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Alleviating the Corrosion of Steel Reinforcement due to Electrochemical Chloride Extraction by Special Electrode Configuration

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This paper aims to alleviate the corrosion of steel in the mortar due to the electrochemical chloride extraction (ECE) through a special electrode configuration. In the ECE treatment with the special electrode configuration, two auxiliary electrodes embedded in the anodic and cathodic electrolytes were serviced as the anode and cathode, respectively. Besides, the steel in the mortar was grounded to reduce the cathodic polarization and the stray current corrosion. By a comparative experiment, the effectiveness of the ECE treatment with the special electrode configuration is evaluated by the chloride profile, potential evolution, half-cell potential, corrosion current density (I_{corr}) (decided by electrochemical impedance spectroscopy (EIS)) and visual examination of steel. The results indicate that the ECE treatments with the traditional and special electrode configurations have similar efficiencies of chloride removal. Compared to the ECE treatment with the traditional electrode configuration, the ECE treatment with the special configuration has a higher initial half-cell potential value and lower initial I_{corr} value of steel when the power supply is disconnected. Besides, the half-cell potential value of steel is more rapidly increased and the value of I_{corr} is more rapidly decreased to a stable value, indicating that a quicker repassivation of steel is obtained by using this special electrode configuration. Accordingly, the corrosion risk of steel due to the ECE treatment has been remarkably alleviated. The reason should be mainly attributed to the decrease of steel polarization during the ECE treatment with the special configuration.

Keywords: electrochemical chloride extraction; electrode configuration; electrochemical measurements; corrosion.

1. INTRODUCTION

Due to the porous structure of concrete, the chloride ions are liable to penetrate from the environment to the surface of steel reinforcement in concrete. The intruded chloride ions can disrupt locally the protective layer formed on the steel surface in the high alkalinity of concrete. When the chloride ions reach a critical level, the protective layer will be destroyed so that the steel corrosion is initiated. Accordingly, chloride-induced localized corrosion of the embedded steel is the main cause of premature deterioration of reinforced concrete structures exposed to chloride-laden environment [1-3].

For prolonging the service life of a deteriorated concrete structure, repair procedures are necessary [4, 5]. The electrochemical chloride extraction (ECE) as a non-destructive repair technique has attracted more and more attentions due to its easy practice, high efficiency and low costs. ECE is traditionally required to mount an anode at the concrete surface and use the steel reinforcement to act as the cathode. A high current density (DC) for a few weeks is implemented. The applied current results in the chloride ions in concrete away from the steel bar toward the anode, and thereby the chloride ions are removed from concrete. ECE treatment can remarkably reduce the chloride content near the reinforcement, leading to the reduction of corrosion current density or the re-passivation of steel, therefore the service life of chloride contaminated concrete structure will be significantly prolonged [6,7]. Despite this, it has to point out that the ECE treatment can increase the corrosion risk of steel at the initial time when the treatment is finished [8, 9]. The reason may be mainly due to the strong cathodic polarization [5] (the potential of steel is approximately -1.2 V vs. SCE). Generally, several months have to be taken to carry out the de-polarization and make the repassivation of the steel [10-14]. It is significant to increase the safety of ECE treatment and reduce the corrosion risk due to the application of ECE treatment.

This paper aims to alleviate the corrosion of steel reinforcement in mortar due to electrochemical chloride extraction by a special electrode configuration. In the special configuration, two auxiliary electrodes embedded in the anodic and cathodic electrolytes were serviced as the anode and cathode, respectively. Additionally, the steel in the mortar was grounded to reduce the cathodic polarization and stray current corrosion. By a comparative experiment, the effectiveness of such special configuration is evaluated by the chloride profile, potential evolution, half-cell potential, corrosion current density (I_{corr}) (decided by electrochemical impedance spectroscopy (EIS)) and visual examination of steel.

2. EXPERIMENTAL

2.1. Preparation of the samples

Table 1. Oxide composition of cement (% w/w).

Oxide	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	Total Cl	SO_3	Ignition loss
Composition (wt. %)	57.27	24.99	9.32	3.11	0.86	0.83	0.28	0.05	1.13	2.16

The cement applied in our work was No. 42.5 ordinary Portland cement made in China. Its oxide composition was indicated in Table 1. The fine aggregate was river sand with a fineness modulus of 2.6. Tap water was used in mortars, and distilled water was utilized to prepare various electrolytic solutions for the subsequent electrochemical treatments.

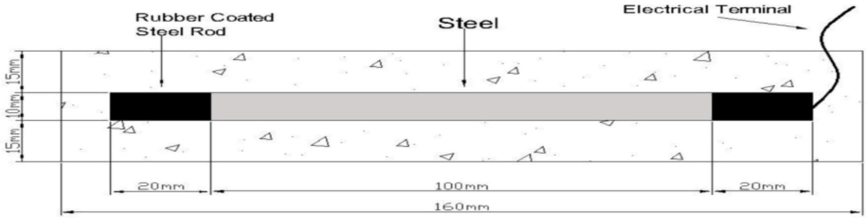

Figure 1. Schematic view of the specimen employed.

The mortar samples with the size of 40 mm×40 mm×160 mm were fabricated with one rebar (1-cm-diameter, 10-cm-long) embedded in each specimen (Fig.1). To simulate the chloride contaminated concrete, the chloride ions with content in 2.0 % by mass of cement was added in the mortar specimen. Water/cement ratio of 0.55 and sand/cement ratio of 2.5 has been employed. Moreover, after one day of casting into the moulds, all the paste samples were demolded, and then cured in a 95% humidity chamber at 20 ± 2 °C for 28 days.

2.2. Electrochemical treatments

A rectangular electrolytic tank (24 cm ×16 cm × 6 cm) made from acrylic sheet was separated into two identical compartments by placing the as-fabricated mortar specimen in the middle of the tank. To conduct the ECE treatment with the special electrode configuration, the saturated calcium hydroxide solution was prepared to use as cathodic and anodic electrolytes. Platinized titanium meshes were applied as the anode and cathode. In addition, the steel in the mortar specimen was grounded to be guarded against corrosion. And then, the chloride ions were removed from mortar through the applied current and the steel was grounding protection. Detailed experimental configuration for the special electrode configuration was indicated in Fig.2 (a). DC regulated power supply was employed for the electrochemical treatment.

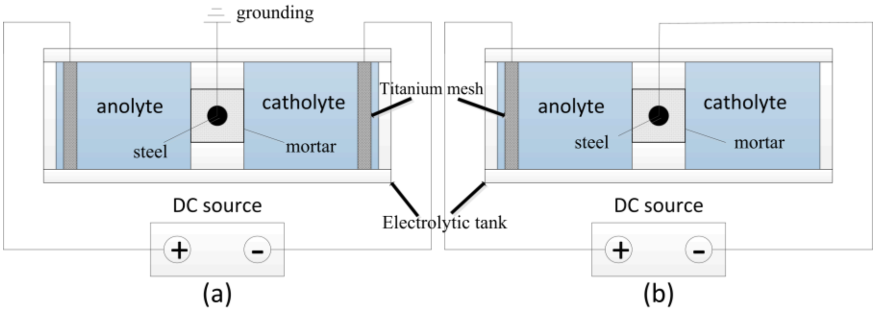

Figure 2. Detailed experimental configurations for the ECE treatments: (a) special electrode configuration (b) traditional electrode configuration.

The applied current density was 4.0 A/m^2 related to the rebar area (a preferable current density through pre-experiments), and conduction time was 28 d. In contrast, the steel in the mortar specimen was directly connected to the cathode of DC power during the ECE treatment with traditional electrode configuration (Fig.2 (b)). The mortar specimen was put into the saturated calcium hydroxide solution. All the other conditions were identical to those for the special electrode configuration. All the treatments were performed at the ambient temperature. Besides, the electrolytic solution of calcium hydroxide was periodically replaced every two days to maintain a stable composition.

2.3. Measurements

2.3.1. Potential evolution of steels

The electrochemical potential of the steel was monitored periodically during ECE treatments. The saturated calomel electrode (SCE) as the reference electrode was placed over the steel in mortar. Then, the electrochemical potential was monitored with a recorder connected to a computer.

2.3.2. Chloride profile

After the ECE treatments, the mortar specimens were cut into slices every 5mm from the steel to anolyte or catholyte. Subsequently, the slices were powdered until passing through the sieve of 0.16 mm. Then, 20 g powders were added into 200 ml nitric acid solution so as to determine the total Cl^- content. The mixtures were vigorously stirred for a period, and then left to stand for 24 h. The chloride remaining was measured by the potentiometric titration with 0.01M silver nitrate ($AgNO_3$).

2.3.2. Electrochemical measurements after ECE treatments

After the ECE treatments, half-cell potential tests were conducted, following the ASTM C-876 [15] guidelines, to determine the likelihood of active corrosion. The potential difference between the working electrodes (steels embedded in mortar samples) and a copper sulphate reference electrode (CSE) placed on the surface of the samples was measured using a high-impedance voltmeter.

Determine the polarization resistance (R_p) values of steels after the ECE treatments. The steel bar, the platinum electrode and the SCE were served as the working electrode, the auxiliary electrode, and the reference electrode, respectively. The EIS in the frequency range from 10 mHz to 100 kHz were performed periodically on the samples. The perturbing signal applied was 10 mV (rms). The potentiostat was PARSTAT 2273 (AMETEK Corporation, USA) and data analysis was carried out by ZsimpWin software by fitting the experimental data in a constant phase element (CPE) model.

The polarization resistance (R_p) obtained from the EIS was introduced into the following expression for calculating the current density (I_{corr}):

$$I_{corr}/B=R_p \quad (1)$$

Where B is a constant, its value has been determined by means of calibration against mass loss measurements). The values of 52 mV and 26 mV are often used in the calculation of B for the bare steel in the passive and active states, respectively [16, 17].

2.3.4 Visual examination of steel

After the electrochemical measurements, the samples were broken and the visual observations of the steels were made to confirm the superficial state.

3. RESULTS AND DISCUSSION

3.1. Potential evolution of steel

Fig.3 depicts the potential evolutions of the steels in mortars during the ECE treatments with the traditional and special electrode configurations. Before the ECE treatments, the potential values of steels are about -450 mV vs. SCE. However, the potential of steel for the ECE treatment with the traditional electrode configuration is sharply decreased towards more negative values immediately after the power is supplied. After a conduction period (2 ~ 4 days), the potential for the sample attains a stable value. The final potential value lies in the range of -1200 mV to -1300 mV vs. SCE, which is in good agreement with previously published results in the literatures [10]. This result indicates that the steel in the mortar is strongly polarized during the ECE treatment with the traditional electrode configuration. The strong polarization accelerates corrosion of steel and destroys the protective oxide film that is formed on the steel surface.

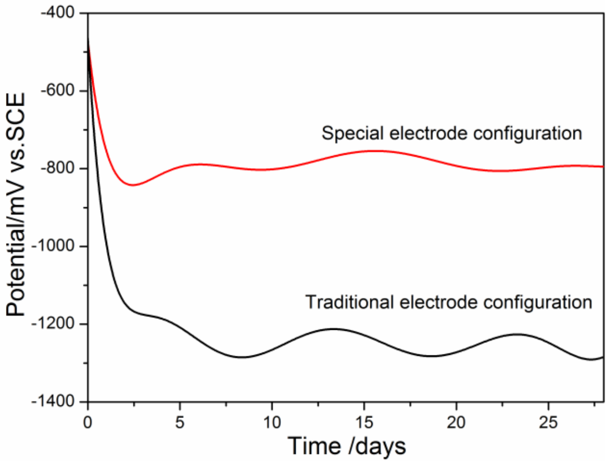

Figure 3. Potential evolutions of steels during the ECE treatments with the traditional and special electrode configurations.

However, the stable value of potential for the ECE treatment with special electrode configuration is only about -800 mV vs. SCE, which is significantly higher than the value for ECE treatment with the traditional electrode configuration. Besides, a quick change of potential from the initial value to ultimate stable value is obtained, which is similar to the sample the ECE treatment with the traditional electrode configuration. The lower absolute value of steel potential indicating that the weaker polarization of steel after the ECE treatment with the special electrode configuration. Therefore, the accelerating corrosion phenomenon could not be observed after the ECE treatment with special electrode configuration. Comparing our results with those in Ref. [8], the depolarization of steel after the ECE treatment with the special electrode configuration might be quicker than that after the ECE treatment with the traditional electrode configuration.

3.2. The chloride profile

After the ECE treatments, the chloride contents at different depths are determined on the samples, as shown in Fig.4. The chloride contents of similar depth from the steel surface to anolyte are almost similar for the ECE treatments with the traditional and special electrode configurations. The efficiencies of chloride removal both are about 60%. Only a little higher efficiency for the ECE treatment with the traditional electrode configuration is obtained. However, the chloride content at the similar depth from steel surface to catholyte for the ECE treatment with the special electrode configuration is significantly lower than the chloride content for the ECE treatment with the traditional electrode configuration. The reason can be due to the fact that there is no electric field between steel and the catholyte during the ECE treatment with traditional electrode configuration [18]. In contrast, during the ECE treatment with special electrode configuration, the electric current flows from the anolyte to the steel and then flows to the catholyte. Therefore, the ECE treatment with the special electrode configuration does not have a negative influence on the efficiency of chloride removal.

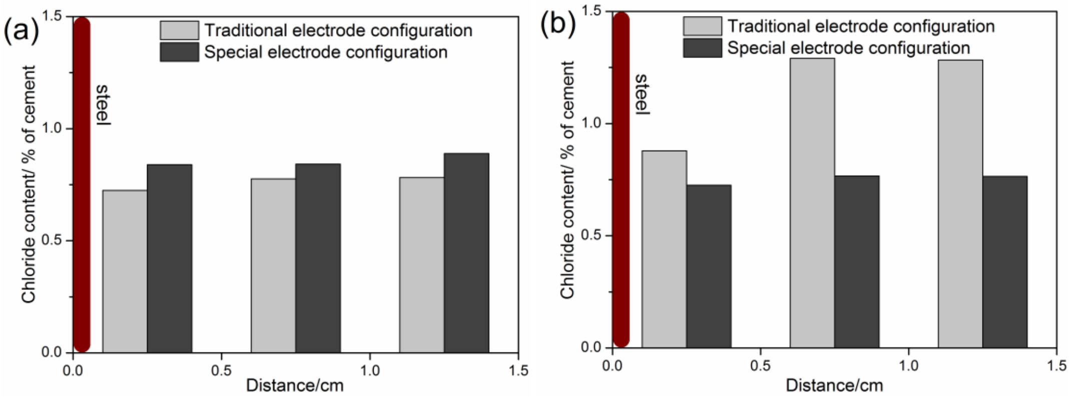

Figure 4. Chloride distribution in mortar samples from the steel surface to the anolyte (a) and to the catholyte (b).

3.3. Electrochemical measurements after ECE treatments

Fig.5 shows the evolutions of half-cell potential with time for the steels after the ECE treatments with the traditional and special electrode configurations. The ASTM C876 [15] standard has determined three half-cell potential levels to identify the corrosion probability of steel in mortar. That is, when the half-cell potential > −0.20V (vs. CSE), the corroded probability of steel in mortar is less than 10%; when the half-cell potential < −0.35V (vs. CSE), the corroded probability of steel in mortar is higher than 90%; when it locates in the middle region, the probability is uncertain.

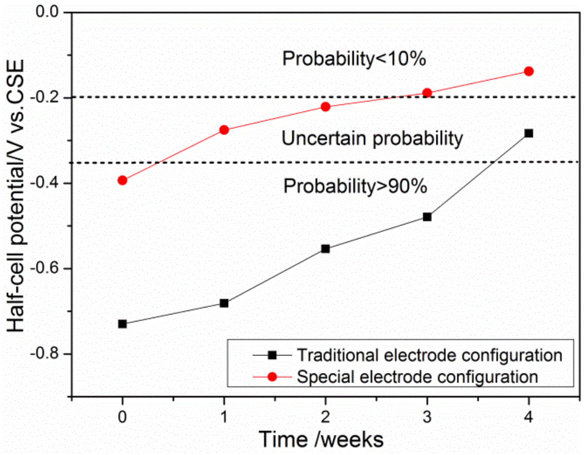

Figure 5. Evolutions of half-cell potential with time for the steels after the ECE treatments with the traditional and special electrode configurations.

According to ASTM C876 standard, half-cell potential of steels at the initial time after ECE treatments with the traditional and special electrode configurations are lower than -350 mV vs. CSE, indicating that steels are in an active corrosion state. But the value of half-cell potential at the initial time after the ECE treatment with special electrode configuration is higher than that after the ECE treatments with the traditional electrode configuration. As time increased, the half-cell potential all tends to the nobler direction. It also can be observed that the half-cell potential value of steel after the ECE treatment with special electrode configuration is increased to more than -200 mV vs. CSE during a short period. This shows that the half-cell potential of steel after the ECE treatment with the special electrode configuration is leading to more easily to the region of potential where corrosion probability is less than 10% [13]. According to some previous works [8, 18, 19], we observe that the application of the ECE treatment with the special electrode configuration brings the corrosion potential of the steel to the zones that could indicate their repassivation in a short time.

The impedance spectra at different times after the ECE treatments with the traditional and special electrode configurations are depicted in Fig. 6 and Fig.7, respectively. As indicated in Fig.6 and Fig.7, the Nyquist plots comprise two distinct arcs in high and low frequencies, which are associated with mortar response and steel surface response, respectively. The phase angle plot shows that the value of the phase angle is high at low frequency in the initial, and then it drops with the increase of time. Besides, the phase angle value of high frequency was about a constant value. The |Z| plot shows the value of the phase angle and |Z| after the ECE treatment with the special electrode configuration are higher than the value after the ECE treatment with the traditional electrode configuration. And, the |Z| value is rapidly increased with time. These results suggest that the samples undergo complicated evolutionary processes and the properties of test samples are changed after the ECE treatments with the traditional and special electrode configurations [5].

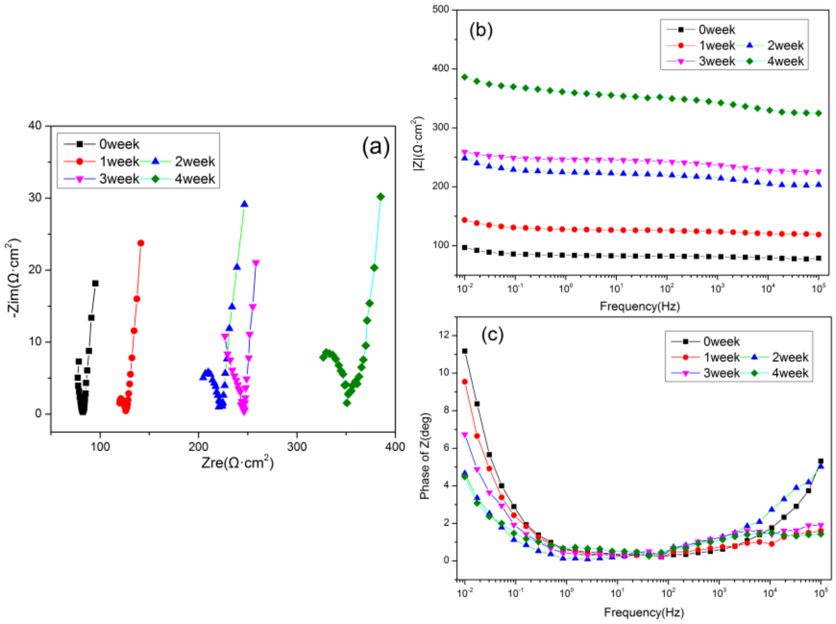

Figure 6. Impedance spectra for samples after the ECE treatment with the traditional electrode configuration: (a) Nyquist plots (b) Bode |Z| plot (c) Bode phase plot.

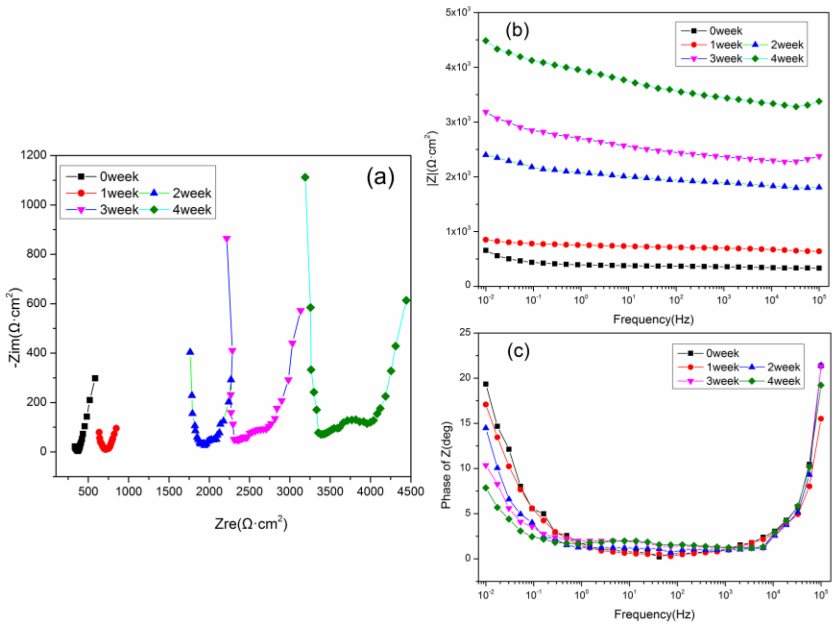

Figure 7. Impedance spectra for samples after the ECE treatment with the special electrode configuration: (a) Nyquist plots (b) Bode |Z| plot (c) Bode phase plot.

According to the evolution characteristics of the EIS spectra of the steels in mortars after the ECE treatments with the traditional and special electrode configurations, the corresponding equivalent circuit (EC) model was proposed to fit the EIS data [18], as showed in Fig.8.

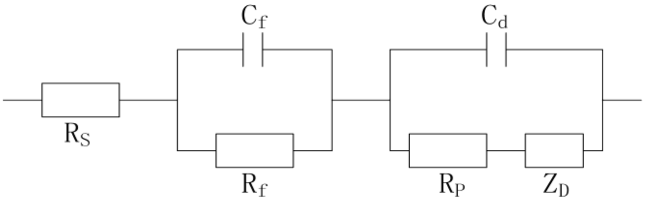

Figure 8. Equivalent circuit used in numerical fitting of the impedance data.

In this equivalent-circuit, R_s is the series resistance, which accounts for the ionic conduction in the electrolyte filling the pores; the parallel circuit (C_f, R_f) accounts for the high frequency relaxation process; the double layer capacitance (C_d) and the polarization resistance (R_p) represent the dissolution processes at the steel/mortar interface. Finally, Z_D stands for the Warburg resistance of the semi-infinite diffusion process [20-22]. The fitting parameters of the polarization resistance of steel (R_p) are presented in Fig.9.

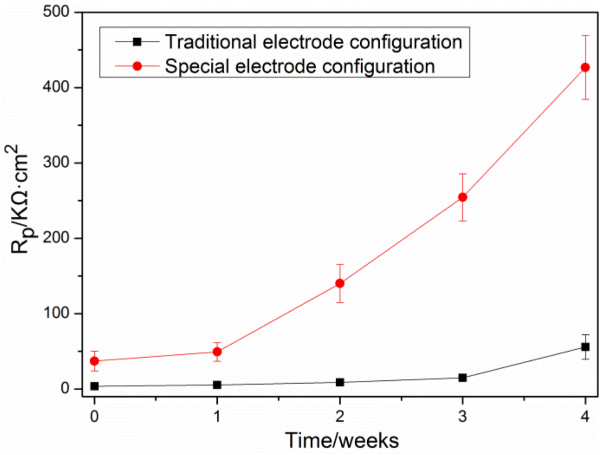

Figure 9. R_p of steel after the ECE treatments with traditional and special electrode configurations.

R_p is increased slowly initially and then increased significantly from the three weeks after the ECE treatments with traditional electrode configuration. However, the value of R_p is increased significantly from the one week after the ECE treatments with special electrode configuration. Furthermore, the value of R_p after the ECE treatment with special electrode configuration is higher than the value after the ECE treatment with traditional electrode configuration. It is well known that the value of R_p is reversely proportional to the corrosion rate [23, 24]. Thus, the corrosion rate will be reduced after the ECE treatment with the special electrode configuration.

Fig.10 shows the evolution of I_{corr} with time for the steels after the ECE treatments with the traditional and special electrode configurations. According to the criteria for estimating the corrosion of steel [25], the steel is in passive condition when $I_{corr}<0.1\ \mu A\cdot cm^{-2}$, the corrosion extent of steel is low to moderate when $0.1<I_{corr}<0.5$ μA·cm^{-2}, the corrosion extent of steel is moderate to high when $0.5<I_{corr}<1.0$ μA·cm^{-2}, the corrosion extent of steel is high when $I_{corr}>1.0$ μA·cm^{-2}.

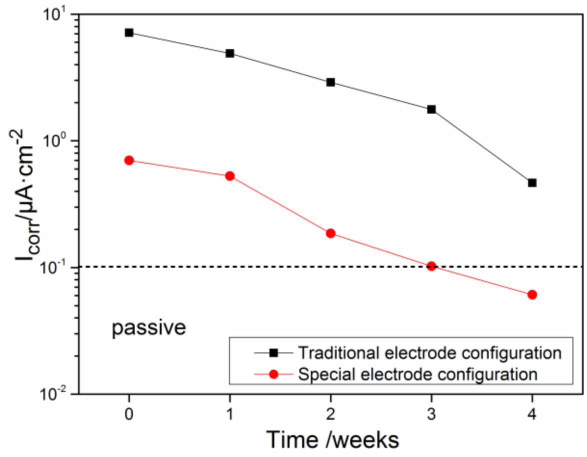

Figure 10. Evolutions of I_{corr} with time for the steels after the ECE treatments with the traditional and special electrode configurations.

As can be observed in Fig.10, the I_{corr} values of steels measured immediately after halting the ECE treatments with traditional and special electrode configurations are significantly greater than the corrosion rate limit for passive steel. The I_{corr} value of steel is about 8 μA·cm^{-2}, if it is monitored immediately after halting the ECE treatment with the traditional electrode configuration. This implies that ECE treatment with the traditional electrode configuration might increase the corrosion current density and the steel has a high corrosion-risk. In the work of Green et al. [13], it is also shown that the corrosion rate increases after the application of the ECE treatment. After the ECE treatment with the special electrode configuration, the I_{corr} value of steel is reduced to more lower than 1.0 μA·cm^{-2}. Due to the relative lower I_{corr} of steel, it can move more easily to the region of I_{corr} where the steel is in passive condition. Therefore, the corrosion rate is reduced by the ECE treatment with the special electrode configuration. It should be mainly attributed to the weaker polarization of steel during the ECE treatment with the special configuration [13, 19].

Moreover, the corrosion rate of steel is decreased with time. Comparing to the Ref. [5, 13, 23], it could be concluded that steel is gradually passivated. After one month, the I_{corr} value of steel after the ECE treatment with the traditional electrode configuration is maintained at a high level. Thus, the repassivation of steel after the ECE treatment with traditional electrode configuration needs a long time (more than one month). In contrast, three weeks after the ECE treatment with the special electrode configuration, the I_{corr} value of steel lower than 0.1μA•cm^{-2} [5, 26]. It is indicating that the passive state of steel is obtained within three weeks after the ECE treatment with the special electrode configuration. Based on these, the ECE treatment with the special electrode configuration can help the steel more rapidly recover to a safe condition.

3.4 Visual examination of steels

Fig. 11 shows the visual inspection images of steels in the mortar before and after the ECE treatments with the traditional and special electrode configurations. It should be pointed out that the corrosion happened on the steel surface before the ECE treatment is severe because of the high chloride content [8]. In contrast, the visual inspection of the steels after the ECE treatment with the traditional configuration and after the ECE treatment with special electrode configuration have clean surface without any sign of corrosion products. These results are similar to the product reported in other works [11, 27]. From this result, it can be proved that the ECE treatment with the traditional configuration and the ECE treatment with the special electrode configuration both have the high efficiencies of chloride removal. Although it is difficult to find the difference in the corrosion condition of steel from the visual inspection between after the ECE treatment with the traditional configuration and after the ECE treatment with the special electrode configuration, the corrosion rates of the steels are different from the electrochemical measurements.

Figure 11. Visual inspection images of steels in the mortar before the ECE treatment (a), after the ECE treatment with the special electrode configuration (b) and after the ECE treatment with the traditional electrode configuration (c).

4. CONCLUSIONS

The results obtained in this work allow us to draw the following conclusions:

(1) The potential of steel during the ECE treatment with the special electrode configuration has a relatively lower absolute value than the ECE treatment with traditional electrode configuration, which is only about -800 mV vs. SCE. It is indicating that the polarization of steel is relatively weaker.

(2) The chloride removal efficiencies of the ECE treatments with traditional and special electrode configuration both are about 60%.

(3) After the ECE treatment with the special electrode configuration, the initial half-cell potential value of steel is higher and the initial value of I_{corr} is lower when the power supply is disconnected. Therefore, the ECE treatment with the special electrode configuration significantly decreases the corrosion risk of steel.

(4) The half-cell potential and I_{corr} of steel after the ECE treatment with the special electrode configuration is more rapidly attained to the stable value than those after the ECE treatment with the traditional electrode configuration. The repassivation of steel is obtained within three weeks after the ECE treatment with the special electrode configuration. However, the repassivation of steel after the ECE treatment with the traditional electrode configuration does not be found in the study.

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References

1. P.K. Mehta, *ACI. Mater. J.*, 126 (1991) 1-32.
2. X. Shi, N. Xie, K. Fortune, J. Gong, *Constr. Build. Mater*., 30 (2012) 125-138.
3. J. Xu, Y. Song, L. Jiang, W. Feng, Y. Cao, W. Ji, *Constr. Build. Mater*., 104 (2016) 9-15.
4. E. Otero, J.A. González, A. Cobo, M.N. González, *Mater. Corros*., 52 (2001) 581-589.
5. G. Fajardo, G. Escadeillas, G. Arliguie, *Corros. Sci*., 48 (2006) 110-125.
6. M. Sánchez, M.C. Alonso, *Constr. Build. Mater*., 25 (2011) 873-878.
7. H. Shan, J. Xu, Z. Wang, L. Jiang, N. Xu, *Constr. Build. Mater*., 127 (2016) 344-352.
8. I. Martínez, F. Rozas, S. Ramos, M. González, M. Castellote, *Elec.Acta*., 181 (2015) 288-300.
9. T.H. Nguyen, T.A. Nguyen, V.K. Le, T.M.T. Dinh, H.Thai, X.Shi, *Anti-Corr. Meth. Mater*., 63 (2016) 377-385.
10. X.X.Wang, Q.J.Yu, C.L.Deng, J.X.Wei, Z.Y. Wen, J.Wuhan *Univ.Technol*., 22 (2007) 764-769.
11. J.C. Orellan, G. Escadeillas, G. Arliguie, *Cem. Concr. Res*., 34 (2004) 227-234.
12. G.E. Abdelaziz, A.M.K. Abdelalim, Y.A. Fawzy, *Cem. Concr. Res*., 39 (2009) 727-732.
13. W.K. Green, S.B. Lyon, J.D. Scantlebury, *Corros. Sci*., 35(1993) 1627-1631.
14. B. Elsener, *Mater. Corros*., 59 (2008) 91–97.
15. ASTM C876-91 [S].
16. F.C. Andrade, J.A. González, *Mater. Corros*., 29 (1978) 515-519.
17. C.Andrade, C.Alonso, *Mater. Struc*., 37 (2004) 623-643.
18. Yeih, W., Chang, J. J., Chang, C. C. Chen, K. L., Chi, M. C., *Cem. Con. Com*., 74 (2016) 136-146.
19. T.D. Marcotte, C.M. Hansson, B.B. Hope, *Cem. Concr. Res*., 29 (1999) 1555–1560.
20. M.F. Montemor, A.M.P. Simões, M.M. Salta, *Cem. Con. Com*., 22 (2000) 175-185.
21. V. Feliu, J.A.González, C.Andrade, S.Feliu, *Corros. Sci*., 40 (1998) 975-993.
22. J Wei, XX Fu, *J. Mater. Sci. Technol*., 28 (2012) 905-912.
23. C. Andrade, M.C. Alonso, J.A. Gonzalez, *ASTM STP,* 1065(1990) 29–37.
24. S.G. Millard, K.R. Gowers, J.S. Gill, *ACI. Mater. J.*, 128 (1991) 373-395.
25. D.A.Koleva, J.Hu, K.V.Breugel, J.H,W.D.Wit, N.Boshkov, *Mater. Corros*., 60 (2009) 344-354.
26. J. Mietz: *Mater. Corros.*, 46 (1995) 527.
27. N.M. Inekwaba, B.B. Hope, C.M. Hansson, *Cement Concrete Res.*, 26 (1996) 267–282.