameter of 8 mm were embedded in into the concrete. Table 2 shows the chemical compositions of the steel rebars. The mortar samples were cured for 3 months in the following conditions: 95% humidity with 25 ^{o}C.

2.2. Corrosion state evaluation

The corrosion state of the steel bar was measured by electrochemical approaches before and after the electrochemical chloride extraction repair treatment. Corrosion potential (E_{corr}), polarization resistance and electrochemical impedance spectroscopy were used for analysis. Scanning potentiostat 362 from EG&G Instruments was used for polarization resistance analysis. The linear scan sweep rang was set as –20 mV to 20 mV with scan rate of 5 mV/min versus E_{corr}.

2.3. Experiment apparatus set up

The electrochemical chloride extraction treatment was carried out after the detection of the corrosion activation. In this study, calcium nitrite (0.5 M $Ca(NO_2)_2$) was used as the corrosion inhibitor during the electrochemical chloride extraction process. The voltage density used for electrochemical chloride extraction in this study is 10 V which applied using rebar as cathode and an external electrode as an anode. The electrochemical chloride extraction process was carried out for 10 days. The electrochemical behaviours of the rebars were analysed periodically for evaluating the performance of the proposed modified electrochemical chloride extraction process and the re-passivation process of the rebars. After treatment, the sample of the mortar was cut up for visual characterization.

3. RESULTS AND DISCUSSION

The modified electrochemical chloride extraction was performed when the E_{corr} and I_{corr} values below –0.35 V and above 0.2 μA/m^2, respectively, which indicating the corrosion process was occurred on the rebar surface. Cathodic polarization potentials were monitored during the modified electrochemical chloride extraction treatment for rebar.

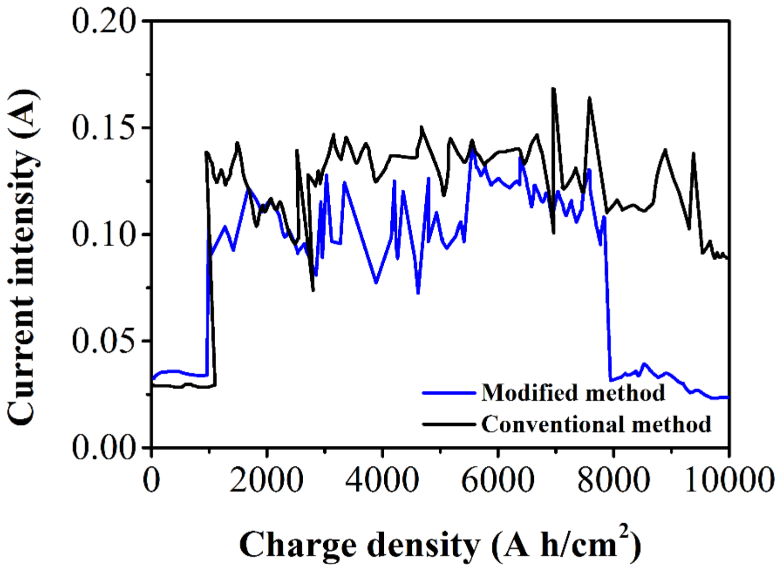

Figure 1. Monitoring of charge density and current intensity during the two types of electrochemical chloride extraction processes.

Figure 1 shows the relationship between the charge density past and current intensity during the electrochemical chloride extraction with addition of nitrites and common electrochemical chloride extraction. It can be seen that the curve of the sample treated using electrochemical chloride extraction with addition of nitrites had a sharp decline on the current response when the charge density reached nearly 9000 A h/cm^2. As reported by the Martínez and co-workers, the sharp decline of the current response could be due to the electro-osmotic flux through the concrete pores, indicating the nitrate ions penetrated into the rebar [14].

The electrochemical behaviours of the rebars were investigated after the electrochemical chloride extraction process. In order to distinguish the difference of proposed modified electrochemical chloride extraction, a conventional electrochemical chloride extraction without addition of nitrites was used as a control group.

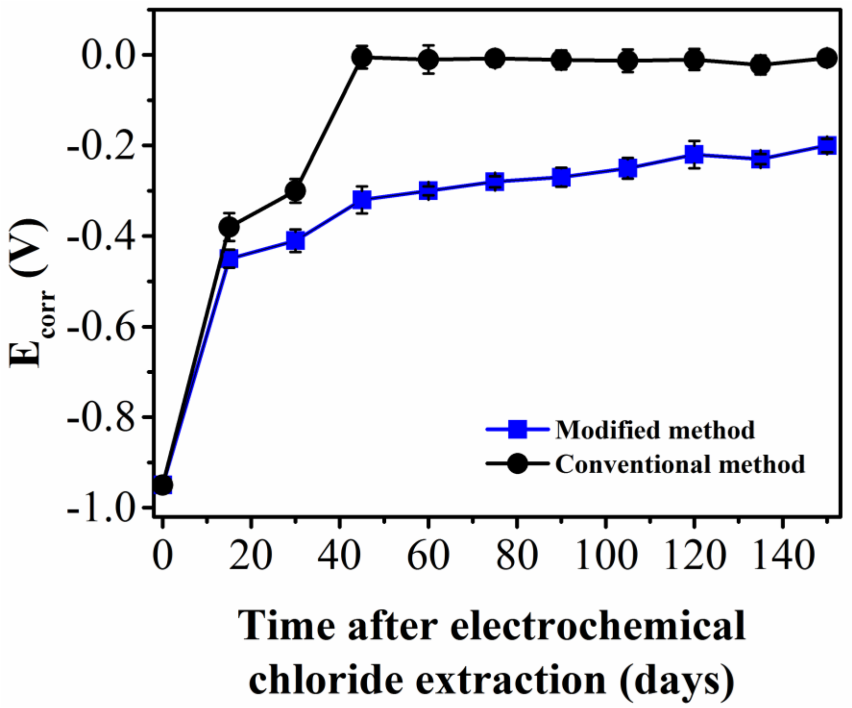

Figure 2. E_{corr} measurements of rebar after two types of electrochemical chloride extraction processes.

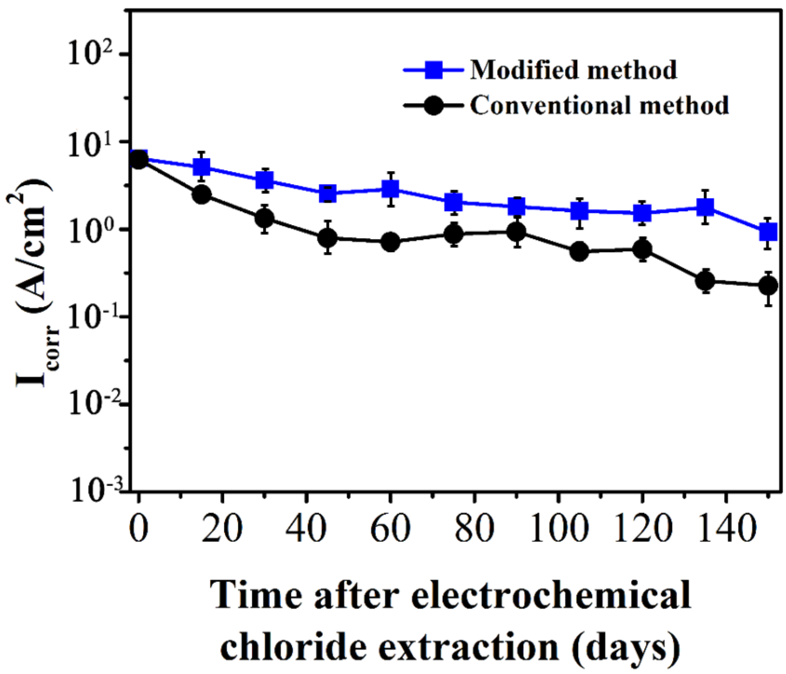

Figure 3. I_{corr} measurements of rebar after two types of electrochemical chloride extraction processes.

Figure 2 shows the plot of E_{corr} values with the time after the electrochemical chloride extraction treatment. The anodic effect of the nitrite was clearly observed in the plot, which the passivation of the rebar was much faster formed in the mortar after the modification electrochemical chloride extraction treatment compared with that of the mortar used the conventional electrochemical chloride extraction treatment. The effect of the nitrite in the passivation of the rebar after the electrochemical chloride extraction was also confirmed by the corrosion current density records. Figure 3 shows the plots of the corrosion current density measurements along with the time after the electrochemical chloride extraction treatment. As shown in the figure, the corrosion current density of the rebar after 10 days of the modified electrochemical chloride extraction treatment could reach to less than 0.15 $\mu A/cm^2$, suggesting the passivation of the rebar was achieved while the value of the mortar after conventional electrochemical chloride extraction treatment was 5 times higher. In addition, after long time measurements, the difference of the corrosion current density using two electrochemical chloride extraction methods became more cleared. Therefore, the addition of nitrite into the electrochemical chloride extraction process not only accelerates the passivation of the rebar but also provides a long-term protective efficiency. This can be ascribed to the penetration of nitrite during the electrochemical chloride extraction process, which acts as a corrosion inhibitor on the rebar surface. Based on the above observations, the introduction of the nitrite during the electrochemical chloride extraction process could accelerate the passivation of the rebar after the treatment. Moreover, the penetration of the nitrite formed an inhibition layer, which lowers the long-term corrosion process.

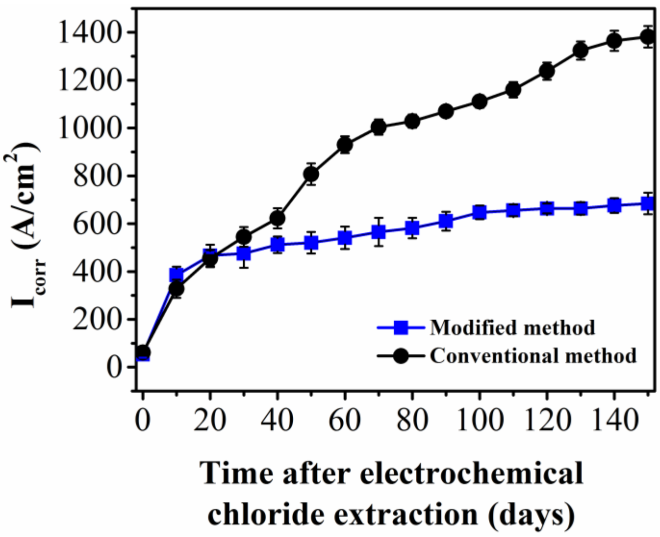

Figure 4. Calculation of cumulative charge using two types of electrochemical chloride extraction processes.

The rebars were polarized at the electrochemical chloride extraction process which could provide an immunity corrosion region [29]. This can be ascribed to the increasing of pH environment surrounding the rebar was achieved by the oxygen oxidation and the formation of hydroxyl ions. However, this condition dramatically changed after the electrochemical chloride extraction process finished. High corrosion rates were detected from the rebar commonly after a few days of the electrochemical chloride extraction process end [30]. The introduction of the nitrite using electronic filed migration showed an enhancement of the passivation process of the rebar. This phenomenon probably due to the attachment of the nitrite on the rebar surface and consequently prevent the corrosion process caused by residue chlorine ions. We further calculated the mass loss of the rebar after two types of electrochemical chloride extraction treatments using Faraday equation. It can be observed that the mass loss of the rebar after conventional electrochemical chloride extraction treatment was much higher than the sample after modified electrochemical chloride extraction treatment.

Visual analysis of the rebars was carried out for observation of the effectiveness of the chlorine ions movement and nitrite penetration. Theoretically, the chlorine ions should be extracted from the rebar and concrete towards external anode while the nitrite should penetrate from the mortar surface towards rebar inner core. The visual analysis showed no clear sign of corrosion, confirming the proposed modified electrochemical chloride extraction method could be used for effectively repairing reinforcement.

Table 3. Chlorine and nitrite ions Elemental analysis of the rebars after modified electrochemical chloride extraction and conventional electrochemical chloride extraction.

Treatment method	Chlorine ions (%)	Nitrite ions (%)
Modified electrochemical chloride extraction	0.18	0.17
Conventional electrochemical chloride extraction	0.35	N/A

Table 3 shows the elemental analysis of the chlorine and nitrite ions in the rebars after two electrochemical chloride extraction treatments.

4. CONCLUSION

In conclusion, we proposed a modified electrochemical chloride extraction treatment process for reinforcement repairing. The modified process includes an addition of nitrites solution during the chloride ions removal process for corrosion inhibitor penetration. Compared with the conventional electrochemical chloride extraction treatment process, our proposed approach not only more effective for chloride ions removal but also could accelerate the passivation of the rebar. Moreover, the proposed modified process also showed a long-term inhibition effect towards rebar due to the formation of an inhibition protective layer.

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