ORGANIC CORROSION INHIBITOR OF TRIETHYLENETETRAMINE INTO CHLORIDE CONTAMINATION CONCRETE BY BIDRECTIONAL ELECTROMIGRATION REHABILITATION

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ABSTRACT

Triethylenetetramine (TETA), as a corrosion inhibitor for steel in aqueous media was introduced into chloride-contaminated concrete specimens by using a novel method called bidirectional electromigration rehabilitation (BIEM). An electric field was applied between embedded steel cathodes and external anodes to inject the corrosion inhibitor from external electrolytes into the concrete and at the same time to extract the chloride ions from the concrete cover zone.After the treatment, the specimens were drilled to determine the concentration profiles of the corrosion inhibitor, chloride and hydroxyl ions within the concrete. Effects of variations in the applied current density, duration of electrolysis, water/cement ratio, initial chloride content and surface carbonation on the concentration profiles of the proposed ions were determined. Electrochemical chloride extraction (ECE) in which saturated $Ca(OH)_2$ solution was used as an external electrolyte was applied as control experiments. As is expected, chloride content decreased and alkalinity increased after the treatment. Also, the concentration of the inhibitor injected around the embedded steel bars was adequate to provide corrosion protection. The results can provide a direction in designing the BIEM process.

KEYWORDS

Cement, Organic corrosion inhibitors, Steel corrosion, Dissociation constant; Migration

INTRODUCTION

Reinforcement corrosion is one of the main causes for the deterioration of concrete structures (P. T. Miyagawa 1991; K. Mehta and R. W. Burrows 2001). The reinforcing steel in concrete structures exposed in the marine environment or suffering de-icing salt may corrode when the chloride concentration around the steel bar reaches the threshold value, leading to the performance degradation or even early structural failure (Djerbi, Bonnet and Khelidj 2008; Song *et al.* 2010). It is important to protect the steel from corrosion in order to extend the service lives of the chloride contaminated reinforced concrete structures.

In recent years, electrochemical methods have been widely applied in rehabilitation for existing reinforced concrete structures (Martínez *et al.* 2009). Among those electrochemical rehabilitation techniques and

electrochemical chloride extraction (ECE) are most widely studied and used in repairing chloride-contaminated structures. The drawback of these methods, however, is that, firstly, the treatment cannot remove all chlorides in the concrete; secondly, the treatment itself does not provide a permanent solution as chloride ions could come back again after the treatment ceases (Fajardo *et al.* 2006; Miranda *et al.* 2006; Yeih *et al.* 2006). In order to protect the reinforcing steel from corrosion in addition to the removal of chlorides, suggestions have been made to use corrosion inhibitors that can be applied on the surface of concrete cover (Miranda *et al.* 2006). These kinds of inhibitors are mostly based on particular amines and alkanolamines or their compounds, which are claimed to be capable of diffusing considerable distances through concrete by capillarity when applied on the surfaces of the structures (Morris and Vázquez 2002; Morris *et al.* 2003). Although these corrosion inhibitors proved to be effective in preventing reinforcement from corrosion within concrete structures (Nmai 2004; Ormellese *et al.* 2011), it should be emphasized that the surface-applied inhibitors can hardly penetrate to the depth of embedded steel reinforcement, reaching adequate concentrations to provide corrosion protection when the concrete cover is too thick or the concrete compaction is too high (Montemor *et al.* 2003; Bolzoni *et al.* 2006). Then the possibility of using electrical fields to accelerate their ingress in concrete has been explored. Since 2005, Sawada, et al. (Sawada *et al.* 2005; Sawada *et al.* 2007; Kubo *et al.* 2008) have succeed in promoting the injection of corrosion inhibitors into carbonated concrete specimens, significantly reducing the corrosion rates of steel bars.

The present authors (Zhang 2012; Zhang *et al.* 2013) have preliminarily explored this kind of method and proposed the remedial technique of bidirectional electromigration rehabilitation (BIEM) through which chloride ions are successively removed along with the injection of inhibitors into the ordinary reinforced concrete specimens. Triethylenetetramine (TETA) was used which is an amined-based corrosion inhibitor for the electrochemical process considering the anticorrosion effectiveness, electrochemical migration capabilities and environmental friendliness. It is known that the effectiveness of electrochemical treatment is influenced by many elements such as circulated charge and specimen type (Li and Page 2000). Nevertheless it is still unclear which conditions are necessary to cause significantly enhanced rates of field-induced injection of the corrosion inhibitor and extraction of chloride ions through various types of concrete. Therefore it is difficult to apply the technique appropriately in field situation.

To obtain a deeper understanding of the bidirectional electromigration rehabilitation, experiments are undertaken with concrete specimens mixed with chloride salt. The concentration profiles of chloride ions, hydroxyl ions and corrosion inhibitor in the concrete cover were measured before and after the electrochemical process was applied. Influence of some key factors on the electrolysis procedure such as current density, treatment duration, water/cement ratio, initial chloride content, surface carbonation were investigated. The effects of the bidirectional electromigration rehabilitation and electrochemical chloride extraction were also compared. It is hoped that this investigation would provide some guidance for practical application of this remedial technique.

TECHNICAL PRINCIPLE

The technical principal of BIEM was illustrated in Fig 1. The electrical field is applied between the embedded steel as cathode and the external anode immersed in the electrolyte contacting to the surface of the concrete specimen. Under the electric field action, the cationic species of corrosion inhibitor would migrate into the concrete cover to the cathode while chloride ions in the concrete would migrate out of concrete to the anode (Zhang 2012). The corrosion inhibitor would form a protective film around the embedded steel bars. It can isolate the corrosive substances such as chloride and oxygen when its concentration reaches to an adequate value

(Nmai 2004). Moreover, alkalinity of the pore solutions close to the embedded steel bars would be enhanced as a result of the generation of hydroxyl ions at the cathod, which favours the steel repassivation. \
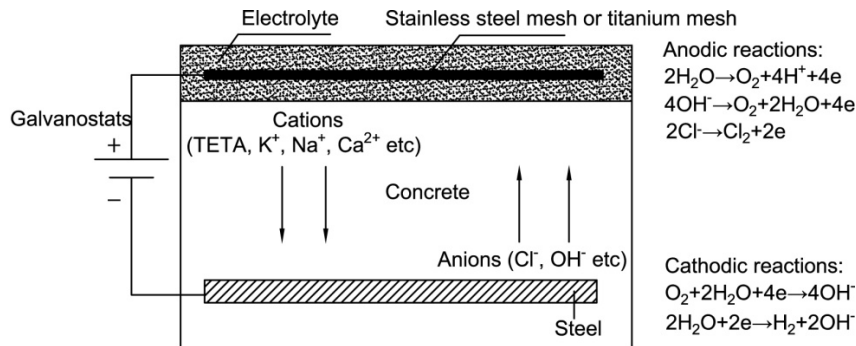

Fig. 1 Schematic of technical principal of BIEM

As described above, the selection of appropriate corrosion inhibitors is the key to the success of the electrochemical treatment. The corrosion inhibitor suitable for BIEM should provide enough corrosion protection under the condition of chloride ions. It should also exist predominantly as cationic species in aqueous media under certain condition. The amine or alkanolamine based corrosion inhibitor would be a good choice if these requirements are taken into consideration (Sawada *et al.* 2005; Sawada *et al.* 2007; Kubo *et al.* 2008; Zhang 2012). The degree of hydrolysis of the organic corrosion inhibitors is governed by their dissociation constants (pK_a) and the solution pH (Sawada *et al.* 2005). When the solution pH is equal to pK_a, the amount of cationic species is equal to that of molecule species. As the pH value decreases, the number of cationic species goes up and that of molecule species goes down. As the pH value increases, the situation goes contrarily. Since pH value of the pore solution in concrete is generally larger than 12.5, the corrosion inhibitor of large pK_a should be chosen to accelerate its injection into concrete.

EXPERIMENT PROGRAMME
Specimen Preparation

Ordinary Portland cement (OPC) mixed with NaCl was used to make the concrete specimens. The mix proportion of the concrete is shown in Table 1. Specimens of dimensions 150×150×300mm were cast with two mild steel bars, which were 12mm in diameter at intervals of 50mm and cover depths of 40mm from one face (see Fig. 2). The specimens were demoulded 24h after casting and cured for a minimum period of 3 months to ensure that the cement was properly hydrated. The end surfaces of the steel bar were connected with electric wire and masked with epoxy resin.

Table 1 Mix proportion of concrete

Type	Max size of aggregate (mm)	Water (Kg/m³)	Cement (Kg/m³)	Fine aggregate (Kg/m³)	Coarse aggregate (Kg/m³)	Mixed NaCl proportion*
1	16	220	406.4	643.1	1049.3	1%, 3%, 5%
2	16	220	457.6	577.6	1072.6	3%
3	16	220	508.8	562.3	1044.2	3%

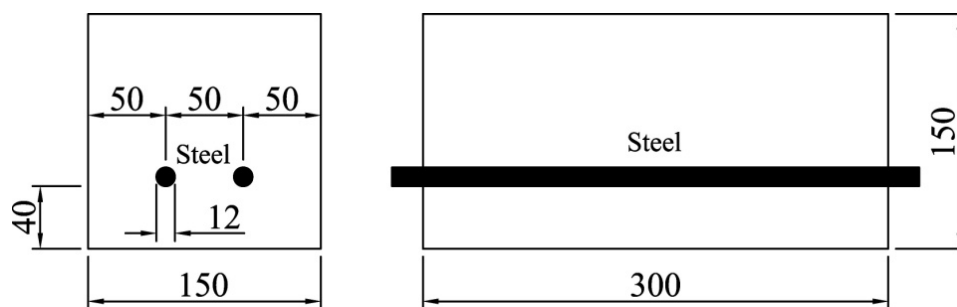*：mass ratio of NaCl to cement

Fig. 2 Schematic of the reinforced concrete specimen (dimensions are in mm)

Treatment of specimens

The types of specimens and their treatment methods are shown in Table 2.The specimens were subjected to electrolysis by means of the experimental arrangement illustrated in Fig. 3. The bottom surfaces of the specimens were immersed in the external electrolyte containing TETA (1mol/L) to a depth of 1mm. Side surfaces of those specimens were sealed with wax to prevent ions exchange. The pH of the electrolyte was controlled to about 10 by phosphoric acid (Zhang 2012). The anodes used in the experiment were made of Type 316 stainless steel mesh while the cathodes used were the embedded steel bars in the specimens. The circuit was then completed and current densities were galvanostatically controlled at 1, 3 or 5A/m^2 of the steel cathode surface area. The periods of the treatment are betwee 7 and 30 days for different specimens. Saturated Ca(OH)$_2$ solution was used as the electrolyte for those specimens subjected to ECE. The pH value of the electrolytes was monitored and if it went down to 7 the electrolytes were renewed. All chemicals used were of analytical-reagent grade with the exception of TETA which was >95% pure.

Table 2 Specimens types ant their treatment methods

Specimen	Concrete type	Mixed NaCl	Treatment method	Treatment duration (d)	Current density (A/m^2)	Pre-carbonation*
C30-3-0	1	3%	--	0	0	No
C35-3-0	2	3%	--	0	0	No
C40-3-0	3	3%	--	0	0	No
C30-1-0	1	1%	--	0	0	No
C30-5-0	1	5%	--	0	0	No
C30-3-B15-1	1	3%	BIEM	15	1	No
C30-3-B15-3	1	3%	BIEM	15	3	No
C30-3-B15-5	1	3%	BIEM	15	5	No
C30-3-B7-3	1	3%	BIEM	7	3	No
C30-3-B30-3	1	3%	BIEM	30	3	No
C35-3-B15-3	2	3%	BIEM	15	3	No
C40-3-B15-3	3	3%	BIEM	15	3	No
C30-1-B15-3	1	1%	BIEM	15	3	No
C30-5-B15-3	1	5%	BIEM	15	3	No
C30-3-C7-3	1	3%	ECE	7	3	No
C30-3-C15-3	1	3%	ECE	15	3	No
C30-3-C30-3	1	3%	ECE	30	3	No

CA30-3-0	1	3%	--	0	0	YES
CA30-3-B15-3	1	3%	BIEM	15	3	YES
CA30-3-C15-3	1	3%	ECE	15	3	YES

Pre-carbonation*: pre-carbonation means the surface of the specimen is carbonated by means of accelerated carbonation treatment within 28d.
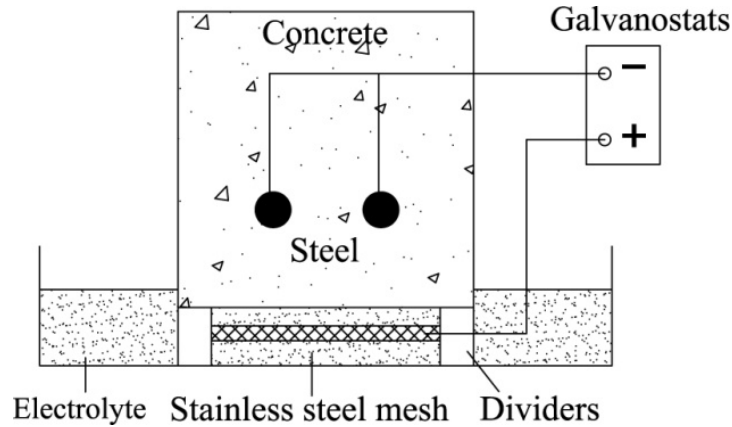

Fig. 3 Schematic of experimental arrangement for bidirectional electromigration rehabilitation (BIEM)

Penetration Profiles of Corrosion Inhibitors, Chloride and Hydroxyl Ions

The specimens were dried in shade after the treatments. Concrete powders were taken out every 5mm along the migration path from different parts of treated surfaces by means of a 10mm drill in diameter. The drilling position was shown in Figure. 4. The powder less than 0.075mm in size was taken through a sieve to determine the content of organic corrosion inhibitor which had penetrated into the concrete blocks. A 20mg sample was weighed and wrapped for each sample to measure the corrosion inhibitor content by means of a Thermo Finnigan Flash 1112 EA organic element analyzer. The residual powder under 0.3mm in diameter was used to determine the Cl^- and OH^- concentration by titration. A 5g sample was mixed with 100ml deionized water and was stored for 24h, then the supernatant liquor being used for titration. The Mettler-Toledo T50A atomatic ptentiometric titrator was applied in the experiment. The titrant for Cl^- titration was 0.01mol/L $AgNO_3$ solution and that for OH^- titration was 0.04mol/L HCl solution. The electrode for Cl^- titration was Plug & Play combined silver ring electrode with ceramic frit for argentometric titrations and that for OH^- titration was Plug & Play combined pH electrode with ceramic frit for direct pH measurements and acid/base titrations in aqueous solutions.
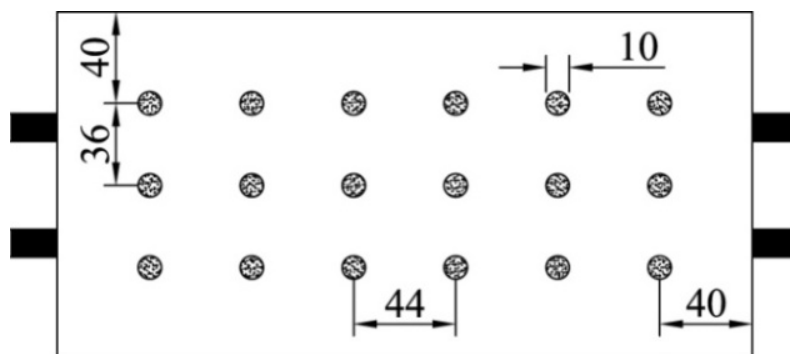
Fig. 4 Schematic of the drilling position on the treated surface (dimensions are in mm).

RESULTS AND DISCUSSION

Concentration profiles of chloride ions, hydroxyl ions and corrosion inhibitor in the concrete cover and the value of OH^-/Cl^- and $TETA/Cl^-$ determine the probability of steel corrosion largely and thus are important in evaluating the effectiveness of the electrochemical remedial techniques. Therefore they were measured in the experiment with given current density, treatment duration, water/cement ratio (w/c), mixed chloride content or surface carbonation as control parameters. Moreover, the effects of ECE and BIEM were also compared particularly.

Influence of Current Density

As illustrated in Figure. 5(a)-(c), the concentration profiles of Cl^- , OH^-, TETA change with current densities applied. In this group of specimens, Type 1 concrete with 3% NaCl was used and the treatment time is 15 days.

The residual Cl^- concentration in the specimens decreases with the increase of current density. Obviously, the increase of current density could intensify the effectiveness of chloride extraction as the circuit charge increased. However, the residual Cl^- in outermost layer was even higher than that in untreated specimens when the current density is less than $3A/m^2$, which means that the electric field applied was not enough to drive the Cl^- out completely resulting in the accumulation of Cl^- in the outer layer of the specimens. The removal efficiency of Cl^- was defined as the ratio of the difference between the initial Cl^- concentration and the residual Cl^- concentration to the value of the initial Cl^- concentration in the vicinity of the embedded steel and this efficiency was used in this paper to evaluate the effect of chloride extraction of the electrochemical process. As indicated in Fig 5(a), the removal efficiency of Cl^- increased from 21% to 65% and finally to 78% as the current density changed from $1A m^2$ to $3A/m^2$ and then to $5A/m^2$. This implies that when the current density increases to a certain level, it is more difficult to increase the extraction effectiveness of Cl^- by means of rising current density.

Change of the water-soluble OH^- concentration accords with the alkalinity change in the concrete. The alkalinity around the steel suggested its possibility of further corrosion in some extent. As shown in Fig. 5(b), the alkalinity drops from inside to outside owing to the CO_2 and H_2O in the atmosphere. The alkalinity of the concrete cover was increased with progress of the treatment due to the OH^- generated by the cathodic reaction and the increase rises as the enhancement of current density. Under the applied electric field with current density of $1A/m^2$ the OH^- concentration rose up to 21% but the alkalinity of outer layer concrete has little increased. Nevertheless when the current density increased to $3A/m^2$ and $5A/m^2$, the alkalinity of outer layer concrete increased more obviously. As a result, the possibility of steel corrosion would be reduced and the resistant ability for the structure to carbonation would be improved.

The migration of the corrosion inhibitor was also affected by the current density as described in Fig. 5(c). Within the first 20mm from the embedded steel bars the concentration of TETA kept almost the same in a relatively low range, but it increased a lot in the outer 20mm layer. The concentration of TETA in the specimens also increased with the increase of current density. It is known that the organic corrosion inhibitors act ineffective in preventing steel from corrosion when their concentrations are too low (Eydelnant *et al.* 1993). Only as the concentration of the inhibitors is no lower than that of chloride ions in pore solution, the corrosion inhibitors can provide adequate protection for the reinforcement (Elsener *et al.* 1999). As shown in Fig. 5(c) when the current density increased from $1A/m^2$ to $3A/m^2$, the concentration of inhibitors penetrated to the surface of the steel increased by

176%. However, this increase was only 16% when the current density varied from $3A/m^2$ to $5A/m^2$ while the increase of the inhibitor concentration close to the treated surface exhibited more.

The relationship between the ratios of different constituents and current density is shown in Fig. 5(d). The minimum ratio of the concentration of corrosion inhibitor to that of the chloride ions when the inhibitor is able to provide effective protection for reinforcement is defined as the effective value of the corrosion inhibitor. As discussed above, the effective value was believed to be 1 in most cases (Elsener $et\ al.$ 1999). As shown in Fig. 5(d), when the current density reached $3A/m^2$, (TETA)/Cl$^-$ exceeded 1. OH$^-$/Cl$^-$ near the steel also increased with the increase of the current density contributing to more effective corrosion protection for the reinforcement (Mammoliti $et\ al.$ 1996; Castellote $et\ al.$ 2000). It follows that the increase of current density played positive role in the increase of the concentration of TETA and OH$^-$ and the decrease of Cl$^-$, but the effect was limited. It is significant to set proper current density accordingly.
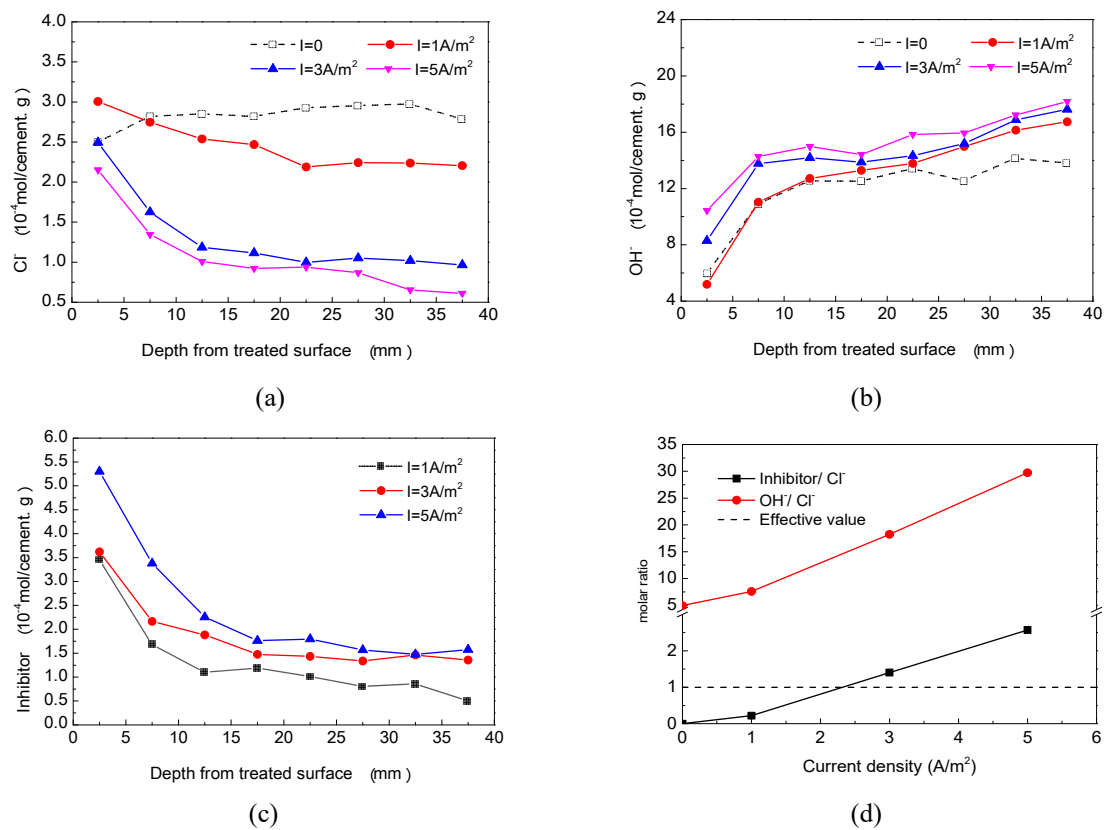

Fig. 5 Concentration profiles/ ratios in specimens after BIEM for different current densities. (a) Concentration profiles of Cl$^-$. (b) Concentration profiles of OH$^-$. (c) Concentration profiles of inhibitor. (d) Ratios of proposed constituents close to the steel reinforcement.

Influence of Treatment Duration

The concentrations of Cl$^-$, OH$^-$, TETA were plotted with the variation of treatment time in Fig. 6(a)-(c). Type 1 concrete with 3% NaCl was used and the current density was kept at 3 A/m^2.

The residual Cl$^-$ distributed relatively uniformly in the range of 20mm in front of the embedded steel bars and increased gradually to the treated surface (Fig. 6(a)). As the treatment duration prolonged, more Cl$^-$ were extracted. In the layer close to the steel bars, 38% of Cl$^-$ were removed after 7 days. When the treatment time

increased to 15 days and 30 days, the percentage of Cl⁻ removed reached to 65% and 85% respectively. The concentration of Cl⁻ in the outermost layer exceeded the initial concentration by 35% after 7 days' treatment because the Cl⁻ migrated to the anode under the influence of applied electrical field. In that case, the concentration difference of Cl⁻ between the inner part and the outer part of specimen was enhanced, leading to the acceleration of counter-migration of Cl⁻ to the reinforcement after the treatment (Chatterji 1995).

The distribution tendency of OH⁻ in the concrete cover zone remains almost the same after BIEM with a little decrease in the concentration difference (Figure. 6(b)). The alkalinity increased with the treatment time increasing. The increase of water-soluble OH⁻ around the steel was 14% after 7days and 28% after 15days. And after 30 days, the increase reached 35%. It implies that as the treatment duration prolonged, the increase of alkalinity slowed down.

The concentration of corrosion inhibitor in concrete cover zone increased along with the treatment time (Figure. 6(c)). In the layer close to the surface, the concentration of TETA kept increasing with the progress of the treatment. However, in the vicinity of the embedded steel bars, the story of the concentration enhancement was different. The concentration of TETA close to the reinforcement increased by 44% from 7 days to 15 days through the electrolysis procedure while it increased by only 20% from 15 days to 30 days. This was attributed to the fact that the OH⁻ continuously generated through the cathodic reaction increased the concrete alkalinity. As a result, the cationic species of TETA in concrete pore solution was reduced with the raise of pH, making it more difficult for the corrosion inhibitor to migrate into the concrete cover zone (Sawada *et al.* 2005).

The relationship between the ratios of different constituents and current density is shown in Fig. 6(d). After the specimen was treated for 15 days, the value of (TETA)/Cl⁻ exceeded 1, suggesting active effectiveness in preventing steel from corrosion. The ratio of OH⁻ to Cl⁻ also increased with the increase of treatment time, which was favoured in the repassivation of the corroded steel bars.

(a)　　　　　　　　　　　　　　　　　　(b)

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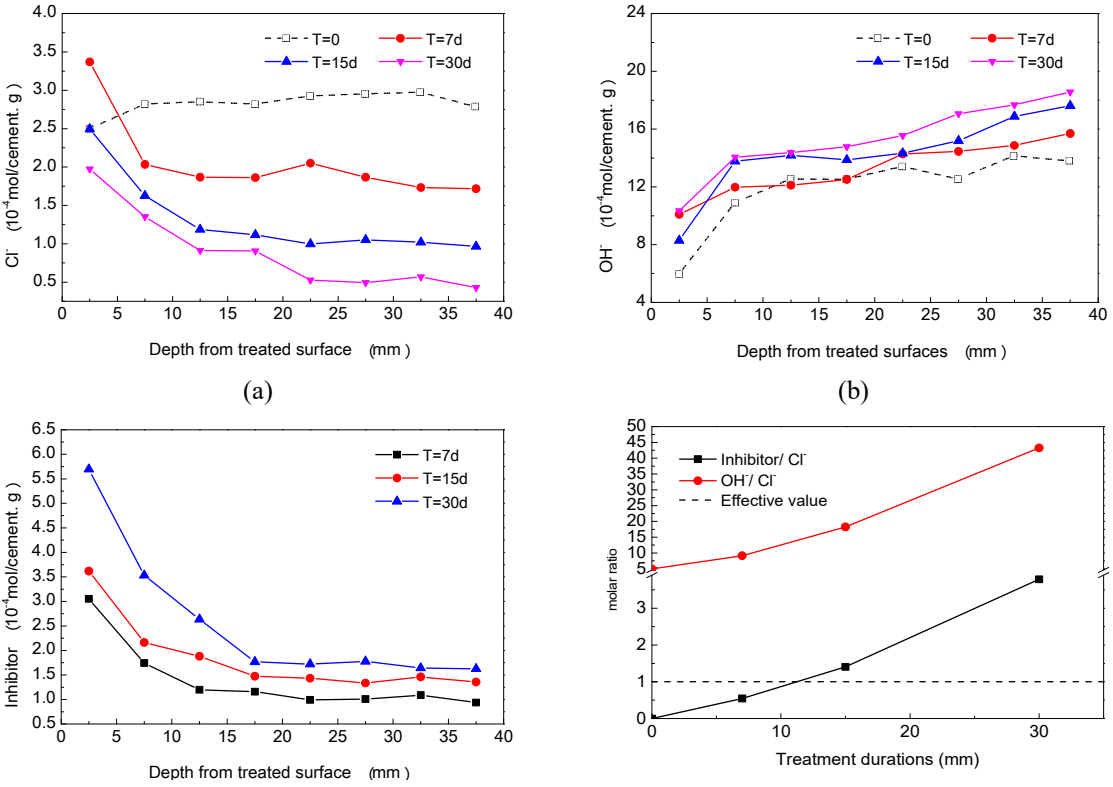
Fig. 6 Concentration profiles/ ratios in specimens after BIEM for different treatment durations. (a) Concentration profiles of Cl$^-$. (b) Concentration profiles of OH$^-$. (c) Concentration profiles of inhibitor. (d) Ratios of proposed constituents close to the steel reinforcement.
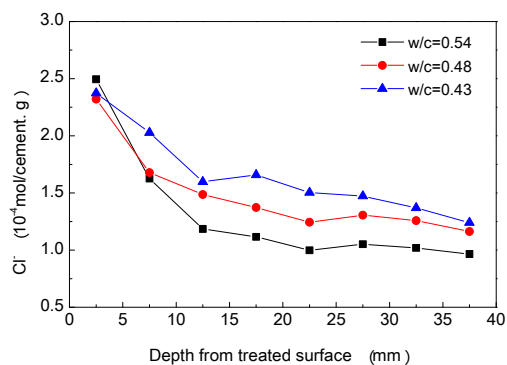
Influence of Water/cement Ratio

The concentration profiles of Cl-, OH- and TETA in specimens of different water/cement ratios are shown in Fig. 7(a)-(c). In this group, concrete of Type 1, 2 and 3 was used. The mixed ratio of NaCl was 3% for each type. The current density exerted was $3A/m^2$ and the treatment lasted for 15 days.

As illustrated in Fig. 7(a), the residual concentration of Cl$^-$ decreased as the water/cement ratio increased. With a higher w/c ratio, the concrete was always having a lager porosity and lower compactness. As a result, the resistance to the migration of Cl$^-$ migration was reduced and then the diffusion coefficient of Cl$^-$ increased (Costa and Appleton 1999). However, residual concentration of Cl$^-$ in the outermost layer did not change much as the w/c changed.

The overall concentration of OH$^-$ increased with w/c. The initial OH$^-$ concentration for the concrete with higher w/c was higher. Therefore when the w/c decreased from 0.48 to 0.43, the concentration of OH$^-$ increased inconspicuously. Yet the increase of OH$^-$ was relatively obvious when the w/c decreased from 0.54 to 0.48.

As indicated in Fig. 7(c), the concentration of TETA in front of the steel bars enhanced with the increase of w/c. Nevertheless in the outermost layer close to the surface, the concentration kept almost the same for different w/c. As mentioned above, the concrete with higher w/c had lower compactness and alkalinity, leading to a higher concentration of cationic TETA in the pore solution. Hence the efficiency of TETA migration was higher in those concrete with higher w/c.

The ratios of different constitutes in the concrete cover were illustrated in Fig. 7(d). When w/c was greater than 0.48, the ratio of TETA to Cl$^-$ was larger than the effective value. However, as w/c was equal to 0.43 the ratio of TETA to Cl$^-$ was less than the effective value, in which the current density and treatment time should be extended accordingly. The water/cement ratio had little effect on the ratio of OH$^-$ and Cl$^-$ in the process of BIEM.
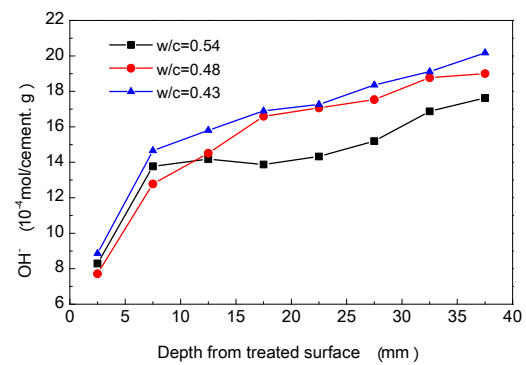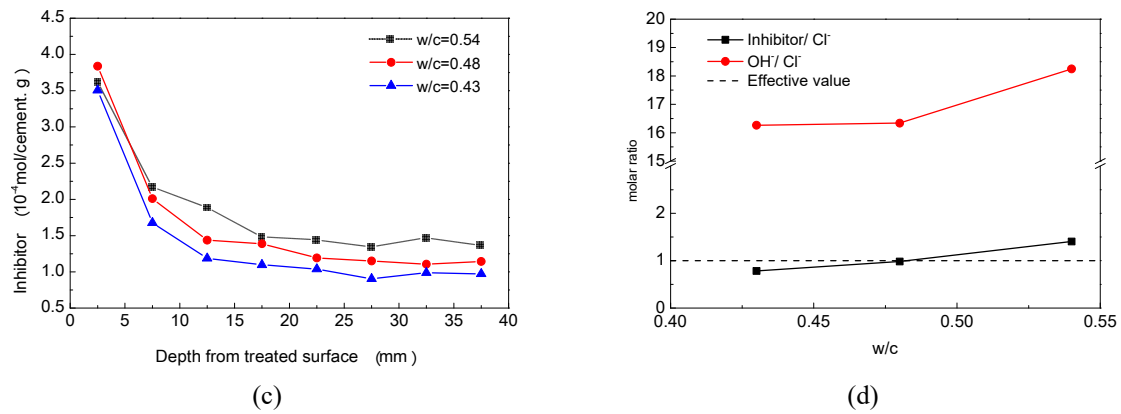

(a)   (b)

Fig. 7 Concentration profiles/ ratios in specimens after BIEM for different water/cement ratios. (a) Concentration profiles of Cl⁻. (b) Concentration profiles of OH⁻. (c) Concentration profiles of inhibitor. (d) Ratios of proposed constituents close to the steel reinforcement.

Influence of Initial Chloride Content

For those specimens mixed with different initial quantities of NaCl, the concentration profiles of Cl⁻, OH⁻ and TETA after BIEM were shown in Fig. 8(a)-(c). Type 1 concrete was used to manufacture these specimens but with NaCl mixed at three different contents, corresponding to 1%, 3% and 5%. For this group, the circuits were galvanostatically controlled at $3A/m^2$ for a period of 15 days.

As illustrated in Fig. 8(a), the extraction efficiency of chlorides in concrete increased with the initial chloride concentration. For the specimens with 1% NaCl mixed, the proportion of extracted chlorides in front of the steel bars was about 44%. And for those with 3% NaCl, the proportion was only 65%. When the mixed ratio of NaCl was increased to 5%, the proportion reached to 78%. It follows that the efficiency of BIEM would be higher for those structures heavier polluted by chloride.

The concentration of OH⁻ in concrete cover kept increasing from outside to inside after the treatment (Fig. 8(b)). The overall concentration of OH⁻ was lower in the specimen mixed with 3% NaCl. However, the alkalinity of the specimen mixed with 5% NaCl was highest barely for that near the embedded steel bars.

As shown in Fig. 8(c), there was no obvious relationship between the migration of TETA and initial NaCl mixed content. It implies that the initial chloride content of the concrete had little influence on the efficiency of TETA ingression.

After the electrochemical process, the value of OH⁻/Cl⁻ and TETA/Cl⁻ was relatively higher in the specimen with 1% NaCl. The low initial concentration of Cl⁻ might be the main reason. It suggests that the bidirectional electromigration rehabilitation may have better effect on those concrete structures with less chloride. There was little difference of these two ratios between the specimens with 3% and 5% NaCl. Nevertheless, the process proved to play an active role in preventing the reinforcement from corrosion since the ratios of corrosion inhibitors to chloride ions all exceeded 1 in all cases.
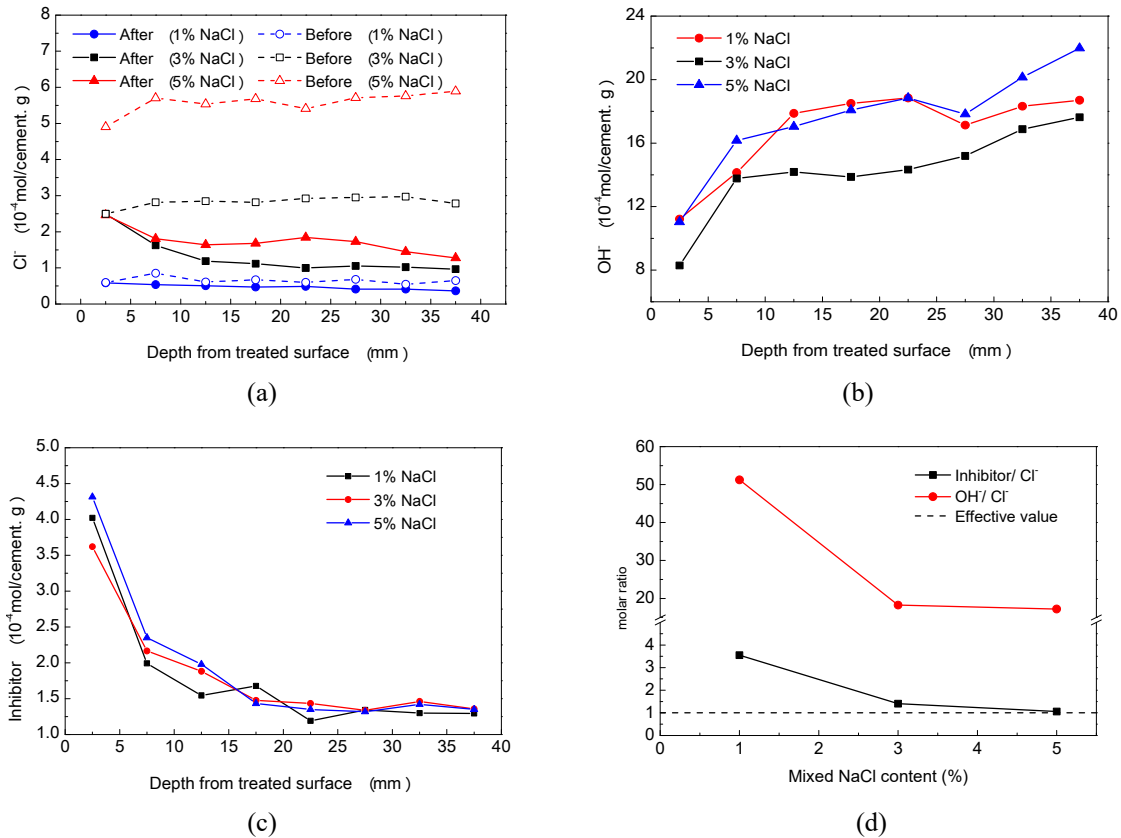
Fig. 8 Concentration profiles/ ratios in specimens after BIEM for different mixed NaCl contents. (a) Concentration profiles of Cl⁻. (b) Concentration profiles of OH⁻. (c) Concentration profiles of inhibitor. (d) Ratios of proposed constituents close to the steel reinforcement.

Influence of Different Electrolysis

The residual concentration profiles of Cl⁻ and OH⁻ after BIEM and ECE were all illustrated in Fig. 9(a) and Fig. 9(b). The specimens in this group were cast with Type 1 concrete with 3% NaCl. Current density applied in the experiment was 3 A/m^2.

As indicated in Fig. 9(a), the residual chloride ion distributions were different after two processes of BIEM and ECE. The overall concentration of Cl⁻ in the whole concrete cover was reduced evenly. By contrast, the residual concentration of Cl⁻ in the outer layer of the specimens was relatively higher than in the inner layer after BIEM. One of the possible explanations is that many cationic TETA species accumulated in the outer layers of the specimens where the cations united with chloride ions. That led to the difficulty in extraction of Cl⁻ thoroughly. After 7 days' treatment, residual Cl⁻ concentrations around the steel after BIEM and ECE were approximately equal. When the treatment duration extended to 15 days and 30 days, the effect of BIEM was better than ECE in removal of Cl⁻. It suggests that BIEM had higher efficiency on removal of Cl⁻ close to the steel than ECE. For better effect of Cl⁻ extraction in the overall concrete cover zone, especially in outer layer, a process of short-time ECE after BIEM might be a good supplement.

It is reflected in Fig. 9(b) that the distribution trend of alkalinity in the specimens after ECE was almost in accordance with that after BIEM. Yet the level of the concentration enhancement of water-soluble hydroxyl after ECE was a little higher than that after BIEM. BIEM had a better effect than equal-time ECE on increasing the

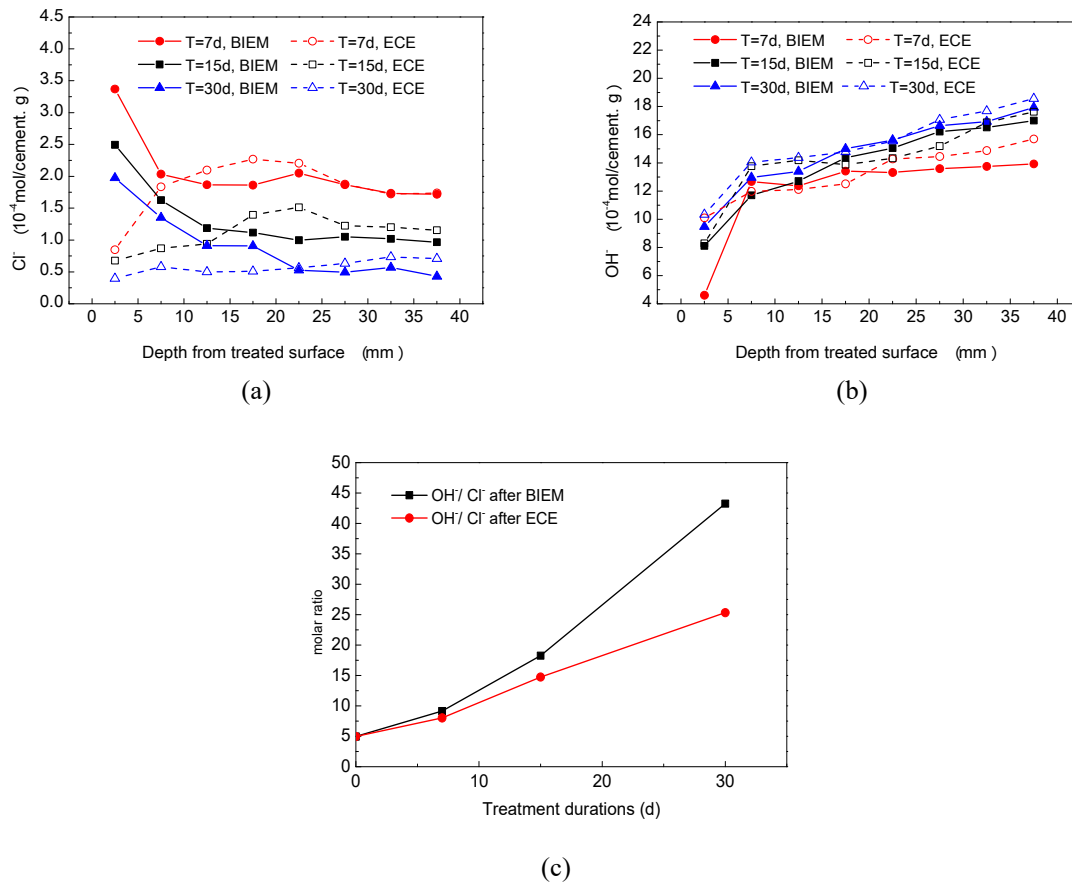ratio of OH⁻ to Cl⁻ , as illustrated in Fig. 9(c).

(a)

(b)

(c)

Fig. 9 Concentration profiles/ ratios in specimens after treatments of different kinds (BIEM and ECE). (a) Concentration profiles of Cl-. (b) Concentration profiles of OH-. (c) Ratios of proposed constituents close to the steel reinforcement.

Influence of Surface Carbonation

The carbonation depth of the specimens experienced pre-carbonation was 13.7mm in average measured by the phenolphthalein test. The carbonated and non-carbonated specimens were all subjected to ECE and BIEM at current density of $3A/m^2$ for a period of 15 days. The concentrations of Cl⁻, OH⁻ and TETA in the concrete cover after treatment were plotted in Fig. 10(a)-(c).

The distribution trends of residual concentration of Cl- in the surface carbonated specimen decreased from outside to inside according with that in non-carbonated specimen. In the 20mm close to the embedded steel bars, the residual Cl⁻ concentration was a little higher in carbonated specimen than in non-carbonated specimen after BIEM. For ECE, however, the Cl⁻ extraction efficiency was much higher in carbonated specimen than in non-carbonated specimen. In general, the effect of ECE was a little better than BIEM on the removal of chloride ions within the concrete cover zone.

Influenced by CO_2 and H_2O, the alkalinity of concrete in the 15mm near to the treated surface decreased sharply. The increase of OH⁻ after BIEM was more substantial in surface carbonated specimen, especially the first 15mm close to the treated surface. It appears to be a little different between carbonated and non-carbonated specimens in increase of alkalinity after ECE. The BIEM-caused increase of alkalinity was lager in the surface carbonated

specimen than in non-carbonated specimen.

The efficiency of TETA migration was much better for carbonated specimen than those non-carbonated, especially in outer part close to the concrete surface which had been carbonated. In the layer close to the reinforcement, the concentration of inhibitors in surface carbonated specimen was 33% higher than that in non-carbonated specimen. This phenomenon was attributed to the decrease in alkalinity close to the concrete surface, leading to a rise in number of cationic TETA species. Therefore the migrating ability of TETA was improved. Yet the inner part of the specimen had not been influenced by carbonation so the increase of TETA was limited.

As shown in Fig. 10(d), the values of TETA/Cl$^-$ and OH$^-$/Cl$^-$ were both higher in the surface carbonated specimen than in non-carbonated specimen. Actually the number of specimens in this experiment was not large enough to get more reliable patterns and conclusions.
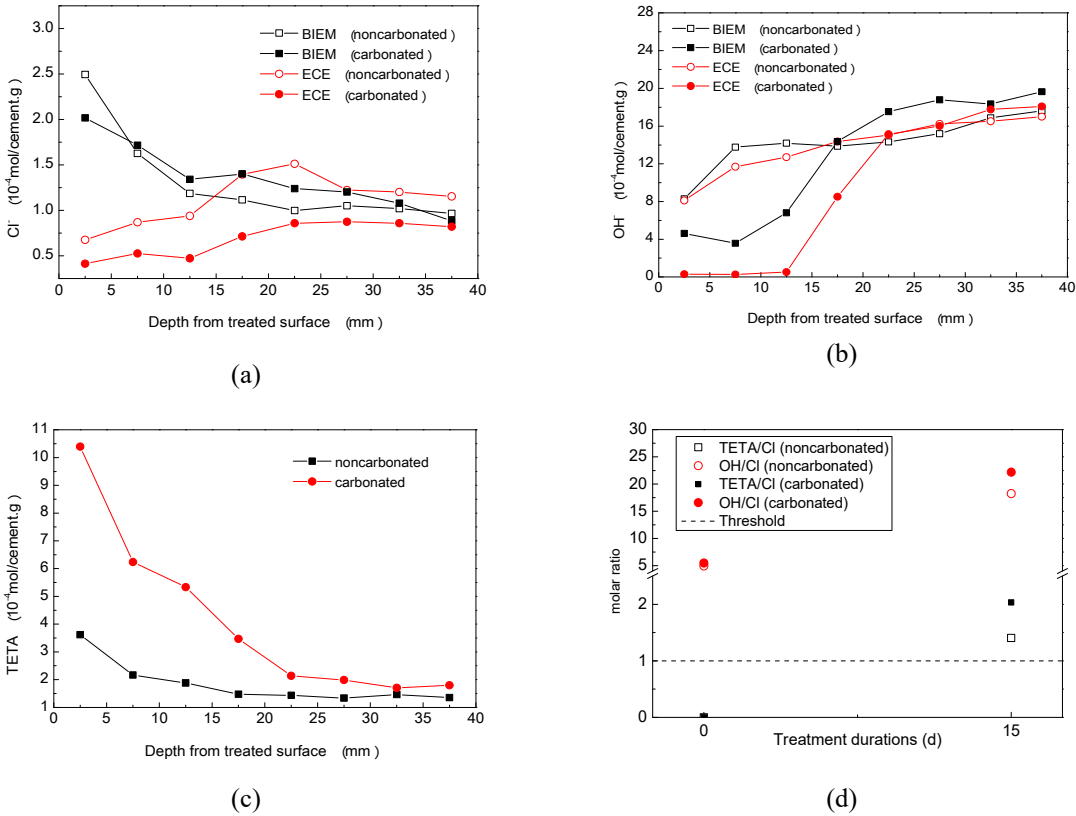

(a)

(b)

(c)

(d)

Fig. 10 Concentration profiles/ ratios in specimens after BIEM for different surfaces (carbonated or non-carbonated). (a) Concentration profiles of Cl$^-$. (b) Concentration profiles of OH$^-$. (c) Concentration profiles of TETA. (d) Ratios of proposed constituents in front of the steel reinforcement.

CONCLUSIONS

The main conclusions of this investigation may be summarized as follows:

Specimens of ordinary concrete were subjected to bidirectional electromigration rehabilitation (BIEM) and the concentration profiles of Cl$^-$，OH$^-$ and corrosion inhibitor were determined in the experiment. The results showed that TETA acted as corrosion inhibitor was capable of being effectively injected into both carbonated

and non-carbonated concrete of the sort investigated by means of the relatively short-term electrochemical treatment of BIEM. The concentration of inhibitor around the embedded steel reinforcement was adequate to provide corrosion protection. At the same time, the ratio of OH^- to Cl^- was raised a lot owing to the fact that the concentration of chloride ions decreased and that of hydroxyl ions was increased in the concrete cover, which favoured the repassivation of reinforcement.

(1) The electricity parameters should be taken into account in design of the electrochemical process. The efficiencies of Cl^- extraction, OH^- enhancement and TETA migration increased as the current density and/or the treatment time increased in the process of BIEM. A low current density or a short treatment duration helped little in the rehabilitation while too high current density or too long treatment were unnecessary. It is significant to choose appropriate electricity parameters according to the actual situation and the goal of rehabilitation.

(2) The quality of the concrete also affected the electrical treatment to some degree. The efficiencies of Cl^- extraction, OH^- enhancement and TETA migration decreased as the w/c of specimens decreased. A lower w/c means denser internal structure of concrete and higher alkalinity, which was unfavorable for the transfer of certain particles in the electrochemical process. It implies that different electricity parameters should be chosen according to different w/c.

(3) Another key factor for the electrochemical process was the initial chloride content in the specimens. The specimens containing more chloride owed higher proficiency in Cl^- extraction through BIEM. The alkalinity increased most in specimens mixed with 3% NaCl and in specimens mixed with 1% and 5% NaCl, the alkalinity increases were lower comparatively. The initial content of chloride in specimens had little influence on the migration of TETA.

(4) There existed significant difference between BIEM and ECE in the changes of Cl^- and OH^- concentration. The residual concentration of Cl^- in outer layer of specimen was higher than that in inner layer after BIEM. Nevertheless the distribution of Cl^- was more uniform in the specimen after ECE. The alkalinity increases in the overall concrete cover zone after the two kinds of remedial techniques differed little. Yet for the alkalinity enhancement near the steel bars, ECE proved to be a little bit better.

(5) The chloride contaminated concrete structures in need of rehabilitation in the practical condition are usually carbonated to a certain depth. The migration efficiency of corrosion inhibitor in carbonated concrete was higher than that of non-carbonated one.

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