

Influences of Fly Ash, Slag and Silica Fume on Electrochemical Chloride Removal Treatment with Simultaneous Migration of Silicate Ion

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The paper aims to investigate the effects of fly ash (FA), slag (SL) and silica fume (SF) on the electrochemical chloride removal treatment with simultaneous migration of silicate ion, which was to alienate the Cl^- from the reinforcement and inject SiO_3^{2-} into the mortar to interact with $\text{Ca}(\text{OH})_2$, respectively. The mortars (20% and 30% FA, 30% and 50% SL, 5 % and 10% SF) contaminated by 2.0 wt.% chloride were prepared. The chloride extraction efficiency and corrosion properties of steel reinforcement in sodium chloride solution after the electrochemical treatment were measured to evaluate the effects. Results show that this electrochemical treatment is effective in extracting chloride from the mortar with various admixtures and prolong the initial time of corrosion for the steel in mortar with various admixtures. With the increase of FA content in mortar, the extracted chloride efficiency and the initial time of corrosion for rebar in mortar were increased. In contrast, with the increase of SL or SF content in mortar, the extracted chloride efficiency and the initial time of corrosion for rebar were decreased.

Keywords: electrochemical chloride removal; electrochemical measurement; corrosion.

1. INTRODUCTION

Concrete has been the most widely used structural material, owing to its performance and versatility. However, due to the porous structure of concrete, aggressive substances in the environment, such as chlorides and sulfate, are easily to diffuse into concrete structure. Concrete subjected to severe environment can thus suffer from deterioration (e.g. corrosion of reinforcement, freezing and thawing damage, sulfate attack). Among these deteriorations, corrosion of reinforcement is the key factor causing the reduction of concrete service-life, especially for the concrete structure exposed in the chloride-contaminated environment [1, 2].

For prolonging the service life of chloride-contaminated concrete, a repair method is required to be carried out. In recent years, electrochemical chloride extraction (ECE) treatment has attracted more and more attentions for repairing reinforced concrete in order to prolong its service life, due to its merits of fast, high-efficiency and little influence on the environment. This treatment involves the application of an electric field for chlorides removal from contaminated reinforced concrete and restoring passivity to the reinforcement [3-6]. Despite it, the corrosion of reinforcement in the reinforced concrete after this treatment may still happens [7]. Due to the porous structure of concrete, the chloride ions inevitably diffuse into the porous concrete when the reinforced concrete structure expose to a chloride-contaminated environment [8]. The ECE treatment cannot remove the chloride ions from the concrete completely [9-11]. Accordingly, chloride ions from the environment can make chloride ions content in the concrete exceed chloride threshold value, resulting in the corrosion of reinforcement for the second time.

In our previous investigation, the ECE treatment with simultaneous migration of silicate ion has been proposed [12, 13]. During this electrochemical treatment, the chloride ions around the reinforcement migrated from the cathode towards the anode, leading to the de-chlorination of the mortar. The SiO_3^{2-} ions in the cathodic compartment were driven into the mortar pores, and reacted with $\text{Ca}(\text{OH})_2$ to generate the additional C-S-H, leading to the mortar densification. The cathodic reaction generated OH^- constantly, improving the alkalinity of mortar pore fluid around the reinforcement and assisting in restoring passivity to the reinforcement. In comparison with the ECE treatment, this electrochemical treatment has similar chloride removal efficiency. When the mortar still exposed to a chloride-contaminated environment, it can extended corrosion initiation time of reinforcement for the second time.

Mineral admixtures, such as fly ash (FA), slag (SL) and silica fume (SF), have been widely used to replace partially the cement due to its low costs, environment protection and resource conservation [14, 15]. However, the influences of mineral admixtures on the ECE treatment with simultaneous migration of silicate ion is not studied so far. For the concrete with various mineral admixtures, the effectiveness of ECE treatment with simultaneous migration of silicate ion is required to be evaluated for its application in real environment. The paper aims to investigate the effects of fly ash, slag and silica fume on the electrochemical chloride removal treatment with simultaneous migration of silicate ion. The mortars (20% and 30% FA, 30% and 50% SL, 5 % and 10% SF) contaminated by 2.0 wt.% chloride were prepared. The chloride extraction efficiency and corrosion properties of steel reinforcement in sodium chloride solution after the electrochemical treatment were measured to evaluate the effects.

2. EXPERIMENTAL

2.1 Materials and specimen preparation

The cement applied in this work was No. 42.5 ordinary Portland cement (OPC) supplied by CONCH cement Co. Ltd in China. Its oxide composition is listed in Table 1. Oxide composition of

FA, SL and SF is listed in Table 2. The fine aggregate was river sand with a fineness modulus of 2.1. Tap water was used in mortars, and distilled water was adopted to prepare various electrolytic solutions using in the subsequent electrochemical treatment.

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

Oxide	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	SO ₃	Ignition loss
%	22.97	9.28	59.68	3.10	1.03	1.73	1.23	0.98
w/w								

Table 2. Oxide composition of used admixtures (% w/w)

	SO ₂ /%	Al ₂ O ₃ /%	Fe ₂ O ₃ /%	CaO/%	Ignition loss /%
FA	51.2	18.5	14.7	4.2	0.2
SL	38.7	11.1	0.9	33.4	3.2
SF	91.3	-	-	<1	2.4

The mortar samples with the size of 4cm×4cm×16cm were fabricated with a rebar (1-cm-diameter, 10-cm-long) embedded in each specimen. NaCl was added to the mixing water (2.0 wt.% Cl⁻ by mass of binder). Water/binder ratio of 0.55, and sand/binder ratio of 2.5 have been employed. Cement was partially replaced by FA, SL and SF. Table 3 summarizes all the mixed compositions. After one day of casting in plastic molds, all mortars were de-molded, and then cured in a 95% humidity chamber at 20±2°C for 27 days.

Table 3. Mix proportion

	Cement (g)	Water (g)	Admixture (g)	Sand (g)	NaCl (g)
FA20%	400	275	100(FA)	1250	10
FA30%	350	275	150(FA)	1250	10
SL30%	350	275	150(SL)	1250	10
SL50%	250	275	250(SL)	1250	10
SF5%	475	275	25(SF)	1250	10
SF10%	450	275	50(SF)	1250	10

2.2 Electrochemical treatment

A rectangular electrolytic tank (24cm×16cm×6cm) made from organic glass was separated into two identical compartments by placing the as-fabricated mortar in the middle of tank, of which the width side was paralleled to the length one of the mortar. Titanium meshes were served as the anode and cathode. The rebar connected to the negative pole of the power supply in order to prevent the rebar

from corroding. Electrolytic solutions of sodium silicate with the concentrations of 0.05 mol/L and saturated calcium hydroxide were added into anodic and cathodic compartments, respectively. Fig. 1 shows the experimental configuration for this electrochemical treatment. The applied current density was $2A/m^2$ (related to the rebar area), and conduction time was 28d. The temperature was controlled at $20\pm 2^\circ C$ in the water bath. Besides, the electrolytic solution of sodium silicate was periodically replaced every three days to maintain a stable composition.

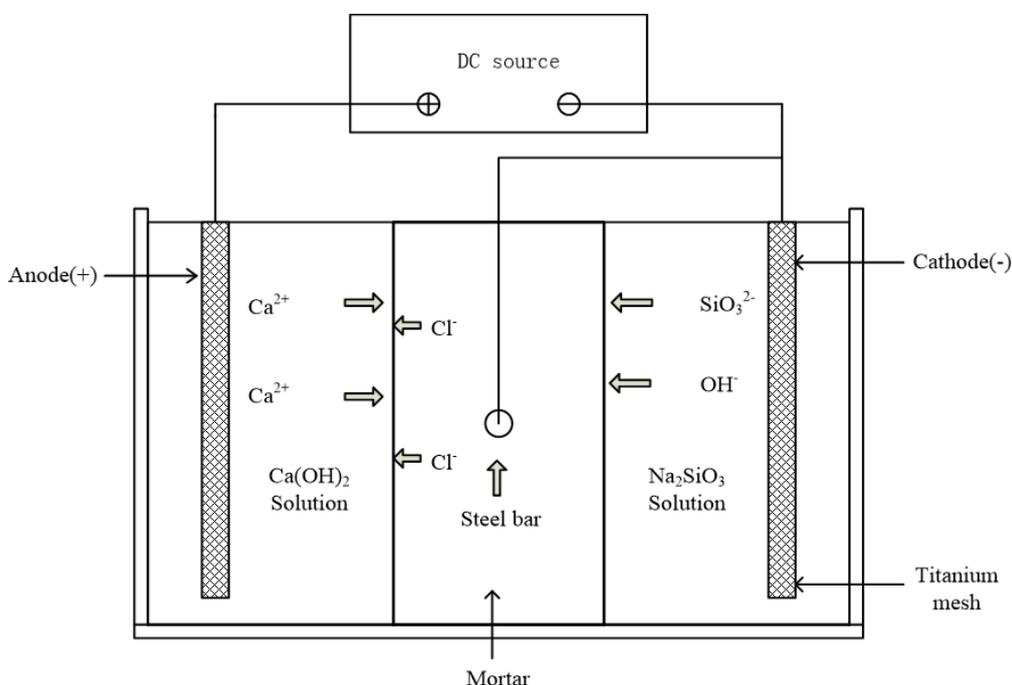


Figure 1. Detailed experimental configuration for the electrochemical treatment.

2.3 Measurement

2.3.1 Extracted chloride efficiency

The extracted chloride efficiency corresponds to chloride extraction percentage, which was measured by potentiometric titrating with silver nitrate ($AgNO_3$) periodically at 4d, 8d, 12d, 16d, 20d, 24d and 28d during the process of this treatment. The chloride extraction percentage is calculated by the following formula:

$$X(t) = \frac{B(t)}{A} \times 100\% \quad (1)$$

where $X(t)$ is the chloride extraction percentage for a specific remediation time; A is the initial chloride ion content and $B(t)$ is the chloride ion extraction content for the specific remediation time.

2.3.2 Corrosion potential and corrosion current density

The mortar samples were immersed in 10% (by mass) sodium chloride solution after this electrochemical treatment. The corrosion potential and corrosion current density were measured using PARSTAT 2273 (AMETEK corporation, USA). A platinum electrode and saturated calomel electrode (SCE) were connected to work as an auxiliary and reference electrode, respectively. The EIS in the frequency range from 10 mHz to 100 kHz was performed periodically on the samples. The perturbing signal applied was 10 mV. The obtained EIS spectra were analyzed with an equivalent-circuit (see Fig.2) for obtaining the values of polarization resistance (R_p) by ZsimpWin software, and then the polarization resistances (R_p) were introduced to Stern–Geary formula to calculate the corrosion current (I_{corr}). The Stern–Geary equation is

$$I_{corr} = \frac{B}{R_p} \tag{2}$$

where I_{corr} is the corrosion current density, B is a constant, assumed to be 26 mV (active state) and 52mV (passive state) [16, 17].

In this equivalent-circuit, R_c 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 [18-20].

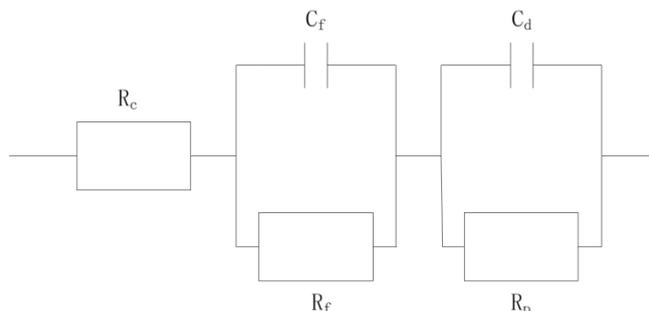


Figure 2. Equivalent circuit of reinforcement mortar.

3. RESULTS AND DISCUSSION

3.1 Extracted chloride efficiency

Fig.3 presents the chloride extraction percentages of the ECE treatment with simultaneous migration of SiO_3^{2-} for mortars with various mineral admixtures (FA, SL and SF). The chloride extraction percentages of the ECE treatment with simultaneous migration of SiO_3^{2-} for mortar with 20% and 30% FA are shown in Fig.3 (a). The chloride extraction amount of mortar with 30% FA was higher than that with 20%. The reason is that FA particles cannot be combined perfectly with the hydration products of cement, and the activity of FA is relative low. Accordingly, the compactness of mortar with high FA content was lower than that of the mortar with low FA content. Under the applied

electric field, the chlorides were easy to extracted in mortar with high FA content. This results are also correspond to the previous literature. It has been found that the electrochemical realkalization depth increases with an increase in the fly ash content [21, 22]. With the increase of FA content in mortar, the extracted chloride amount increased obviously. Fig.3 (b) shows the chloride extraction percentage of the ECE treatment with simultaneous migration of SiO_3^{2-} for mortar with 30% and 50% SL. The amount of chloride extraction during this treatment increased as the increase of SL content in mortar. The results are also correspond to the previous study, which indicates that the mortar with 30% SL has the highest resistance [23]. Under applied electric field, the chloride ions in mortar with 50% SL content were migrated easier than that in mortar with 30% SL content. Compared the mortar with 30% FA and SL, the chloride extraction percentage of the electrochemical treatment for mortar with FA was higher than that with SL. During this treatment, the activity of SL was relative higher, when compared to the FA, so that the chloride in the mortar with FA was easily to be removed under the electric field [22]. Fig.3 (c) shows the chloride extraction percentage of the ECE treatment with simultaneous migration of SiO_3^{2-} for mortar with 5% and 10% SF. As shown in Figure, the chloride extraction percentage of mortar with 5% SF was higher than that with 10% SF. The reason is that as the SF content increased, the electrical conductivity of mortar decreased [22]. In addition, due to hydration of SF, the produced C-S-H adsorbed parts of chloride ions in mortar, resulting in fewer amount of chloride extraction during the treatment [24]. Accordingly, with the increase of SF content in mortar, the chloride extraction percentage was decreased. According to the results above, this electrochemical treatment extracted the chlorides from the mortar with FA, SL and SF effectively. With the increase of FA content in mortar, the extracted chlorides amount of this treatment was increased, and with decreasing of SL content or SF content in mortar, the extracted chlorides amount was increased.

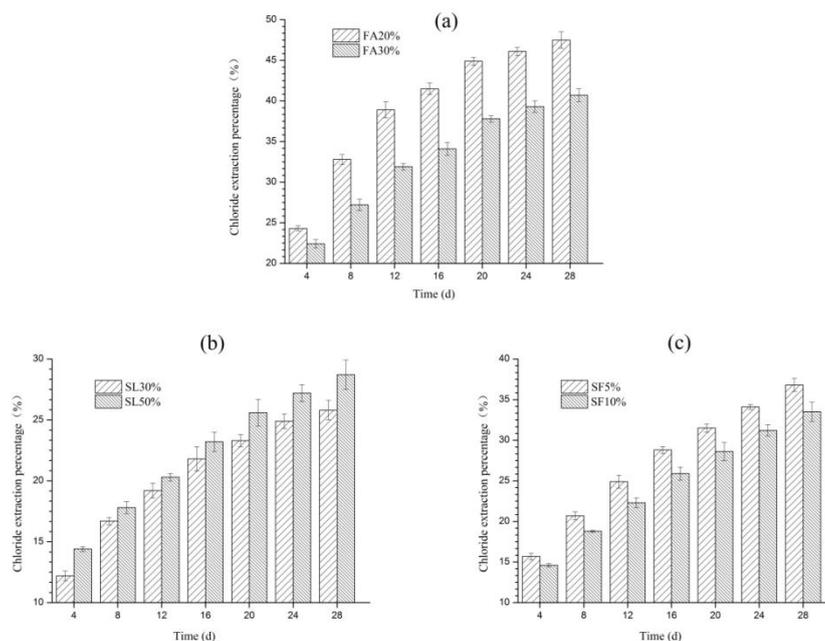


Figure 3. Chloride extraction percentage of mortars with various mineral admixtures (FA, SL and SF) (a) FA (b) SL (c) SF.

3.2 Corrosion performance after the electrochemical treatment

3.2.1 Corrosion potential

Fig.4 shows the corrosion potentials of mortar with various admixtures (FA, SL and SF) in sodium chloride solution. The corrosion potentials of mortar with 20% and 30% FA in sodium chloride solution are shown in Fig.4 (a). At the initial time of saltwater exposure, the corrosion potentials of these mortar specimens were relative low result from the polarization of rebar after the application of electric field. With the increase of immersion time, the corrosion potentials of these mortar specimens increased obviously.

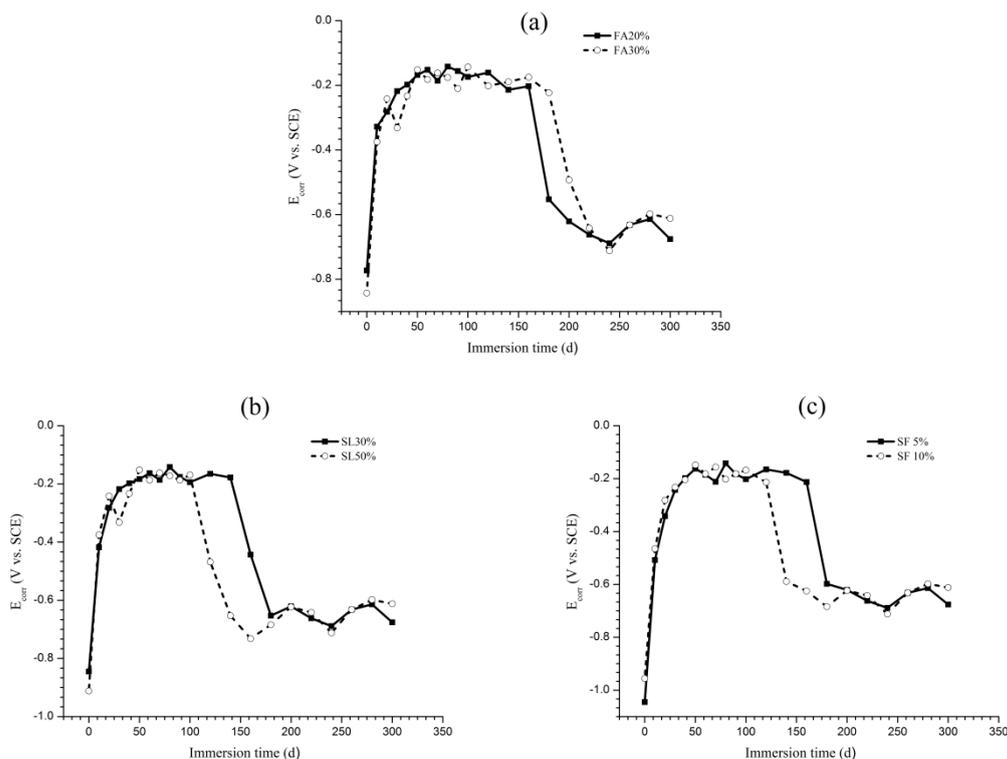


Figure 4. E_{corr} evolution after the electrochemical chloride extraction with simultaneous migration of SiO_3^{2-} for mortars with various mineral admixtures in sodium chloride solution (a) FA (b) SL (c) SF.

Then the corrosion potential of the mortar with FA after the treatment exhibited gentle variations during the period of 30d to 160d. After that period, a potential of mortar sample with 20% FA decay towards more negative value was detected, indicating that the rebar in mortar sample with 20% FA was out of passive condition [18]. Furthermore, the potential of mortar with 30% FA still showed a smooth change, indicating that the rebar was in passive condition. At the immersion time of 180d, the potential showed a decrease obviously, revealing active corrosion occurred at this time. Fig.4 (b) shows the corrosion potentials of mortar with 30% and 50% SL in sodium chloride solution. Similar to the result of FA in Fig.4 (a), the rebar in mortar with SL were polarized after these treatments, and then the potential increased to about -200mV at the time of 30d. After that period, the

potential were in the range 220 to 140 mV during the period of 30d to 100d, corresponding to a state of passivity. Then a decrease of the potential of mortar with 50% SL was detected at the immersion time of 100d, and this was characteristic of out of passive state. The rebar in mortar with 30% was out of passive condition at the immersion time of 140 d. Fig.4 (c) shows the corrosion potentials of mortar with various SF in sodium chloride solution. In the initial time of immersion, the rebar in mortar restored passivity. Then the rebar in mortar with 5% and 10% SF content was at active corrosion state successively, and the corrosion initial times of rebar in the mortar with 5% and 10% SF was 140d and 120d, respectively. The results indicate that with the increase of FA content, the initial time of corrosion for the steel was increased. In contrast, with the increase of SL or SF content, the initial time of corrosion for the steel was decreased.

3.2.2 Electrochemical impedance spectra

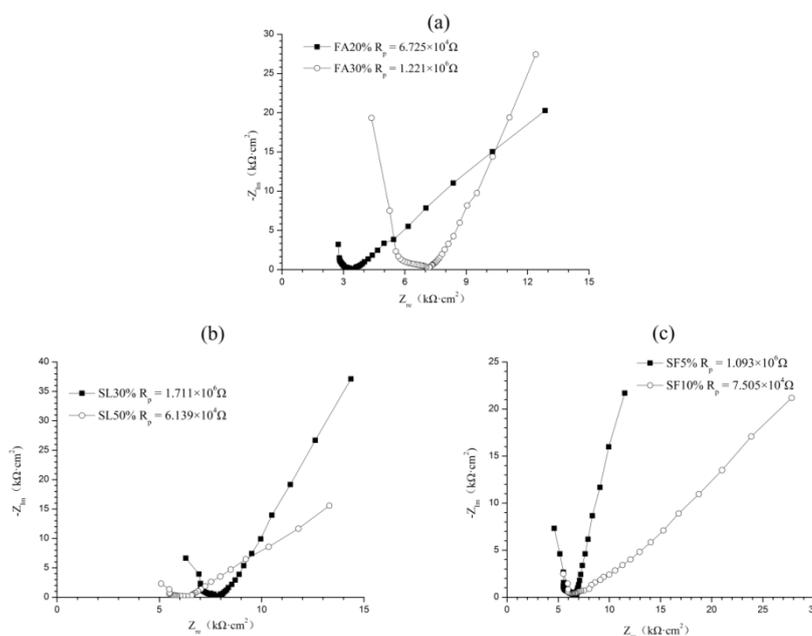


Figure 5. Nyquist plots for the mortars after the electrochemical chloride extraction with simultaneous migration of SiO₃²⁻ for mortars with various mineral admixtures (a) FA (b) SL (c) SF.

Fig.5 (a), Fig.5 (b) and Fig.5 (c) show the Nyquist plots for mortars with 20% and 30% FA at the immersion time of 160d, the Nyquist plots for these mortars with 30% and 50% SL at the immersion time of 100d and the Nyquist plots for these mortars with 5% and 10% SF at the immersion time of 120d, respectively. The range of high frequency in the EIS for the sample in an electrolytic solution indicates the interface resistance between the mortar and rebar, and the section of low frequency corresponds to the charge transfer resistance, which is equal to the polarization resistance (R_p) [25]. By comparing of the capacitive loop diameters of low frequency section in Fig.5, the comparison of capacitive loop diameters for mortars with various admixtures after this treatment as follows: 30% FA > 20% FA, 30% SL > 50% SL, 5% SF > 10% SF. The calculated R_p values were

corresponding to the capacitive loop diameters of low frequency section in these figures, and the comparisons of R_p value for mortars with various admixtures after this treatment as follows: 30% FA > 20% FA, 30% SL > 50% SL, 5% SF > 10% SF. The I_{corr} of mortars with 20% FA, 50% SL and 10% SF after this treatment calculated by Stern–Geary formula were higher than $0.1\mu\text{A}/\text{m}^2$, indicating that the active corrosion of rebar occurred [26]. However, the I_{corr} of mortar with 30% FA, 30% SL and 5% SF after this treatment were far lower than $0.1\mu\text{A}/\text{m}^2$, and these rebars still were in passive state.

3.2.3 Corrosion current density

Fig.6 shows the corrosion current densities of mortar with various admixtures (FA, SL and SF) in sodium chloride solution. Due to the strong polarization of rebar after this electrochemical treatment, the higher corrosion current densities at the initial of saltwater exposure were detected. The corrosion current densities of mortar with 20% and 30% FA in sodium chloride solution are shown in Fig.6 (a). During the salt immersion (from 30d to 160d), the corrosion current densities of mortars with various FA were lower than $0.1\mu\text{A}/\text{cm}^2$, indicating that the rebar restored passive condition [26]. After the immersion time of 160d, the corrosion current densities of mortar with 20% FA increased obviously, indicating that the rebar was out of passive condition and the corrosion risk of rebar raised. However, the mortar with 30% FA after this treatment was out of passive condition at the immersion time of 180d. The reason is the remained chloride content near rebar was increased with an increase of FA. However, the increasing FA content led to more compact structure of mortar [21, 22]. The chlorides in external environment were difficult to diffuse into mortar, resulting in the prolonging the initial time of corrosion for rebar in the mortar. Fig.6 (b) shows the corrosion current densities of mortar with 30% and 50% SL in sodium chloride solution. The rebar in mortars with 30% and 50% SL after this electrochemical treatment was out of passive condition at the immersion time of 140d and 100d, respectively. It is because with an decrease of SL, the remained chloride content near was decreased and the compactness of mortar was improved [22, 23]. The compact structure can prevent chlorides diffusing into mortar, leading to the prolonging the initial time of corrosion for rebar in the mortar. Fig.6 (c) shows the corrosion current densities of mortar with 5% and 10% SF in sodium chloride solution. The rebar in mortars with 5% and 10% SF after this electrochemical treatment was out of passive condition at the immersion time of 120d and 140d, respectively. Combined with the results of corrosion potential, it can be found that this electrochemical treatment was more effective on prolonging the initial time of corrosion for rebar in the mortar with increasing content of FA, or decreasing content of SL or SF. This trend occurs because remained chloride content near was increased with a decrease of SF. Few chlorides were required to diffuse into mortar for rebar corrosion in mortar with higher content of SF.

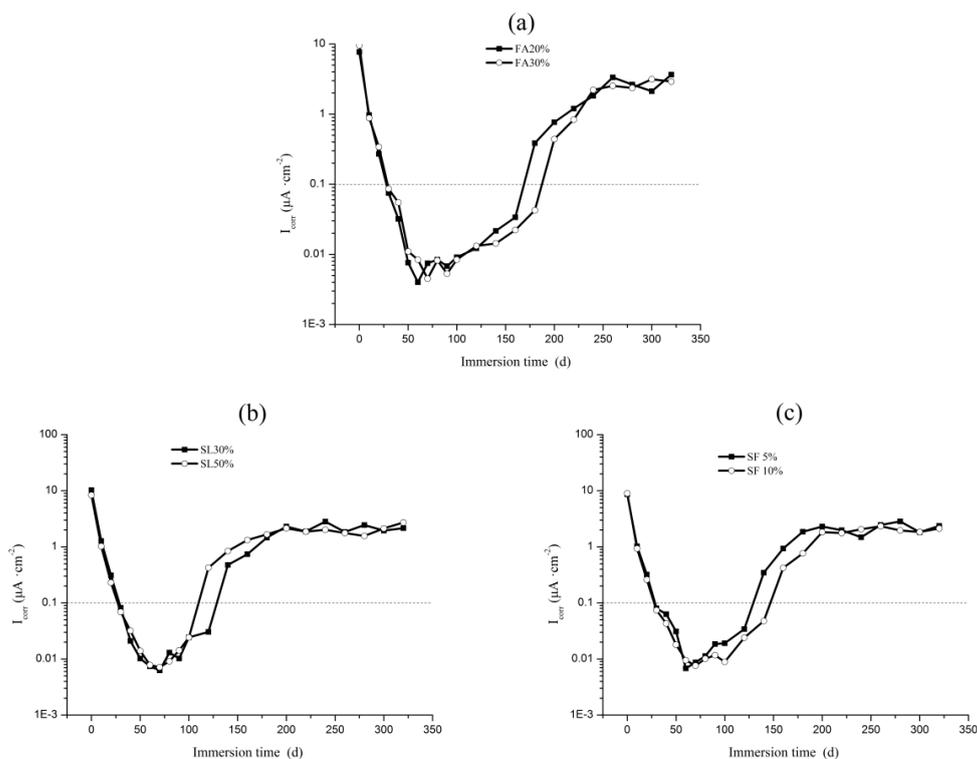


Figure 6. I_{corr} evolution after the electrochemical chloride extraction with simultaneous migration of SiO_3^{2-} for mortars with various mineral admixtures in sodium chloride solution (a) FA (b) SL (c) SF.

4. CONCLUSIONS

In summary, the effects of fly ash (FA), slag (SL) and silica fume (SF) on the electrochemical chloride removal treatment with simultaneous migration of silicate ion were investigated. The chloride extraction efficiency and corrosion properties of steel reinforcement in sodium chloride solution after the electrochemical treatment were measured to evaluate the effects. The conclusions may be summarised as follows:

(1) This electrochemical treatment can extract the chloride ions from the mortar with FA, SL and SF, and prolong the initial time for rebar in mortar with FA, SL and SF effectively, especially for mortar with FA.

(2) Higher chloride extraction percentage can be attained with increasing content of FA. In contrast, with the increase of SL or SF content in mortar, the extracted chloride efficiency of this electrochemical treatment was decreased.

(3) With the increase of FA content in mortar, the initial time of corrosion for rebar in mortar was increased. In contrast, with the increase of SL or SF content in mortar, the initial time of corrosion was decreased.

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References

1. X. Shi, N. Xie, K. Fortune and J. Gong, *Constr. Build. Mater.*, 30 (2012) 125.
2. J. Xu, Y. Song, L. Jiang, W. Feng, Y. Cao and W. Ji, *Constr. Build. Mater.*, 104 (2016) 9.
3. G. Fajardo, G. Escadeillas and G. Arliguie, *Corros. Sci.*, 48 (2006) 110.
4. C. Arya, Q. Said-Shawqi and P.R.W. Vassie, *Cem. Concr. Res.*, 26 (1996) 851.
5. M. Sanchez and M.C. Alonso, *Constr. Build. Mater.*, 25 (2011) 873.
6. B. Elsener and U. Angst, *Corros. Sci.*, 49 (2007) 4504.
7. X.X. Wang, Q.J. Yu, C.L. Deng, J.X. Wei and Z.Y. Wen, *J. Wuhan. Univ. Technol.*, 22 (2007) 764.
8. S. Muthulingam and B.N. Rao, *Corros. Sci.*, 93 (2015) 267.
9. P. Garces, M.J.S. De Rojas and M.A. Climent, *Corros. Sci.*, 48 (2006) 531.
10. J.C. Orellan, G. Escadeillas and G. Arliguie, *Cem. Concr. Res.*, 34 (2004) 227.
11. I.M.A. Abuawad, I.L. Al-Qadi and J.S. Trepanier, *Constr. Build. Mater.*, 84 (2015) 437.
12. H. Shan, J. Xu, L. Jiang and Z. Wang, *Constr. Build. Mater.*, 127(2016) 344.
13. J. Xu, H. Shan, C. Zhang, L. Jiang, L. Tang, Y. Xu and N. Xu, *Mag. Concr. Res.*, 68 (2015) 69.
14. C. Tasdemir, *Cem. Concr. Res.*, 33 (2003) 1637.
15. M. L. Berndt, *Constr. Build. Mater.*, 23 (2009) 2606.
16. C. Andrade and C. Alonso, *Mater. Struct.*, 37 (2004) 623.
17. C. Andrade and J.A. Gonzalez, *Mater. Corros.*, 29 (1978) 515.
18. M.F. Montemor, A.M.P. Simoes and M.M. Salta, *Cem. Concr. Compos.*, 22 (2000) 175.
19. V. Feliu, J.A. Gonzalez, C. Andrade and S. Feliu, *Corros. Sci.*, 40 (1998) 975.
20. W. Aperador, R. Mejia de Gutierrez and D.M. Bastidas, *Corros. Sci.*, 51 (2009) 2027.
21. Z.G. Zou, J. Wu, W. Yu and Z. Wang, *J. Mater. Civil. Eng.* 29 (2017) 04017124.
22. C.J. Shi, *Cem. Concr. Res.*, 34 (2004) 537.
23. C. Dehghanian, *Corrosion*, 55 (1999) 291.
24. H. Zibara, R.D. Hooton, M.D.A. Thomas and K. Stanish, *Cem. Concr. Res.*, 38 (2008) 422.
25. J. Xu, L. Jiang and J. Wang, *Constr. Build. Mater.*, 23 (2009) 1902.
26. L. Li and A.A. Sagues, *Corrosion*, 57 (2001) 19.

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