Review of Recent Developments of Electrochemical Chloride Extraction on Reinforced Concrete in Civil Engineering

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Received: 17 April 2014 / Accepted: 8 May 2014 / Published: 19 May 2014

Reviewing about the progresses of electrochemical chloride extraction (ECE) was carried out to learn more about the current achievements in ECE in this passage. Principles of ECE were introduced after the corrosion of reinforced concrete was descried. And the recent developments of ECE were summarized including the factors affecting the ECE; the impacts on the concrete microstructure, cohesion between the steel rebar and concrete, and performance of the concrete; and the side effects. Then the field tests and applications were also introduced to make a further research. The study reveals that current research were not enough to promote the wider application of ECE. And finally orientations for further research were also put forward explicitly based on this research, which would guide and facilitate the future study of ECE and enlarge its application.

Keywords: reinforced concrete; chloride; electrochemical extraction; progresses; orientations;

1. INTRODUCTION

Nowadays deterioration of reinforced concrete caused by steel rebar corrosion has become a great disaster in the field of civil engineering [1]. Many things may lead to such corrosion but the chloride ion intrusion has been proved the main cause based on statistics of engineering failures [2].Traditional repair work was to clear the rust of steel rebar, and then make some coating on the steel rebar and finally cover it with less permeable concrete or mortar[3]. This method was too complex, and couldn't clear the penetrated chloride and lower the cohesion between the rebar and concrete. Therefore the electrochemical chloride extraction has become a suitable and reliable option in concrete repairing nowadays.

Electrochemical chloride extraction (ECE) is the method to discharge the harmful chloride ion
in the concrete through applying external electric field, which would also reactivate and repair the passivation in the concrete surface; it is a newly invented technology without destroying the structure of the concrete. And this method is easy to be conducted with high efficiency but low cost and non-destructive. This technology was firstly advocated by the Federal Highway Administration in the U.S.A in 1970s, and the first electrochemical chloride extraction tests were conducted in Ohio and Kansas [4]. After that, related researches works were conducted in European and the U.S.A [5]. The company named Norcure has proved that this newly repairing method can save much of time and cost, and applied for a patent in 1988 at the name of Norcure™ [6]. And the first application of ECE was in the Burlington highway repairing work in Ontario of Canada. According to the estimation of Norcure, ECE has been widely used in British, German, Japan, North Europe and North American etc from 1987 to 1998, and the repairing area were up to 182,000 square meters [7]. In addition, the recommended norm was also built in Europe in 1994; and then this method was specified as the national norm in Norway in 1995, and the similar national norm was established in British in 2000[8].

However, the application of this technology was still underdeveloped in some of the country, for example, it was not until 1996 that China began the first ECE tests [9]; Besides, some problems are still need to be solved, for example, the specifications and guide books was lacked in actual engineering application; and the requirements for the designer and constructors are too high; and some of the side effects were still existing. All this demonstrates that the present research of ECE was not enough, and more studies should be put forward to accelerate the application of the ECE, which is also the aim of this paper.

In this paper, principles of electrochemical chloride extraction was first introduced after the corrosion of reinforced concrete was described; And the research progresses of ECE were presented including the factors affecting the ECE; the impacts on the concrete microstructure, cohesion between the steel rebar and concrete, and performance of the concrete; then the side effects of ECE were also presented. And the orientations of this technology were finally put forward to guide the future research.

2. PRINCIPLES OF ELECTROCHEMICAL CHLORIDE EXTRACTION

2.1. Corrosion of reinforced concrete

The steel rebar is reactivated after the passivation is destroyed [10]. The electrochemical reaction begins when enough water and oxygen exists. And it includes four basic processes in below [11]:

(1) Anode reaction. The iron atoms leave from the crystal lattice and become the surface adhesive atoms. And the atoms leave the double electric layer and generate ion $Fe^{2+}$, and the equation is:

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$

(2) Electron transmission. The ion released in the anode move to cathode from the steel rebar;

(3) Cathode reaction. The oxygen moves to the surface of steel rebar by penetrating, diffusion and adhesion, then it absorbs the electron released from the anode, and the equation is:
\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \]  \hspace{1cm} (2)

(4) Forming of the corrosive product. The ion \(Fe^{2+}\) generated in the anode moves into the deeper zone of surrounding concrete through the diffusion and penetration. Meanwhile the ion \(OH^-\) formed in the cathode move to the anode through the pore of the concrete and the contact surface of concrete and steel rebar; it combined with the ion \(Fe^{2+}\) and produces the \(Fe(OH)_2\). And the final product depends on the supply of oxygen, the equation is:

\[ Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \]  \hspace{1cm} (3)

The \(Fe(OH)_2\) will further oxidized to be \(Fe(OH)_3\) when there is enough oxygen; and the \(Fe(OH)_3\) will degrade into soft and porous \(Fe_2O_3\) after dehydration, the process is:

\[ Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \]  \hspace{1cm} (4)
\[ 2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O \]  \hspace{1cm} (5)

When the oxygen is not enough, the \(Fe(OH)_2\) will become as black \(Fe_3O_4\) as below:

\[ 6Fe(OH)_2 + O_2 \rightarrow 2Fe_3O_4 + 6H_2O \]  \hspace{1cm} (6)

Although the depolarization agent is not limited to the oxygen, for example, the hydrogen could also serve as depolarization agent. But the reinforced concrete is often located in the medium or alkaline solution environment with dissolved oxygen, the ultimate product was subject to the richness of oxygen in general. And the corrosive products were scanned clearly by G.S. duffo and W. Moris [12].

2.2. Theory of electrochemical chloride extraction

The ECE treatment includes the direct current power supply and external anodes to generate a constant current or potential [13]. During the ECE treatment, the corrosion products are electrochemically reduced at the steel rebar (cathode) in addition to the reaction represented by Equation 2 [14]. Furthermore, hydrogen gas is evolved at the reinforced steel because of the low potential that is induced by the high current density as the equation shows as below [15]:

\[ H_2O + 2e^- \rightarrow 2OH^- + H_2 \uparrow \]  \hspace{1cm} (7)

The electrochemical reactions occurring at the external anode are represented by the following two equations:

\[ 2H_2O \rightarrow 4H^+ + O_2 \uparrow + 4e^- \]  \hspace{1cm} (8)
\[ 2Cl^- \rightarrow Cl_2 \uparrow + 2e^- \]  \hspace{1cm} (9)

The reaction represented by Equation 9 can be suppressed by keeping the PH (power of hydrogen value) of the electrolyte sufficiently high above approximately 9 [16].

From the Equation 8, it is also found that the oxygen is consumed at the beginning; then the hydroxyl ion \(OH^-\) and chloride \(Cl^-\) move to the external anode through the pores and holes of concrete. As Equation 9 shows, the chloride would be discharged as the gas from the concrete when the electric field was applied. Thus the chloride \(Cl^-\) is removed gradually as the process continues.

From above, it was learned that three major materials were involved during the ECE process: the electrolyte solution, the external anode and the direct current. The electrolyte solution often uses the saturated \(Ca(OH)_2\) solutions, or 0.1 mole \(NaOH\) solutions or the 0.1 mole \(Na_2BO_3\) solutions etc.
The anode could be the ordinary iron wires or some stainless wires or even titanium ones. And researches have demonstrates that the stainless and titanium wires were the most frequently used nowadays [18]. The current used was very important for the ECE technology; if the current density was too high the concrete would be destroyed [19].

3. INDOOR RESEARCH AND ACHIEVEMENTS

3.1. Factors of electrochemical chloride extraction

Some research has revealed that electrochemical chloride extraction would increase with the voltage applied and the numbers of steel rebar [20]. However, only 50% of chloride could be removed [21]. And the thickness of concrete would hamper the extraction of chloride, the bigger water cement ration mean better extraction, and the reasonable arrangement would facilitate the chloride extraction [22]. The ion \( k^+ \) move the fastest among the mental ion and the extraction ratio was about 50% to 60% of the total chloride [23]. But some stated that the chloride calcium aluminates was formed during the ECE after the energy dispersive spectrometer analysis was conducted, which also could be used to explained the chloride could not be eliminated totally [24]. As to the arrangements of steel rebar also had influence on the ECE; and it would be more difficulty to extract the chloride in double-layer steel rebar concrete and some have got the distribution of the chloride in concrete specimen [25].

The traditional material of anode was Ti-RuO\(_2\) wire netting; but application of a conductive cement paste as an anode has become more and more popular in recent years. And Perez found the conductive cement paste anode could work as the traditional Ti-RuO\(_2\) anode [26]; and the anode could be adapted to complex structural geometries with addition of carbon nanofibers [27]; and it is particularly useful to treat sizable vertical surfaces such as structural supports [28]; Additionally, a creative methodology of ultrasonic-electrochemical chloride extraction had been proposed, and the efficiency was approximately 19% higher than traditional ECE treatment [29].

In general, various conditions would affect the ECE results, including the voltage, current density, solution type, anode materials, thickness of concrete and layout of the steel rebar etc. In a research, only a few factors were chosen to be studied in normal situation. However, some of the researches are contradicted, for example, Rob [30] and Yao [31] were totally different to the influence of water cement ratio. It reflects the works done were not enough to make a final conclusion to a specific factor. The best solution would be conducting the orthogonal tests with some of the main factors, then discuss the impact of each factor and rank it in a specific order.

3.2. Impact on the concrete microstructure

Research shows that the content of \( \text{Ca(OH)}_2 \) would increase after ECE treatment, and the new materials was produced near the steel rebar, and it was rich in Na, Ca and Fe [32]. And the porosity in the concrete was larger and more scatter before the ECE treatment [33]. The mercury intrusion test demonstrated that the inner structure of concrete was improved by the ECE treatment, because the pore was blocked by the unsolvable matter nearby [34]. Cheng et al further concluded that
the pore smaller than 30 nm was increasing after the mercury intrusion test was conducted to compared the porosity before and after the ECE treatment[35]. By using the Scanned Electron Microscope, Orellan et al [36]found not only the a fine granular layer rich with sodium and calcium, Iron and hydration products with calcium, but also the thin strips of sodium hydroxide material.

3.3. Impact on the cohesion between steel rebar and concrete

During the ECE process, the hydroxyl ion $OH^-$ and chloride $Cl^-$ move from the cathode to the anode; and the ion $Na^+$ and $K^+$ also move to the cathode and accumulated near the steel rebar, and some of them combined with the hydroxyl ion $OH^-$ to produce the alkaline hydroxide, which would make the concrete become softened. Moreover the high current in cathode would result in the reaction lead to the hydrogen to be released as Equation 7 demonstrates. All the two would make the cohesive force decrease between the steel rebar and the concrete. However, there is no uniform opinion about the decreasing ratio of the cohesive force.

In 1960s, Ewing began the research of ECE’s impact on the cohesive force between the rebar and concrete [37]. In a test conducted by Rasheeduzzafar[38], the movement was large between the rebar and concrete after applying external current of 538 milliampere per square meters for 14 months; and the higher current or the initial chloride content mean larger loss of that cohesive force, which was proved by conducting pull-out tests in 1995[39]. Recent research also revealed that the ECE treatment would lower the cohesive force between the rebar steel and concrete, but the force would recover as the time goes when the ECE treatment ended [40]. Chang [41] found that interface softening was the main cause leading to cohesive forces degrading and the loss was about 40% to 60%, which was different from Deng’s finding that the loss was less than 25% [42]. And Li’s research show that the impact of current density was greater that the amount of electricity; and the current density should be confined to 1 to 4 ampere per square meters[43].

3.4. Impact on the concrete performance

Up to now, it is generally accepted that the compress and shear strength would not be affected by the ECE treatment[21,32] but the permeability and water absorption would be decreased because the structure of the reinforced concrete was more compact after ECE [33]. On the other hand, it has been found that the ECE would slow down the chloride corrosion but accelerate the other corrosion for the oxygen was decreased by the extraction process [34]. And the research of Li has also showed that the ECE technology will recover the passivation on the steel rebar in the concrete [35]. But some also pointed out that the corrosive current would increase after ECE; and the corrosion processes would become more fast when the ECE current was not uniform in the steel rebar. All these have make people understood more about the impact of ECE on the concrete performance. In a word, the ECE is good for the concrete strength and performance in most of the research; but there exist much to be known, so further works should also be putting forward to learn more about the impact.
3.5. Side effects of electrochemical chloride extraction

The electrochemical chloride extraction would increase the pore solution alkali in surrounding concrete, and result in alkali-aggregate reaction when the silicon dioxide exists. The alkali-aggregate reaction could lead to the expansion of the concrete, then the chloride are more easily and fast to penetrate into the concrete, causing the structure of concrete to crack instantly. Mohammad has proved such process after rigid experiments were conducted [48]. And Page et al [49] has discovered that the alkali-aggregate reaction also existed even the reactive aggregates were lower than the normal value; and the alkali silica gel (as Figure.6 shows) would lead to partial expansion and cracks.

In order to avoid the concrete expansion, some professors also try to add something to curb the alkali-aggregate reaction; and Lu et al [50] have found that the adding to lithium salts to electrolyte solution would control the alkali-aggregate reaction.

The other side effect was the hydrogen embrittlement. During ECE treatment it produce the hydrogen at the cathode; and the hydrogen may penetrates into the steel rebar and cause the other side effect named hydrogen embrittlement. Hydrogen embrittlement may lead to the crack or sudden and unpredictable failure of reinforced concrete. Siegwart [51] measured the extension of 22 pre-stressed concrete beams after ECE treatment, and concluded that the hydrogen would result in the hydrogen embrittlement in the steel rebar; and such process has nothing to do with the current density, treatment time and the surface conditions of rebar; thus the ECE technology is not suitable for pre-stressed concrete structure.

4. FIELD TESTS AND APPLICATION

Although ECE has been widely used in European, there were not so many cases reports about its application in literatures. However, this technology has been gained much attention in the developing country. In a recent field research, series of tests were carried out to study the seismic behavior of reinforced concrete pier with ECE treatment [52]. And the results indicated that the ductility coefficients of specimen were all decreasing after ECE treatment, and the specimens decreased by about 23%. This reflects the ductility coefficients were degrading after low cyclic integrative loading; it may be caused by the destruction of inner structure of the reinforced concrete, which was also testified by the other research [53].

Recent application of ECE was conducted in Zhanjiang, the southern port city in People's Republic of China [54]. The field measures also revealed the reduction of chloride ion after ECE treatment; and the relationship between the total electricity quantity and residue chloride ion was also studied. The test results indicated that, the chloride concentrations were all decreasing after the ECE treatment. It demonstrated that the ECE technology is feasible and beneficial to the recovery of the reinforced concrete. Moreover, the results also showed that the ECE makes the all parts of concrete to extract chloride; the chloride concentration drops to nearly the same value no matter it is bottom, external or internal.
After two months, the current potential of the steel rebar were also measured at the different places of the testing beam; it included the bottom, external and internal of the beam. The measurement shows that the current potential before ECE was higher than that after ECE, and the difference between the two was about 100mV, which reflects the ECE technology would lower the corrosion potential. Moreover the corrosion potential after ECE was larger than 150 mV; it means that the possibility of steel rebar corrosion would be lower than 10%; therefore the ECE terminated the corrosion of steel rebar in the concrete effectively and prolong the using time of the structures [55].

5. ORIENTATIONS FOR FUTURE RESEARCH

Electrochemical chloride extraction was a new technology with high efficiency and easy operation lowers cost and non-destructive. It provides a new method to renew the reinforced concrete without damage. And it has obtained many scholars' attentions all over the world. The process of electrochemical chloride extraction is very complex; so much works would be done in future. It includes at least the following.

(1) Determination the electrochemical parameters in ECE treatment. Although abundant works have been conducted to learn the suitable parameters, the current researches were very scattered; and some of them even contradicted each other. The actual mechanism of concrete, chloride and electrochemical parameters are still not very clear. It has hampered the further application of ECE in actually engineering.

(2) Interface mechanism between steel rebar and concrete. Up to now, no uniform opinion was accepted about the decreasing cohesive force between the steel rebar and concrete. And this interfacial characteristics are very important to the strength of reinforced concrete; it should be clear know that whether the ECE would do harm to their cohesive force or even strength; and how does it happen and what should be done to prevent or lessen such degrading.

(3) Application of ECE in special environment. As the development of society, human being has stepped into every corner of the world. And the extreme environments were often encountered, for example, the deicing environment, the vibration environment in subway station, and the wet-dry circulation marine environment etc. Those special occasions are also very important for the further usage of ECE and it needs more specific tests and researches to unveil the unique mechanism.

(4) Strengthen the field test and numerical simulation. Current researches were more inclined to conduct indoor tests, and the conclusions were also made based on the scaled models. But the actual situations are different, and sometimes even contradict to indoor'. Thus more field tests and numerical simulations should be conducted to learn more about the real processes of ECE, which may be helpful to reveal the mechanism of ECE in detail.

(5) Develop new materials and technique. Most of the present jobs were all confined to use the traditional material and technique of ECE. To improve the efficiency and effect of ECE, new materials and technique should be introduced and applied in the field of ECE. Those problems existed may be solve if the proper materials and technique is adopted.
6. CONCLUSION

In this paper, reviewing about electrochemical chloride extraction was conducted; the main conclusions were as follow.

(1) Various conditions would affect the ECE results, current works were not enough to make a final conclusion to a specific factor. The orthogonal tests with the main factors are needed to discuss the impact of each factor and rank them in a specific order.

(2) Research shows that the ECE treatment would improve the inner structure of concrete but also have side effects like alkali-aggregate reaction and alkali-aggregate reaction. It depends on many factors and more researches should be conducted.

(3) The ECE would not affect the strength but permeability and water absorption; and this technology will recover the passivation on the steel rebar in the concrete. And it would also lead to the decreasing of cohesion between concrete and steel rebar. And the current density was greater than the amount of electricity in leading such results.

(4) Field tests and application proved the effectiveness and efficiency of ECE. Further similar works should be conducted in a more extensive way.

(5) Future works should lay more emphasis on electrochemical parameters determination, interface mechanism between steel rebar and concrete, special application, strengthening the field test and numerical simulation, and new materials and technique developing etc.

ACKNOWLEDGMENTS
This work was supported by Shanghai International Shipping Service Center Development Co. Ltd and Shanghai Harbor Engineering Design and Research Institute Co. Ltd, which is gratefully acknowledged. And the comments from the reviewers are greatly appreciated too.

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