

Study on the Performance of new Imidazoline Electromigration Inhibitor in Reinforced Concrete

Chonggen Pan¹, Chao Yang¹, Jianghong Mao¹ and Weiliang Jin^{1,2}

¹Ningbo Institute of Technology, Zhejiang University, Ningbo, China

²Institute of Structural Engineering, Zhejiang University, Hangzhou, China

ABSTRACT

Steel bars inside reinforced concrete easily become corroded in high chloride environments, bidirectional electromigration rehabilitation is an important method of repairing the durability of reinforced concrete, it can migrate chloride out of concrete and transfer electromigration inhibitor to the surface of the steel bar under the action of an electric field. In this paper, autonomous synthesis electromigration inhibitor was used with bidirectional electromigration rehabilitation to repair the durability of reinforced concrete. Specifically, the effect of a new imidazoline corrosion inhibitor on chloride migration, corrosion potential, and reinforcement of concrete strength was explored. The research results showed that the dechlorination effect and electrochemical dechlorination made no significant difference on the surface of the concrete, where chlorine removal efficiency was more than 70% and the location of steel efficiency of chlorine was more than 90%. The autonomous synthesis electromigration inhibitor was found to be excellent at facilitating chloride migration and ameliorating corrosion, meanwhile, it had a negligible impact on the concrete strength.

Keywords: Reinforced concrete; Durability; Bidirectional electromigration rehabilitation; Imidazoline inhibitor; Chloride

1.0 INTRODUCTION

The invention of reinforced concrete is considered a major revolution in civil engineering, where reinforcement makes up for the lack of tensile and bending in concrete and concrete provides a dense, alkaline working environment for the reinforcement. Over time in high chlorine environments, reinforced concrete experiences severe damage. Chloride ions cause the reinforcement passivation film to become destroyed and the reinforcement to become corroded. Chloride ions enter the concrete structure through the use of sea sand rather than river sand or the penetration of chloride ions in the environment into the concrete, such as through seawater immersion (Kang, 2018; Yu, 2011). When rebar becomes corroded, the volumetric expansion rate of the rust ranges from 2.26% to 3.46%, which results in cracking of the concrete and, eventually, the rib from the inside.

Concrete in extreme environments, such as the sea and saline lake areas, frozen polar environments, and temperature differences experienced by desert regions, suffers from chloride ion erosion and easily becomes unserviceable early. Generally, the service life of concrete is about 50-100 years, although many domestic marine concrete projects have lasted 10-20 years and some have lasted only a few years. Australia investigated the corrosion of coastal wharves and found severe corrosion of the steel

bars (Ai, 2013). In the Nordic countries, Canada, Australia, and many other countries, the corrosion of steel by chloride is a common occurrence in many construction projects; therefore, large amounts of money have been spent on the associated repair and replacement of materials (Zhang, 2007). The durability of marine-engineering materials is influenced by factors such as steel corrosion, freeze-thaw cycles, chemical corrosion, and marine microbial action. In particular, China's losses from marine environment corrosion account for 10% of the investment in construction, steel corrosion was the main form of reinforced concrete structure damage (Ze, 2014).

Bidirectional electromigration rehabilitation is an important method of repairing the durability of reinforced concrete. This technique discharges chloride ions from concrete and moves inhibitor into the vicinity of the reinforcement under the action of an applied electric field, where, upon arrival at its destination, the inhibitor adheres to the surface of the steel through physical and chemical adsorption (Jin, 2017; Xu, 2015). At present, the corrosion inhibitors suitable for use in bidirectional electromigration rehabilitation are mainly amine, alcohol amines compounds. The electromigration inhibitor forms a protective film on the surface of the reinforcing steel bar and blocks the pores, and it can reach the reinforcement surface through pores in the concrete through siphonage and electric fields,

where the non-polar group of the inhibitor arranges on the reinforcing steel surface to form a hydrophobic layer. This layer of protection can prevent metal ions and corrosion medium, water, and oxygen from penetrating the metal surface, thus playing a role preventing rust and "second corrosion" (Liu, 2008; Han, 2013). When the inhibitor reaches a certain concentration on the surface of the reinforcing steel, it will form a dense protective film that can separate corrosive medium, such as chlorine ions and oxygen, from the steel bars as a means of preventing damage (Chen, 2012). Electrolysis occurs when ions are transferred. A large amount of OH⁻ is produced on the surface of the reinforcement, which improves local basicity and is beneficial to the passivation of the steel bar (Hong, 1999; Luo, 2006).

Alcamines inhibitor has a weak electromigration ability and cannot migrate to the surface of steel quickly or effectively. Under high alkaline conditions, the degree of ionization of alcamines inhibitor is limited and is not enough to dissociate rust, thus limiting its inhibiting effect. Imidazoline inhibitors are newly trending in the field of electromigration inhibitor research. Wang and Shu synthesized a series of imidazoline inhibitors containing with diethylenetriamine, triethylenetetramine using different processes (Wang 2004). Kang and Li used Zanthoxylum bungeanum seed oil and diethylenetriamine to synthesize an imidazoline derivative, which was then reacted with sodium chloride and benzyl chloride to obtain zwitterionic imidazoline derivatives and cationic imidazoline derivatives (Kang, 2004). Fei synthesized a cationic electromigration type imidazoline corrosion inhibitor and examined its effectiveness (Fei, 2015). The methods currently used to evaluate corrosion inhibitors include the weight-loss, electrochemical, and spectral analysis methods. Both domestic and international researchers typically use electrochemical and weight-loss methods in the laboratory, although new methods are often used to obtain better corrosion resistance. Common methods include colorimetric analysis (Mu, 1986), X-ray photoelectron spectroscopy and surface enhanced Raman scattering (Morito, 1973; Tian, 1995). Liu and Li (2003) used the potentiodynamic method to study the effect of imidazoline corrosion inhibitor on the corrosion resistance of a metal surface and electrochemical impedance spectroscopy to evaluate the carbon steel EIS spectrum for the membrane surface. These authors put forward the characteristics of the equivalent circuit. Zhang and Bai (2003) studied the effect of an imidazoline corrosion inhibitor using the weight-loss method and electrochemical measurements, and they found the introduction of multi-adsorption centers enhanced the surfactant adsorption capacity of the metal surface, thus improving inhibition. Lei and Xiao used weight-loss experiments and a self-made local corrosion simulation probe to study corrosion inhibition by imidazoline (Xiao, 2001). The

corrosion inhibitor were found to have an imidazoline ring structure and displayed effective inhibition. Xun and Zhou used the weight-loss method to study inhibition of corrosion by naphthenic imidazoline derivatives in sulfuric acid medium (Zhou 2006). However, few researchers have studied the effectiveness of imidazoline inhibitor in concrete. Whether imidazoline can migrate to concrete under the action of an electric field and protect the reinforcement is unknown. In the present study, autonomous synthesis electromigration of imidazoline inhibitor was used for bidirectional electromigration rehabilitation and the effectiveness of imidazoline inhibitor in concrete was evaluated. Migration of a new imidazoline inhibitor to concrete under an electric field and its protective effects were explored.

2 0 SYNTHESIS OF IMIDAZOLINE QUATERNARY AMMONIUM SALT

2.1 The route of imidazoline quaternary ammonium salt synthesis

In this paper, a new imidazoline inhibitor with a symmetrical molecular structure and containing two imidazoline heterocycles and two alkyl long chains of lauric acid was synthesized. The imidazoline molecules contained a five-membered heterocyclic ring with two N atoms. The adsorption ability of transition metals is higher than the two N atoms undergo the heterocyclic electron effect, which significantly increasing the electron density of the imidazole heterocyclic ring, and providing sufficient electric and transition metal atomic unoccupied empty d-orbital bonding. The two five-membered heterocycles of bicyclic imidazoline further increased the electron cloud density of the imidazole heterocycles, enabling them to provide enough electrons to bond with transition metal atoms with d-orbitals unoccupied by electrons or completely occupied by electrons. The synthetic route is presented in Fig. 1.

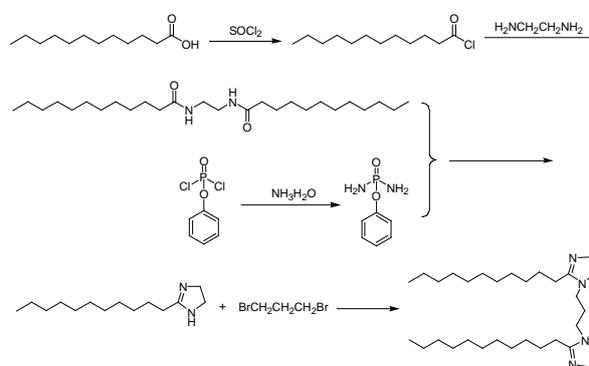


Fig. 1. Route of synthesis

The synthesized double ring imidazoline quaternary ammonium salt inhibitor was a light yellow solid. The

solid product was easily soluble in water and had obvious surface activity.

2.2 Weight-loss method to validate resistance of inhibitor

A saturated pore solution of calcium hydroxide and 0.01 mol/L sodium hydroxide was used to simulate the pore fluid of reinforced concrete. In order to accelerate the corrosion rate, 3% sodium chloride was added to the simulated concrete pore solution.

The steel bar used in this study was ordinary HPB235 rounded steel bar with a 10 × 100 mm diameter. Before the experiment, 800# sand paper was used to remove the rust on the surface of the steel bar, which was then washed with anhydrous alcohol to remove any potentially influencing factors, such as grease. After tests on the steel bar were completed, and vacuum drying was performed. The weight was determined using a high precision electronic balance and the quality of the steel bar specimen recorded. Double ring imidazoline quaternary ammonium salt and three ethylene four amine were used at a concentration of 1 mol/L as inhibitors. For controls, inhibitor was not added and the remaining conditions were unchanged. Each of the 6 rust-treated specimens was placed in the treated steel bar. After soaking for 7 and 14 d, 3 steel samples were removed from each inhibitor solution. The surface corrosion products were washed away, the steel samples were weighed after vacuum drying, and the quality of the reinforcement samples was recorded after corrosion.

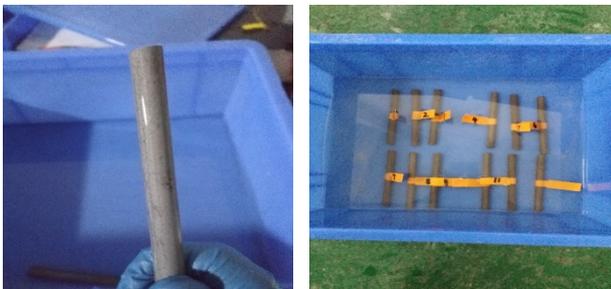


Fig.2. Test process of Weight-loss method

In weight-loss experiments, the corrosion rate called V and corrosion inhibition rate called η calculated using formulas (2-1) and (2-2).

Corrosion rate:

$$V=(m_0-m_1)/s.t \tag{2-1}$$

Corrosion inhibition rate :

$$\eta=[(V_0-V_1)/V_0] \times 100\% \tag{2-2}$$

Type: m_0 and m_1 -quality of steel bar before and after corrosion, respectively (g), s -exposure area (m^2), t -soaking time (h), V_0 and V_1 -corrosion rate in the absence and presence of inhibitor, respectively ($g/m^2.h$). The calculated corrosion inhibition rate

results for the steel bar specimens are shown in Table 1.

Table 1. Corrosion inhibition rates of different inhibitors in simulated concrete pore fluid

Test	Inhibitor	Time	Mass	Rate
Concrete pore solution	-	7	0.0710	-
		14	0.1499	-
Concrete pore solution	TETA	7	0.0585	17.6%
		14	0.1101	26.5%
Concrete pore solution	Imidazoline	7	0.0424	40.3%
		14	0.0916	38.8%

From the above table, it can be seen that, in the simulated concrete pore fluid, three ethylene four amine had relatively little effect on corrosion of the steel bar. After 14 d of immersion, the maximum corrosion inhibition rate was 26.5%, which was far lower than that of the self-made bicyclic imidazoline quaternary ammonium salt corrosion inhibitor. Bicycloimidazoline quaternary ammonium salt corrosion inhibitor incurred good resistance to rust after 7 d immersion, where the corrosion inhibition rate reached 40.3%. After 14 d immersion, the corrosion inhibition rate reached 38.8%. The steel corrosion rate first increased and then decreased with extensions in soaking time, but the overall inhibition of the corrosion rate was far greater than that displayed by the three ethylene amine four-treated steel. Based on the weight-loss method, self-made bicyclic imidazoline quaternary ammonium salt inhibitor has been determined to be more effective than three ethylene four amine and is a good inhibitor for steel bar corroded by chloride salt.

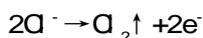
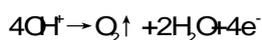
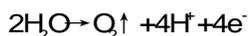
3.0 BIDIRECTIONAL ELECTROMIGRATION REHABILITATION

3.1 Principle underlying bidirectional electromigration rehabilitation

The bidirectional electromigration rehabilitation device used is presented in Fig. 3. The bottom of the tested concrete block was soaked in a well-dispensed inhibitor solution, the steel bar was embedded in the concrete as a cathode, and the stainless steel iron plate was used as an anode in the inhibitor solution. Two electrodes were connected with direct current, the chloride ions in the concrete moved outside the concrete under the action of an electric field, and the external cationic rust resisting group moved to the interior of the concrete.

The anode and cathode reactions were as follows:

Anode reactions:



Cathode reactions:



Hydroxyl ions in the pore fluid can continue to be produced near the cathode steel bar and the steel near the original reinforced alkaline and passive corrosion can be stopped. The nitrogen ions in the inhibitor were stronger and smaller in size than the chloride ions. Therefore, the chloride ions can be isolated on the surface of the reinforcement.

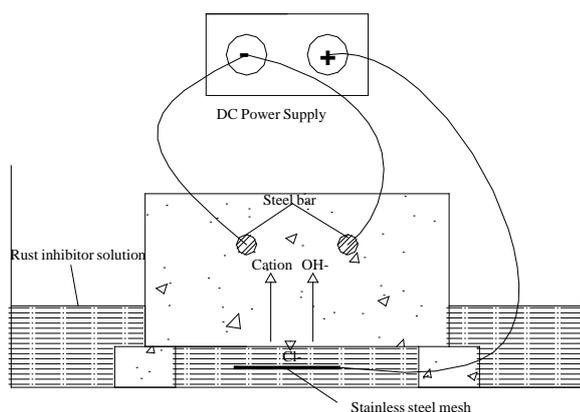


Fig. 3. Principle underlying bidirectional electromigration rehabilitation

3.2 Designing and preparation of concrete block

In this experiment, the strength grade of concrete is C30. The dimensions of the concrete were 150 mm length \times 150 mm width \times 100 mm height. Every concrete block contained two HPB235 round steel reinforcing bars with 10 mm diameters and the thickness of the concrete protection layer was 30 mm as shown in Fig. 4. The concrete blocks were made using three lions P-O 52.5 grade cement, pebbles with diameters of 5.0-18.0 mm, medium coarse sand, and tap water. When pouring the concrete, a final concentration of 3% sodium chloride was added to the cementitious material to simulate a high chloride environment. The composition of the concrete block is presented in Table 2.

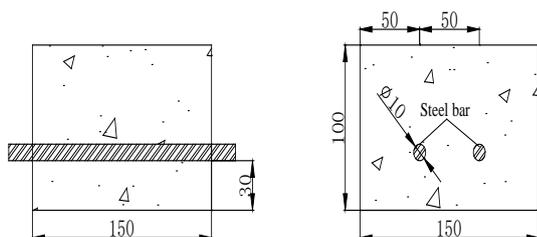


Fig. 4. Concrete block dimensions

Table 2. Components of concrete block

Strength	Water (kg/m ³)	Cement (kg/m ³)	Sand (kg/m ³)	Gravel (kg/m ³)
C30	177	393	534	1297

3.3 Bidirectional electromigration rehabilitation

In order to investigate the effect of the new imidazoline inhibitor on concrete corrosion resistance, experiments comparing different inhibitors were carried out. In the experiments, steel was used as the cathode and external barbed wire was used as the anode. The concrete was energized with a current density of 3A/m² for 14 d. The electrolytes used for bidirectional electromigration rehabilitation are listed in Table 3.

Table 3. Samples of electrolytes

Strength	Samples	Electrolyte (mol/L)	
		New imidazoline	TETA
C30	A	0.3	
C30	B		0.3
C30	C	--	--

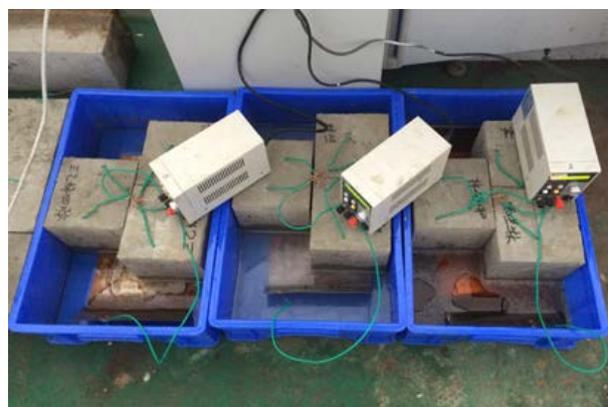


Fig. 5. Test site

After 14 d, the concrete block was removed, and surface was also cleaned and then soaked for 24 h in water. After above step, the potentiodynamic polarization curve was directly measured. After the polarization curve test was completed, the concrete was ventilated and dried. Based on the size of the concrete blocks, impact drill was selected and the concrete powder sample was taken from every 5 mm in depth (Fig. 6). The resulting concrete powder was sifted through a mesh screen with a mesh diameter of 0.3 mm and immersed in deionized water for 24 hours and then the chloride ion content in the deionized water was determined. The inhibitor content in the concrete was also measured. The nitrogen content is usually indicative of inhibitor

content. The concrete powder sample was collected from every 10 mm in depth. Each test sample required 20 mg concrete powder with particles sized $> 80 \mu\text{m}$ to test the inhibitor content. Therefore, the concrete powder was sifted through mesh screen with a mesh diameter of 0.075 mm and concrete powder with particle sizes $> 0.075\text{mm}$ was stored in centrifuge tubes.



Fig. 6. Concrete block powder extraction

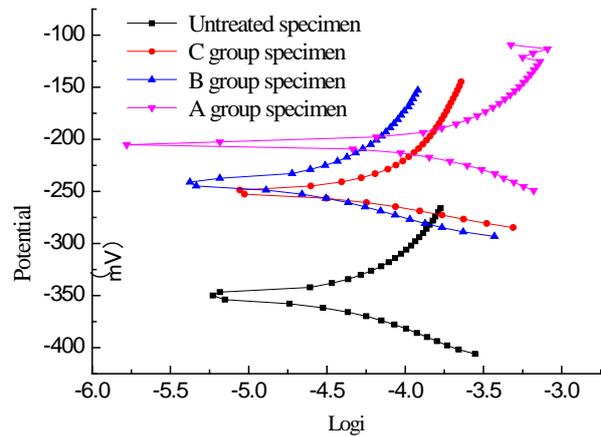
After the concrete powder samples were retrieved from the C30, the test pieces were broken and cement hydration products near the surface of steel bar with diameters of no more than 20 mm were retrieved for analysis by scanning electron microscopy. After the concrete powder sample was collected from the concrete samples, the axial compressive strengths of the concrete blocks were determined.

4.0 RESULTS AND DISCUSSION

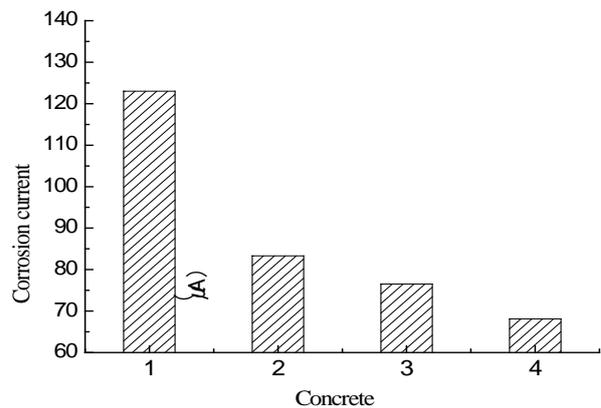
4.1 Corrosion potential and resistance of steel

After powder was removed from the reinforced concrete specimens, the surface of the concrete was cleaned and the concrete was placed in a ventilated area for 72 hours. After excluding the influence of polarization treatment, the potentiodynamic polarization curve was measured.

The potentiodynamic polarization curves were measured using a Reference 600 electrochemical work station, which uses three electrode system. One steel bar in the concrete was used as the working electrode, the other steel bar was used as the auxiliary electrode, and the saturated calomel and the Calomel electrodes were used as reference electrodes. The scanning range of potentiodynamic polarization was -0.07 to 0.07 V in relation to the open circuit potential and the scanning speed was 0.333 mV/s .



(a) Corrosion potential



(b) Corrosion current

Fig.7. Potentiodynamic polarization curve of steel bar

From Fig. 7(a), it can be seen the corrosion potential of the untreated reinforced concrete specimens was the most negative, reaching -350 mV , and the corrosion potentials of the reinforced concrete specimens after electrochemical repair were all moving forward. The positive shift in corrosion potential of the imidazoline quaternary ammonium salt-treated concrete was the largest with a positive shift of 145 mV and corrosion potential of -205 mV . The positive moving amplitude of the corrosion potential of the three ethylene four amine-treated steel bar was 107.3 mV and the corrosion potential reached -242.7 mV . The positive moving amplitude of the corrosion potential of the electrochemical dechlorination-treated steel bar was 100 mV and the corrosion potential reached -251 mV . In general, more positive corrosion-resistance potential of the steel indicates a more extensive area of passivation, which is beneficial to the durability of the reinforced concrete. Based on the positive shift in corrosion potential, the imidazoline quaternary ammonium salt and three ethylene four amine electromigration inhibitors promoted the durability of concrete. From the steel corrosion potential amplitude it can be seen the imidazoline quaternary ammonium salt prevents rust better than three ethylene four amine, and three ethylene four amine is a better inhibitor of rust than electrochemical dechlorination.

Figure 7(b) presents the analysis performed using reinforcement corrosion current software with the electrochemical workstation, where 1, 2, 3, and 4 represent the reinforced corrosion currents of the untreated, electrochemical dechlorination-treated, three ethylene four amine-treated, and imidazoline quaternary ammonium salt-treated reinforced concrete specimens, respectively. It can be seen in the diagram the corrosion current of the untreated reinforced concrete specimens was the largest at 123 μA , while the corrosion current of the imidazoline quaternary ammonium salt-treated specimens was the smallest at 68.1 μA . The corrosion current of the three ethylene four amine-treated samples was 76.5 μA and the corrosion current of the electrochemical chlorination-treated samples was 83.3 μA . The corrosion current of the reinforcement reflects the corrosion rate of the steel bar under no external current. The corrosion rate is proportional to the corrosion current, where the larger the corrosion current, the faster the corrosion rate. Imidazoline quaternary ammonium salt and three ethylene four amine both reduced the corrosion current and slowed down the corrosion rate of the steel bar and protected the durability of the concrete structure. The corrosion current of the imidazoline quaternary ammonium salt was higher than that of three ethylene four amine, indicating imidazoline quaternary ammonium salt was more effective than three ethylene four amine.

Based on the above analysis, imidazoline quaternary ammonium salt and three ethylene four amine inhibit rust, delay corrosion, and increase corrosion resistance of steel bars in concrete, where imidazoline quaternary ammonium salt inhibitor is more effective overall than three ethylene four amine.

4.2 Chloride ion concentrations in concrete

A Chloride-Meter DY-2501 was used to measure chloride ion concentrations in the concrete. The control group consisted of concrete specimens not treated by electrochemical repair and was used to determine the initial chlorine ion concentrations in the chloride-corroded concrete (Fig. 8).

From Fig. 8, it can be seen the chloride ion concentrations in relation to the concrete protective layer thickness ranged from 0.14-0.15% with small fluctuations, indicating the concrete protective layer was evenly distributed along the initial direction of chloride ions and the initial concrete chloride concentration was 0.1446%.

After the electricity was completed, three holes were taken under the area of the steel bar. The chloride concentration was detected by Chloride-Meter DY-2501 and the chlorine ion discharge efficiency was calculated (Figs. 9 and 10).

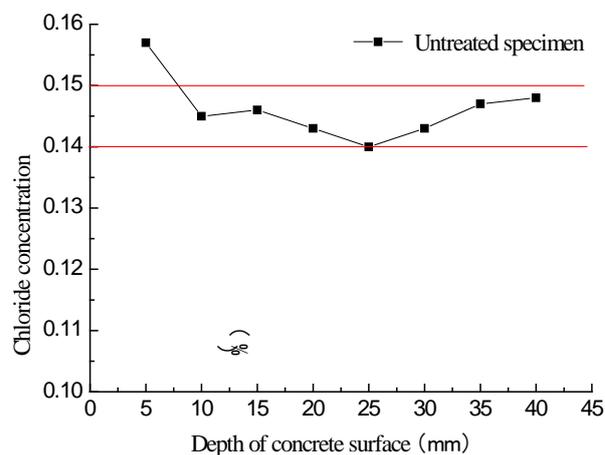


Fig. 8. Initial chloride concentration in concrete

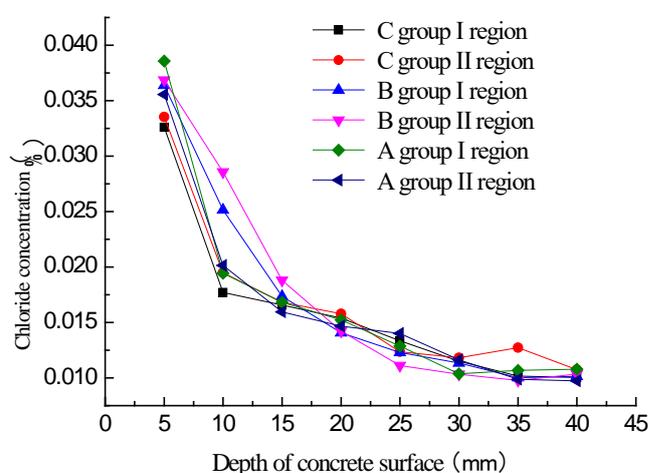


Fig. 9. Chloride concentration

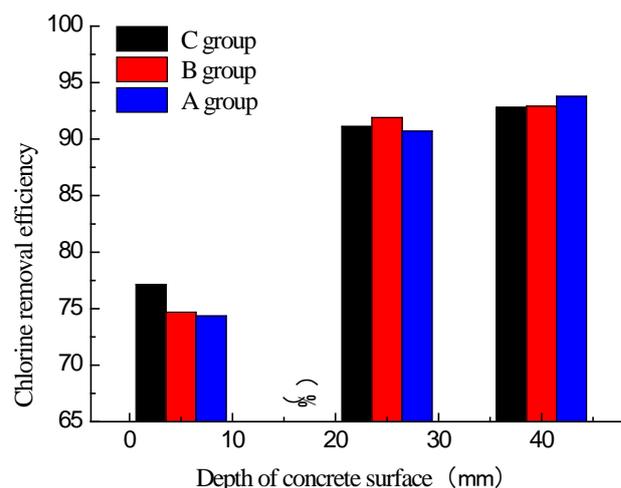


Fig. 10. Chlorine removal efficiency

From Fig. 9, it can be seen the residual chloride concentrations in the specimens treated with the three different electrolytes displayed a decreasing trend along the thickness of the protective layer. Specifically, the residual chloride ion concentration was highest on the surface of the concrete and lowest on the steel bar. No obvious differences were

observed in the internal residual chloride levels in the concrete specimens for the three electrolytes and the residual chloride concentrations at the steel bar were about 0.01%. From the above diagram, it can be seen there were slower changes in and more stable levels of residual chloride ions closer to the steel bar.

Figure 10 is a chlorine removal efficiency diagram for specimens electrochemically treated with different electrolytes at 5, 25, and 40 mm from the surface of the concrete. The dechlorination efficiency was lowest closer to the surface (5 mm), where the efficiencies of the three electrolyte treatments ranged from 70-80%. The removal efficiency of the chlorine-saturated calcium hydroxide solution was slightly higher than the other two solutions tested. The dechlorination efficiency of the imidazoline quaternary ammonium salt solution and three ethylene four amine solution on the surface of the concrete displayed no obvious difference and averaged 77%. The dechlorination efficiencies of the three electrolyte solutions at 25 and 40 mm were higher than 90%. The dechlorination efficiency of three ethylene four amine was slightly higher than the other two treatments at 25 mm and the chlorine removal efficiency was 91.9%. The dechlorination efficiency of imidazoline quaternary ammonium salt was slightly higher than the other two treatments at 40 mm and the dechlorination efficiency was 93.8%. There were no obvious differences in the efficiency of chlorine removal by the three electrolyte solutions.

Based on the above analysis, it was determined based on chlorine removal that imidazoline quaternary ammonium salt and three ethylene four amine were excellent electromigration inhibitors after 15 d electricity treatment. Most of the chloride ions migrated out of the concrete specimens, which is conducive to protecting the durability of concrete structures. There were no significant differences in residual chlorine concentration and chloride removal efficiency between the two inhibitors and the addition of inhibitors only in the saturated calcium hydroxide solution. Therefore, electromigration inhibitor does not affect the migration of chloride ions.

4.3 Inhibitor concentrations

In this experiment, an organic element analyzer (EA1112) was used to measure the concentration of the new imidazoline corrosion inhibitor content in the concrete. Concrete powder (20 g) was weighed using a micro-electronic balance (MX5) and then placed into a special silver tin small cup. The organic element analyzer was used to measure the imidazoline corrosion inhibitor in the concrete (Fig. 11).

As shown in Fig. 11, the inhibitor concentration in the reinforced concrete decreased as the depth from the

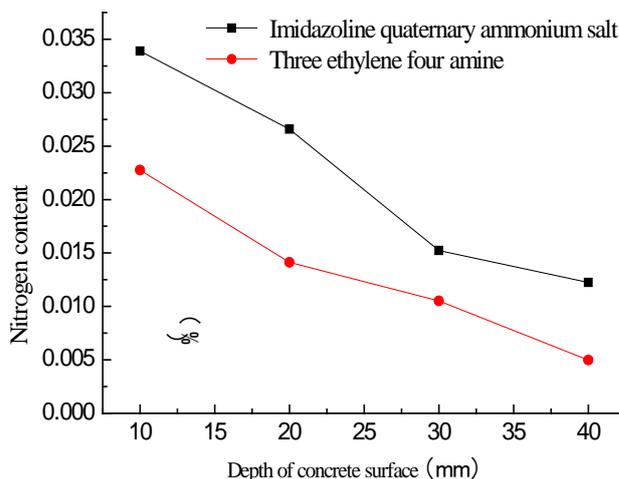


Fig. 11. Corrosion inhibitor content in concrete

concrete surface increased. Specifically, the inhibitor content was highest on the surface of the concrete and lowest on the steel bar. The highest and lowest concentrations of imidazoline quaternary ammonium salt inhibitor in the concrete specimens were approximately 0.035% and 0.013% and the highest and lowest content of three ethylene four amine were 0.023% and 0.005% in concrete, respectively. The amount of imidazoline quaternary ammonium salt inhibitor in the concrete was higher than three ethylene four amine. The surface inhibitor content in concrete was about three-fold that of three ethylene four amine and the content of reinforcing bar corrosion inhibitor was 2.6-fold that of three ethylene four amine. For three ethylene four amine and electrochemical dechlorination, the corrosion potential and current of the concrete bar were very similar. This may be because the three ethylene four amine content on the surface of steel bar was very low and with less effective at rust protection for the reinforcing steel bar. In the experiments, the same concentration of imidazoline quaternary ammonium salt and three ethylene four amine was used with 0.3 mol/L, after treatment, the imidazoline quaternary ammonium salt corrosion inhibitor content in the concrete was higher than that of three ethylene four amine, which indicating the imidazoline quaternary ammonium salt experienced stronger migration under the electric field than the three ethylene four amine.

4.4 Scanning electron microscopy analysis

Figure 12 shows that in the vacuity contrast (untreated) group, the hydration product contained a large amount of needle-shaped ettringite, calcium hydroxide, and more lamellar silicate gel C-S-H. In B group, the needle-shaped ettringite were virtually invisible, but there was a large amount of stacked lamellar calcium hydroxide and comparatively less lamellar silicate gel C-S-H. In the imidazoline quaternary ammonium (Im)-treated group, which consisted of samples treated with bidirectional

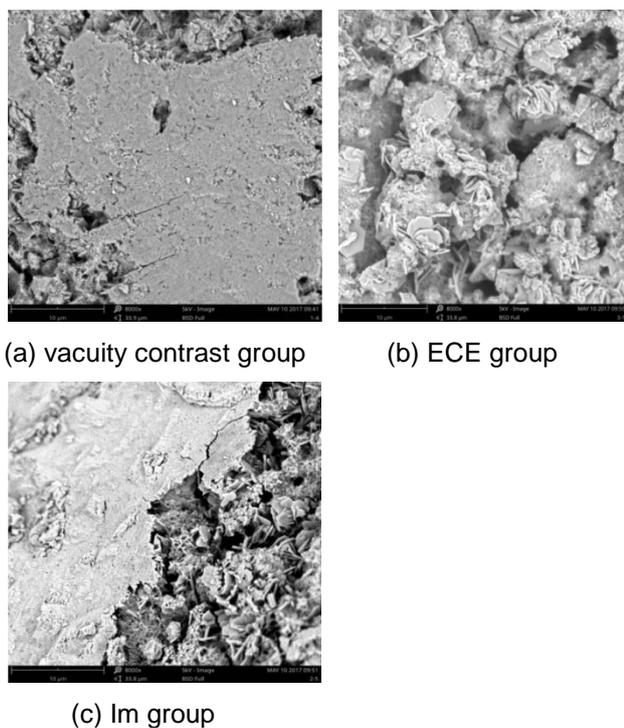


Fig.12. SEM images of different group

electromigration rehabilitation, there was an increase in flake calcium hydroxide near the reinforcement, which is very beneficial for protecting the steel bars. However, the hydration product density of the concrete decreased and the porosity increased in the ECE and Im groups, perhaps due to the production and outward diffusion of hydrogen during energization. Conversely, lamellar silicate gel C-S-H hydrolysis by electricity may lead to expansion of the pores.

5.0 CONCLUSIONS

In the present study, a new imidazoline corrosion inhibitor was synthesized in the laboratory and its effectiveness at increasing corrosion resistance was studied. The conclusions of this study are as follows:

1) The effect of electrochemical treatment with different inhibitors on chlorine salt erosion of reinforced concrete corrosion potential and corrosion current were studied. It was found imidazoline quaternary ammonium salt and three ethylene four amine can be able to make move the corrosion potential forward. The imidazoline quaternary ammonium salt corrosion potential shifted positively to the amplitude ratio of three ethylene four amine. The two inhibitors reduced the corrosion current, where the imidazoline quaternary ammonium salt corrosion current displayed a more significant reduction than alcohol amine inhibitor and was more effective at increasing resistance than three ethylene four amine.

2) Inhibitor from the external solution was found to discharge the majority of chloride ions in the concrete. The dechlorination effect and electrochemical dechlorination made no significant difference on the surface of the concrete, where chlorine removal efficiency was more than 70% and the location of steel efficiency of chlorine was more than 90%, which revealing the electromigration inhibitor did not affect the migration of chloride ions in the concrete.

3) The inhibitor content in the concrete specimens after exposure to electricity was evaluated. The inhibitor content in the concrete specimens decreased along the thickness of the concrete protective layer, meaning the location where the content of the inhibitor on the surface of the concrete was the highest corresponded with where the corrosion inhibitor content in the steel bar was the lowest. The imidazoline quaternary ammonium salt inhibitor content in the concrete was higher than that of three ethylene four amine, indicating the electric migration ability of imidazoline quaternary ammonium salt inhibitor was stronger than the other compounds under an electric field.

Acknowledgement

The authors would like to acknowledge the assistance of Financial support for the research which was provided by Natural Science Foundation of China (No. 51778578), Natural Science Foundation of Zhejiang Province (No. Y17E080072, LY16E090007) and Natural Science Foundation of Ningbo City (No. 2016A610220, 2016A610219)

References

- KANG, W. N., 2013. Investigation of corrosion status of reinforced concrete reinforcement and its causes[J]. *Technology and Enterprise*, (8): 147-147.
- YU, J., 2011. Damage analysis and experimental study of reinforced concrete structures with rebar corrosion[D]. Zhejiang University.
- AI, Z. Y., 2013. The Design and Synthesis of a New Type of Electro-migrating Corrosion Inhibitor and Its Influence on the Composition, Structure and Performances of Reinforced Concrete[D]. South China University of Technology.
- ZHANG M. 2007. Study on the Durability of High-pile Wharf-Test Study about the Effect of Concrete Carbonization Degree on Chloride Diffusion Coefficient[D]. Tong Ji University.
- ZE, L., PAN, C. G., 2014. Research on properties and preparation of resist seawater and corrosion inhibitor[J]. *New Building Materials*, 26 (s10-11): 1787-1790.

- JIN, W. L., HUANG, N., XU, C., 2014. Experimental research on effect of bidirectional eletromigration rehabilitation on reinforced concrete – Concentration changes of inhibitor, chloride ions and total alkalinity[J]. Journal of Zhejiang University(Engineering Science), 48(8):1586-1594.
- XU, C., JIN, W. L.,HUANG, N., 2015. Experimental on repair effect of bidirectional eletromigration rehabilitation on reinforced concrete: changing rule of protective layer strength[J]. Journal of Zhejiang University (Engineering Science) , (06): 1128-1138.
- LIU, Z. Y., LIAO, C. W., ZHOU, W. L., 2008. Maintenance and improvement of durability of reinforced concrete using migrating corrosion inhibitors [J].Journal of the Chinese ceramic society, 36(10): 1494-1500.
- HAN, W. W., TIAN, J. L., CAI, W., 2012.Research progress of steel bar rust inhibitor[C]. The Eighth National Academic Meeting on durability of concrete.
- CHEN, C. C., CAI, J. S., LIU, J. Z., 2015. Use of Aminoalcohol as inhibitor in Chloride-contaminated Steel Reinforced Concrete[J]. Journal of the Chinese ceramic society, (04): 393-399.
- HONG, N. F., 1999. Corrosion and protective technology of rebar in concrete-rebar corrosion by chloric salt [J]. Industrial Construction, 29(10), 60-63.
- LUO, B. D., 2006.Study on correlation and prediction of durability of concrete against chloride ion penetration[D]. ZhongshanUniversity.
- WANG, J. H., SHU, F. C., 2004, Preparation and Evaluation of Imidazoline Derivative as Corrosion Inhibitor[J]. Advances in fine petrochemicals, 5(6): 22-24.
- KANG, H. Y., LI, S. J., 2004, Preliminary investigations synthesis and anticorrosive per for man ces of imidazolined rivatives for omzan thoxy lumbun geanoleum and diethyleneiramine[J]. Speciality petroci emicals, 5: 33-35.
- FEI, F. L., 2015. The investigation on the preparation of a tailored electro-migrating corrosion inhibitor and its corrosion inhibition performance and mechanism[J]. South China University of Technology.
- MU, G. N., 1986. Corrosion of pure aluminium in hydrochloric acid solution[J]. Chemistry, (2): 38-39.
- Morito, N., Suetaka, W. J., 1973. Jpn.Inst.Met [J]. 37: 216.
- TIAN, Z. Q., REN, B., XU, C. X., 1995. Applications and Prospectus of Electrochemical in_situ Raman Spectroscopy[J]. ELECTROCHEMISTRY, 5(1):1.
- LIU, J. P., LI, Z. F., 2003. Electrochemical behavior of an imidazoline filmformed on carbon steel surface [J]. Corrosion science and protection technology, 15(5): 263-265.
- ZHANG, S. C., BAI, Z. M., 2003. Synthesis and performance of corrosion inhibitors with multi adsorption centers [J]. Corrosion science and protection technology, 15(2): 79-81.
- LEI, L. C., XIAO, K., 2001. Preparation and characteristics of a novel imidazolineinhibitor made from naphthenic acid and diethylenetriamine [J]. Corrosion& Protection, 22(10): 420-423.
- ZHU, X., ZHOU, X. Q., 2006. Study on corrosion inhibition of naphthenic Imidazoline derivative in H₂SO₄ solution[J].Applied Chemical Industry, 35(1): 51-53.