

*Short Communication*

## **Investigation of Chloride Transference in Reinforced Concrete Structure using Electrochemical Chloride Extraction Process**

Xingwang Liu, Ning Xue, Hanbo Jia, Yingshuai Wu and Jingjun Ma\*

College of Science and Technology, Agricultural University of Hebei, Huanghua, 061100, P.R. China

\*E-mail: [mjjwjpmartin@sina.com](mailto:mjjwjpmartin@sina.com)

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Electrochemical chloride extraction (ECE) is an effective method for rehabilitating reinforced concrete structure damaged by the corrosion process. The understanding of the chloride transference in reinforced concrete structure during ECE process is essential for further exploring the ECE mechanism and propose the mathematical model. In this paper, we used an embeddable chloride probe and chemical titration analysis for analyzing the chloride content in different depth of the concrete structure during the ECE process. Moreover, the decomposition of bound chlorides during the ECE process was also investigated.

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**Keywords:** Electrochemical chloride extraction; Reinforced concrete; Chloride transference; Current density

### **1. INTRODUCTION**

Corrosion of reinforced concrete structure always is a great concern in the construction industry because its a major cause of the premature deterioration of reinforced concrete [1-5]. Theoretically, the embedded steel will covered with a layer of passivating film for protecting its affected by the corrosion [6-9]. However, the formed passivating film could be broken down by the presence of some species, such as chloride ions and carbonation. For example, a major cause of the durability decreasing of reinforced concrete flyovers in northern China is the corrosion of the reinforcing steel due to the ingress of chloride ions from deicing salts. The passivating film was destroyed by the chloride ions at the alkaline environment [10, 11]1-4. Formation of oxide by-products occupies several times the volume of the original steel, exerting tensile stresses greater than the tensile strength of the concrete. These stresses lead to cracking formation and spalling, further accelerating the corrosion process.

Consequently, the steel cannot be further against the corrosion process at the presence of moisture and oxygen. Therefore, the development of a rehabilitating method is essential.

Electrochemical chloride extraction (ECE), also known as desalination method, is a promising method for lowering chlorides content in the concrete structure. The mechanism of ECE can be described as follows: an anode and electrolyte were placed on the concrete surface and the direct current was applied between the anode and the steel rebar (acts as the cathode). During this process, the cations such as  $\text{Na}^+$  and  $\text{K}^+$  migrate to the steel rebar. On the other hand, the  $\text{Cl}^-$  ions were taken out of the concrete structure [12].

So far, many studies were conducted for the investigating of the ECE process towards different concrete structure. Arya and co-workers studied the system efficiency of the ECE process [13]. A similar work was carried out by Bertolini et al. [14] as well. Polder and co-workers demonstrated the effect of the pore solution on the ECE efficiency [15]. The possibility of the reduction in bond strength was studied by several groups [13, 16-18]. Page and co-workers demonstrated the possible instigation of Alkali Silica Reaction [19]. Some work also conducted the modeling of the extraction process [20]. Although large number of researches have been carried out on the feasibility of applying ECE in laboratory as well as field cases, however, only few reports in regard to the investigation of migration pass way of  $\text{Cl}^-$  ions during ECE process [21, 22]. It is no doubt that the understanding of the  $\text{Cl}^-$  ions transference in reinforced concrete structure during ECE process is essential for further exploring the ECE mechanism and propose the mathematical model [23].

In this contribution, we proposed an embeddable chloride probe was installed into concrete and used for measuring the free chloride concentration change during the ECE process at different depths. In the meantime, the decomposition of bound chlorides during the ECE process was also investigated. The bound chlorides dissolve was observed by Elsener and co-workers [24]. However, the detail monitoring data were rarely reported. Besides the chloride transference analysis, several factors including the water to cement ratio and the impressed current density on the ECE efficiency were studied.

## 2. EXPERIMENTS

### 2.1 Mortar preparation

Ordinary Portland cement 42.5 was used for constructing sample mortars. The sand-to-cement ratio was chose as 3. 0.5 % naphthalene-based superplasticizer was added. In order to investigate the effect of the water to cement ratio on ECE process, the water to cement ratios of 0.5 and 0.65 was used for making mortar samples. The mortar samples were prepared in size of  $40 \times 50 \times 100$  cm (Figure 1). The steel rebar with diameter of 8 mm with 130 mm in length were embedded in into the concrete. In order to investigate the chloride transference, 3 % of NaCl was added into the mortar during the mixing procedure. Embeddable chloride probe was placed into the concrete prior to the casting. After casting and demould, the mortars were placed into a standard curing chamber for 1 month before testing.



**Figure 1.** Photo of prepared mortar sample.

### 2.2 Preparation of embeddable chloride probe

Silver wire was used for fabricating the embeddable chloride probe. In a typical preparation process, a silver wire of 30 mm in length and 0.6 mm in diameter was firstly polished using sand paper for removing the oxidized surface layer followed by ethanol, ammonia and Milli-Q water. The galvanization of AgCl was then carried out at a 0.1 mol/L hydrochloric acid solution using an applied current density of 0.4 mA/cm<sup>2</sup> for 2 h. The galvanization process was only applied for 3/4 of the silver wire. After drying process, the half of the silver wire (includes 1/4 of silver without galvanization) was sealed by epoxy resin. The rest AgCl part was used as the embeddable chloride probe for chloride concentration detection.

For establishing the calibration curve of the chloride probe, different concentrations of NaCl solution with saturated Ca(OH)<sub>2</sub> were prepared. The following equation was then obtained for determining the chloride content:  $E_{\text{Ag}/\text{AgCl}} - E_{\text{SCE}} = -32.69 \text{gC}_{\text{Cl}}^{-1} - 4.25$ , where  $E_{\text{Ag}/\text{AgCl}}$  and  $E_{\text{SCE}}$  are the potential reading of the embeddable chloride probe and the potential of the saturated calomel electrode, respectively.  $\text{C}_{\text{Cl}}^{-1}$  is the concentration of the chloride content.

### 2.3 Electrochemical chloride extraction process

The external anode was made by the titanium mesh, which wrapped on the sample mortar [21]. A maximum current density of 6 A/cm<sup>2</sup> and the maximum possible extraction voltage of 32 V were used for ECE process. The mixture of the 0.1 M NaOH and H<sub>3</sub>BO<sub>4</sub> was used as the electrolyte. The whole ECE process was carried out for 28 days.

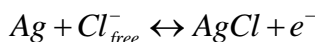
### 2.4 Chloride content determination

The water-soluble and total chloride contents of mortars before and after ECE process was determined according to the standard chemical titration analysis reported by Brian et al. [25]. For chloride content monitoring during the ECE process, the potential changes of the embedded chloride

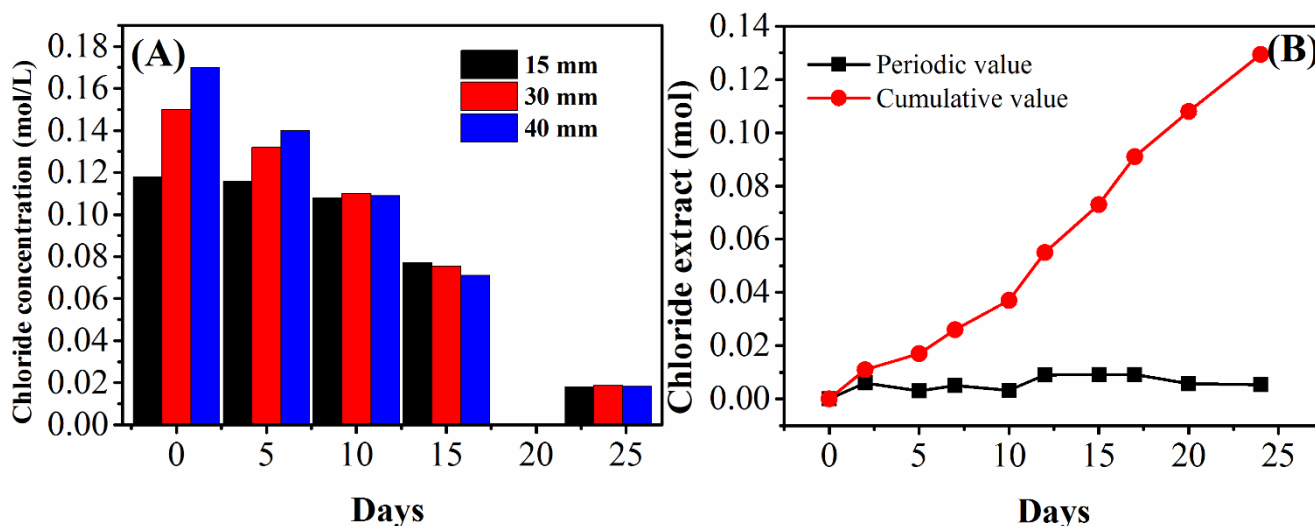
probes were recorded. The free chloride concentration was then calculated using previously proposed calibration equation. The extracted chloride was also determined using chloride probe at electrolyte. The pH condition of the electrolyte was kept at 10.

### 3. RESULTS AND DISCUSSION

The chloride transference was studied during the ECE process. The chloride probes were embedded into the concrete with different distances. The chloride content was monitored by the potential change of the embedded chloride probes. The mechanism of the chloride probes can be described using the following electrochemical equilibrium equation:



Where  $Cl_{free}^-$  is the free chloride. When the ECE process start, the free chloride concentration of the medium consequently changed, which affect the free chloride electrochemical equilibrium and shift the equation. In order to restore the equilibrium, the potential of the chloride probe will be changed. The concentration of the free chloride can be calculated according to the calibration equation proposed in the experimental section. Moreover, the chloride transference status at different area of the concrete during the ECE process can be monitored by the chloride probes embedded at different depths.

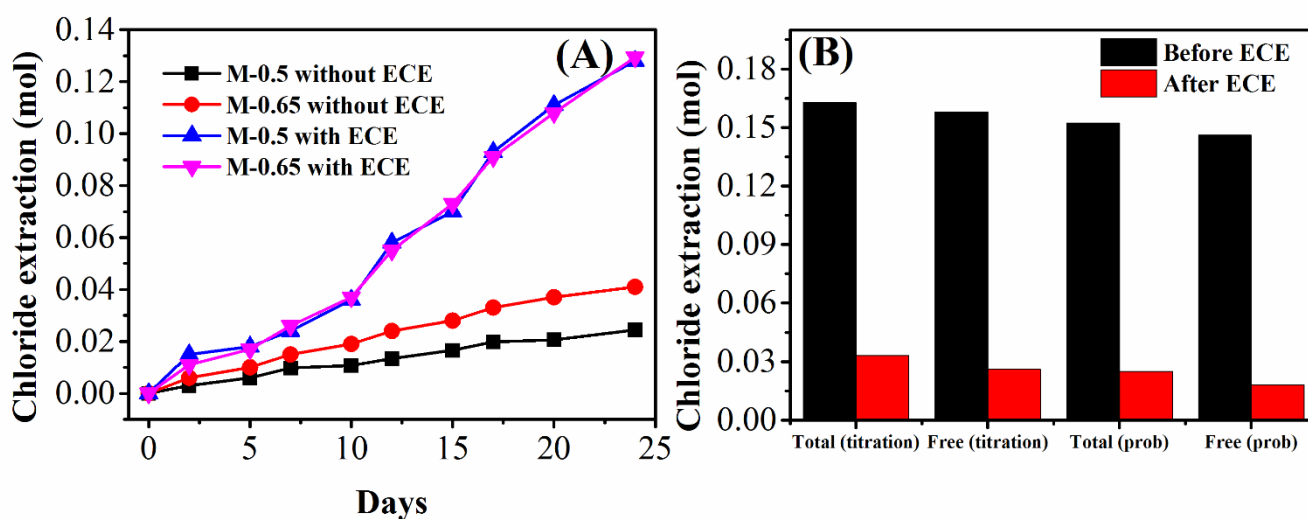


**Figure 2.** (A) Free chloride changes of the concrete with 5, 10, 15 and 24 days of ECE process at the distance to the steel rebar of 15 mm, 30 mm and 40 mm. (B) Cumulative and periodic amounts of extracted chlorides of the mortar.

Figure 2A shows the free chloride of the concrete with 5, 10, 15 and 24 days of ECE process at the distance to the steel rebar of 15 mm, 30 mm and 40 mm. It can be observed that the free chloride content of the outermost part in the concrete showed the significant decline when the ECE process started. It can be ascribed to the big chloride concentration difference between the concrete and

electrolyte. The extraction process started immediately when the electric field applied. The chloride at the outermost part was transferred quickly into exterior electrolyte. On the other hand, the chloride concentration at the innermost part only showed a slight decreasing in the first 10 days of ECE process due to the initial chloride concentration of the innermost part is much less than the middle and outermost parts. Therefore, the transaction of the free chloride cannot be effectively triggered before the concentrations of the middle and outermost parts declined into a certain stage. After 10 days, the decreasing of the chloride concentration can be observed because the chloride concentrations of the middle and outermost parts decreased enough. After 15 days ECE process, the reaming chloride concentrations of three parts were around 0.075 mol/L. This number can be down to 0.018 mol/L after 24 days ECE treatment. Figure 2B shows the cumulative and periodic amounts of extracted chlorides from mortar sample. It can be seen that the extracted chlorides at first 10 days showed larger amounts due to the larger chloride concentration difference between the electrolyte and concrete. After 10 days, the extract performance reached a stable value, suggesting the extraction process will be mainly due to the electric force driving.

We further investigated the effect of the ECE efficiency on the water to cement ratio. The basic principle of the ECE process is based on the applied electric field, which could make the force for moving the charged particles in the inner concrete. The mobility rate can be influenced by two factors including the intensity of the electric field and the resistance of the medium. Therefore, the porosity and adsorption effect of the concrete are important for the ECE treatment efficiency. The water to cement ratios can be responsible for the porosity and adsorption effect of the final concrete. According to the previous study [26], the water to cement ratio higher than 0.42 could result a high permeability of cement-based materials, which could beneficial for the chloride transference. In this study, the water to cement ratios of 0.5 and 0.65 was used for making mortar samples.



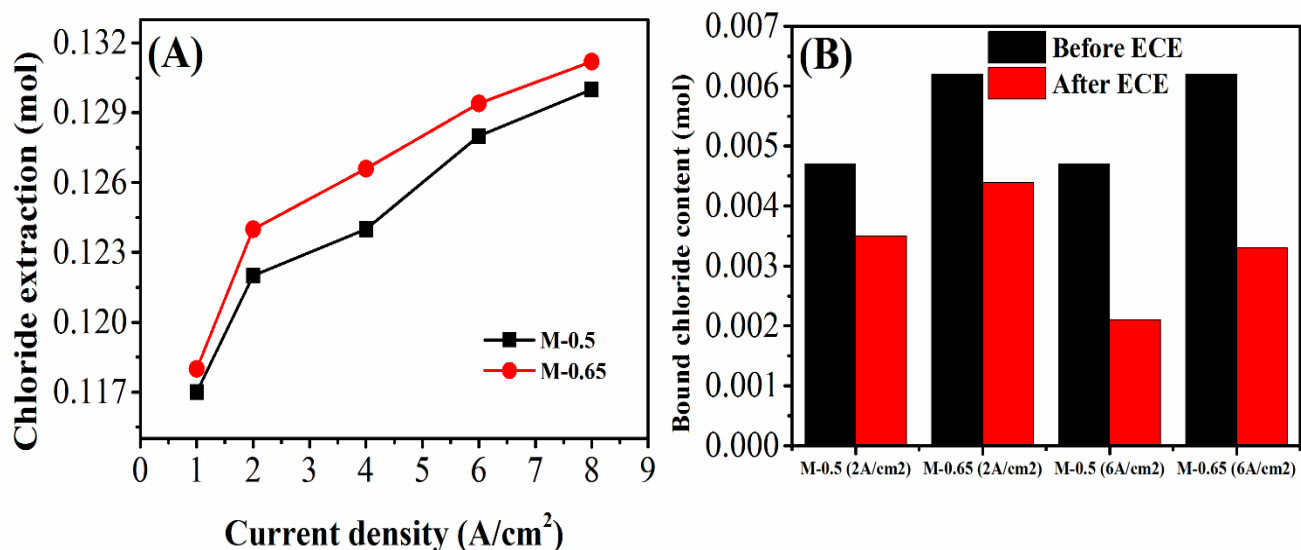
**Figure 3.** (A) Amount of extracted chloride with or without ECE process detected by chloride probes. (B) Total and free chloride contents determined using chemical titration method and chloride probe method.

Figure 3A shows the chloride extraction profiles of the mortars made from water to cement ratios of 0.5 (M-0.5) and 0.65 (M-0.65) placed in an electrolyte with and without ECE process. It can be seen that the chloride extraction process of the M-0.65 showed a much higher performance compared with that of the M-0.5 when no ECE was applied, which proved the high water to cement ratio could result in a porosity and adsorption effect.

Therefore, the free chloride ions in M-0.65 were transferred quickly into exterior electrolyte. On the other hand, the chloride extraction performances of the M-0.5 and M-0.65 showed no big difference when the electric current applied, suggesting the effect of water to cement ratio on ECE process is insignificant. It should be noticed that the water to cement ratio chosen in this study already at a high level, which provides sufficient porosity and adsorption effect for chloride extraction. Moreover, based on Figure 2A and Figure 3A, we can see the chloride can be leached out from the outer parts, while the inner chloride at inner part only can be extracted by the applied electric field. Therefore, under the ECE process, the total extract performance of both mortars were similar.

Figure 3B shows the total and free chloride contents of the mortar sample using chemical titration method and probe monitoring method. It can be seen that the values obtained from the chemical titration method were higher than that of the values collected from chloride probe. This difference can be ascribed as two aspects. For the chemical titration method, overestimation may occur due to the uneven distribution of chlorides in mortar sample. On the other hand, for chloride probe method, the underestimation may occur due to the consumption of the chloride ions through the electrode reaction.

Based on the observation in Figure 3A and 3B, the extraction of the chloride can be effectively enhanced with the impressed current density. The extraction performance in our work showed a better rate than the work reported by Climent et al. [27] using a graphite–cement paste as anode and the work reported by Carmona et al. [28] using a new cement-based anodic system. The porosity and adsorption effect of the concrete are essential. We further studied the effect of the current density on the extraction performance to investigate whether the electric field intensity played an important role. Figure 4A shows the relationship between the current density and extraction efficiency. Both chemical titration method and chloride probe method were used for evaluating the extraction efficiency. As shown in the figure, the increase in the applied current could significantly enhance the extraction efficiency. However, the extraction efficiency is not linear with the applied current density. The unilaterally increasing the applied current density not only leads to energy dissipation but also could result in a loss of interfacial bond strength [29]. Therefore, a current density of  $6 \text{ A/cm}^2$  was used in this study. The possible reason for the superior extraction performance discussed previously could be ascribed to the optimization of current used during the extraction process. As in Climent et al.'s report [27], the current density range they investigated is between 0.5 and  $2 \text{ mA/m}^2$ . Although the balance between the extraction efficiency and energy consumption is an important budgeting control, the extreme longer extraction time also adds an additional cost to the device maintenance.



**Figure 4.** (A) Relationship between current density and extraction efficiency in M-0.5 and M-0.65. (B) Bound chloride content of M-0.5 and M-0.65 before and after ECE process using different current densities

The amount of total chlorides reduced during the ECE process is inconsistent with that of the free chlorides reduced after the ECE process, suggesting some of the non-free chlorides were participated the ECE process. Besides the free chlorides, the bound chlorides (including chemically bound chlorides and physically adsorbed chlorides) also the existence in the concrete by the combination of hydration products or adsorbed on the some structures. The bound chlorides could be dissolved and transferred during ECE treatment. Figure 4B shows the bound chloride content of M-0.5 and M-0.65 before and after ECE process using different current densities. It can be seen that the bound chlorides increased in the water to cement ratio increasing, which had a good agreement with previous report [30]. Under ECE process, the depletion of the free chloride led to the shift of the chemical equilibrium, which could result in a dissolution of the certain amount of bound chloride. The applied electric current also could accelerate the dissolution process. It can be seen that the M-0.65 with 6 A/cm<sup>2</sup> ECE showed the highest dissolution of the bound chlorides.

#### 4. CONCLUSIONS

In this work, we studied the ECE process on different water to cement ratio made concrete with different applied current densities. An embeddable chloride probe was constructed for monitoring the chloride concentration changes during the ECE process. Chemical titration method was also employed for the confirmation of the chloride change. Results suggested that the water to cement ratio could highly affect the chloride leak but only contribute a little when the electric field applied. The higher current density applied could result a higher chloride extraction. Moreover, the chloride transference status at different parts of the concrete was studied. The outmost part showed the first decreasing of chloride content when the ECE process started and the chloride transference of innermost part started

when the chloride concentration matches the chloride concentration of the whole concrete. In addition, we also analyzed the content change of the bound chloride during the ECE process.

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