Organic corrosion inhibitor of triethylenetetramine into chloride contamination concrete by eletro-injection method

C. Xu [a], W.L. Jin [a,b], H.L. Wang [a,*], H.T. Wu [a], N. Huang [a], Z.Y. Li [a], J.H. Mao [b]

[a] Institute of Structural Engineering, Department of Civil Engineering, Zhejiang University, Hangzhou 310058, China
[b] Ningbo Institute of Technology, Zhejiang University, Ningbo 315100, China

HIGHLIGHTS

- TETA as a corrosion inhibitor was capable of being effectively injected into concrete.
- The TETA concentration around the rebar was adequate to provide corrosion protection.
- Both BIEM and ECE will reduce overall porosity in concrete cover.
- Pore distribution in concrete cover will change after BIEM and ECE treatments.
- Surface strength reduction is more obvious for carbonized concrete after BIEM.

ARTICLE INFO

ABSTRACT

Triethylenetetramine (TETA), a corrosion inhibitor for steel in aqueous media, was introduced into chloride-contaminated concrete specimens using a novel method called bidirectional electromigration rehabilitation (BIEM). An electric field was applied between the embedded steel cathodes and external anodes to inject the corrosion inhibitor from the external electrolytes to the concrete specimens and extract the chloride ions from the concrete cover zone. After 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) was applied as a control experiment using saturated $Ca(OH)_2$ solution as an external electrolyte. As expected, the chloride content decreased and alkalinity increased after treatment. The concentration of the inhibitor injected around the embedded steel bars was adequate to provide corrosion protection. Concrete strength and pore distribution were measured before and after the electrochemical process was applied. The ability of TETA to inhibit further corrosion after BIEM treatment was also analyzed. The effects of BIEM and ECE were also compared. The results obtained can provide a direction in designing the BIEM process.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Reinforcement corrosion is one of the main causes of deterioration of concrete structures [1,2]. The reinforcing steel in concrete structures exposed in a marine environment or suffering de-icing salt may corrode when the chloride concentration around the steel bar reaches a threshold value, leading to performance degradation or even early structural failure [3,4]. Therefore, the steel must be protected from corrosion to extend the service life of chloride-contaminated reinforcement concrete structures.

Electrochemical methods have been widely applied in rehabilitating existing reinforced concrete structures [5]. Among the electrochemical rehabilitation techniques available, electrochemical chloride extraction (ECE) is the most widely studied and used technique in repairing chloride-contaminated structures. However, this method cannot completely remove the chlorides in the structure and is only a temporary solution because chloride ions tend to come back after treatment is stopped [6–8]. In addition to the removal of chlorides, the use of corrosion inhibitors that can be applied on a concrete cover surface has been suggested to protect reinforcing steel from corrosion [7]. These inhibitors are mostly based on particular amines and alkanolamines or their compounds, which are capable of diffusing considerable distances through a

concrete when applied on the surfaces of the structures by capillary action [9,10]. Although these corrosion inhibitors are effective in preventing reinforcement from corrosion within concrete structures [11,12], the surface-applied inhibitors can hardly penetrate the depth of the embedded steel reinforcement; thus, adequate concentrations are necessary to provide corrosion protection when the concrete cover is too thick or the concrete compaction is too high [13,14]. The possibility of using electrical fields to accelerate their ingress in concrete has been explored. Sawada et al. [15–17] have succeeded in promoting the injection of corrosion inhibitors into carbonated-concrete specimens, significantly reducing the corrosion rates of steel bars.

The present authors [18,19] have explored this kind of method and proposed the remedial technique of bidirectional electromigration rehabilitation (BIEM), through which chloride (Cl⁻) ions are successively removed along with the injection of inhibitors into the ordinary reinforced-concrete specimens. Triethylenetetramine (TETA), an amine-based corrosion inhibitor, was used during the electrochemical process because of its anticorrosion effectiveness, electrochemical migration capabilities, and environmental friendliness. The effectiveness of electrochemical treatment is influenced by many elements, such as circulated charge and specimen type [20]. Nevertheless, the optimum conditions necessary enhance rates of field-induced injection of the corrosion inhibitor and extraction of Cl⁻ ions through various types of concrete remains unknown. Therefore, applying the technique appropriately in a field situation is difficult.

Experiments were undertaken with concrete specimens mixed with chloride salt to obtain a deeper understanding of the BIEM method. The concentration profiles of Cl⁻ ions, hydroxyl ions, and corrosion inhibitor in the concrete cover were measured before and after the electrochemical process. The influence of key factors, such as current density, treatment duration, water/cement ratio, initial chloride content, and surface carbonation, on the electrolysis procedure was investigated. The effects of the BIEM and ECE were also compared.

The concrete strength after BIEM treatment, corrosion inhibitor retention, and long-term corrosion inhibition performance are also important. In the ECE process, the negative ions in the concrete cover migrate toward the anode under electric field action, whereas the positive ions migrate toward the cathode. During this process, hydration products dissolve and new crystals or sediments are generated. Such transformation also occurs in the BIEM; however, the positive ions that migrate toward the cathode are different. Thus, special attention should be given to the positive ions of the corrosion inhibitor. Such transformation could cause changes in the pore distribution and compactness of the concrete cover, which will further affect the surface strength of the concrete. Scholars in China and other parts of the world have performed relevant studies in ECE. New crystals have been generated in the concrete, and changes in the pore size and distribution of the concrete cover were observed after ECE treatment [21–23]. The concrete strength also changed after ECE treatment, with the concrete strength near the anode higher than that close to the cathode [24]. However, with the exception of the above influences, the TETA corrosion inhibitor may have additional effects on the concrete strength and on the pore structures in the BIEM process.

Scholars have studied the effects of self-migration corrosion inhibitor applied to a concrete surface and organic corrosion inhibitor inside a concrete on concrete strength. However, given the difference of specific corrosion inhibitors or application modes, the test results varied. Söylev et al. [25] showed that no significant effect on concrete strength was observed when amine corrosion inhibitor was applied to a concrete surface as a migration corrosion inhibitor. However, Schutter et al. [26] considered that mixing amine corrosion inhibitor with concrete would reduce concrete strength by 10%–30%. Heren et al. [27] showed that the decline in concrete strength was enhanced by an increase in corrosion inhibitor concentration. To date, no scholars have analyzed the influences of the BIEM repair method that is based on electromigration principle on the performance of concrete materials or structures. In practical application of BIEM, special attention should be given to whether or not the material of concrete directly in contact with the electrolyte containing the corrosion inhibitor on the surface will deteriorate and reduce strength under the influence of physical and chemical changes. Material degradation on the concrete surface may destroy its pore characteristic, which will affect its compactness and cause various corrosive mediums to enter the concrete cover. In addition, decline in surface strength caused by material degradation influences the concrete structure and mechanical properties, causing the concrete cover to easily crack.

This study aimed to investigate the effect of control parameters, such as charging parameters, water/cement ratio, chlorine salt concentration, and carbonization, on surface strength. A comparison on the influence of BIEM and ECE on concrete surface strength was studied. Finally, retention of corrosion inhibitor and long-term corrosion inhibition performance after BIEM treatment were also analyzed.

2. Technical concepts

The technical concepts of BIEM are illustrated in Fig. 1. An electrical field is applied between the embedded steel as cathode and external anode immersed in the electrolyte that contacts the concrete specimen surface. Under electric field action, the cationic species of the corrosion inhibitor migrate into the concrete cover to the cathode, whereas the chloride ions in the concrete migrate out of the concrete to the anode [18]. The corrosion inhibitor forms a protective film around the embedded steel bars and isolates the corrosive substances, such as chloride and oxygen, when its concentration reaches an adequate value [11]. Moreover, the alkalinity of the pore solutions close to the embedded steel bars is enhanced as a result of the generation of hydroxyl ions at the cathode, which favors steel repassivation.

As described previously, 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 chloride ion condition and should also exist predominantly as cationic species in aqueous media under certain conditions. An amine or alkanolamine-based corrosion inhibitor is a good choice if these requirements are taken into consideration [15–18]. This type of corrosion inhibitor is protonated to an extent governed by the solution pH and the dissociation constants (K_a) of their conjugate acids when dissolved in aqueous solutions, as represented in Eqs. (1) and (2). The degree of hydrolysis of the organic corrosion inhibitors is governed by their dissociation constants (K_a) and the solution pH [15]. When the solution pH is equal to K_a, the amount of cationic species is equal to that of the molecular species. As the pH value decreases, the number of cationic species increases and the molecular species decrease. The opposite happens when the pH value increases. Given that pH value of the pore solution in the concrete is higher than 12.5, a corrosion inhibitor with large K_a should be chosen to accelerate its injection into the concrete. Triethylenetetramine (NH_2-CH_2CH_2-$(NHCH_2)_2$-NH_2) was chosen as corrosion inhibitor in this study because of its high K_a value and better ability of anticorrosion.

$$RNH_3^+ \leftrightarrow RNH_2 + H^+. \tag{1}$$

$$K_a = \frac{[H^+][RNH_2]}{[RNH_3^+]}. \tag{2}$$