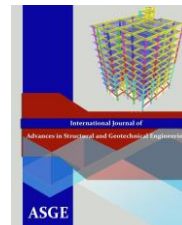




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Chloride Extraction from Portland Cement Concrete: A Review

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ABSTRACT

Several concrete structures are suffering from chloride attack which causes corrosion of the reinforcements. The chloride attack may be due to the presence of chloride in the constituents materials used in manufacturing reinforced concrete. In the common practice, such reinforced concrete structures to be either repaired or replaced and the later is the most common one when chloride content is being high which means much loss for the economy. Several studies have been conducted to investigate the ability of removing the chloride for the contaminated reinforced concrete. This process can prolong the expected life time of the contaminated reinforced concrete structures. This paper is focusing on reviewing the electrochemical chloride extraction (ECE) as an important key to enhance the durability of reinforced concrete structures. The influence of various factors on chloride removal efficiency are reviewed and presented. Various factors including, time of extraction, current density, ratio of cover thickness and side length, initial chloride ion concentration, ratio of cross-sectional area of reinforcement to cross-sectional area of specimen, type of the used electrolyte, type of the used cathode and concrete composition as well as its characteristics are reviewed. Moreover, the advantages, the expected drawbacks, the challenges as well as the expected future of the ECE are reviewed and highlighted.

Key words: Electrochemical Chloride extraction; Reinforced concrete; Anode: Electrolyte: Current intensity; Durability

1. INTRODUCTION

In the field of civil engineering, the degradation of reinforced concrete due to steel rebar corrosion has become a major disaster [1]. Many factors may cause corrosion, but statistics on engineering failures indicate that chloride ion intrusion is the most common cause [2]. Traditionally to repair such defect rust on steel rebar to be removed, then a coating to be added, and eventually the steel rebar to be coated with less permeable concrete or mortar [3]. This process is too difficult, and it is unable to remove the chloride that had penetrated the rebar and reduce the cohesion between the rebar and the concrete. As a result, electrochemical chloride extraction is now available and effective alternative for concrete repair. It is a newly invented technology that reactivates and repairs the passivation in the concrete surface by applying an external electric field; it is a newly invented technology that does not damage the concrete structure. And this approach is simple to implement, resulting in high performance at a low cost. It is also non-destructive [4]. The Federal Highway Administration in the United States first promoted this technology in the 1970s, and the first electrochemical chloride extraction experiments were performed in Ohio and Kansas [4]. Following that, similar study was carried out in Europe and the United States of America [5]. Norcure, a company that has shown that

this modern repairing process would save a lot of time and money, applied for a patent in 1988 under the name Norcure™ [6]. The first time ECE was used was in the Burlington highway repair project in Ontario, Canada. According to Norcure, ECE was commonly used in the United Kingdom, Germany, Japan, North Europe, and North America from 1987 to 1998, with a gross repair area of up to 182,000 square metres [7]. In addition, in 1994, the recommended standard was established in Europe; in 1995, this form was defined as the national norm in Norway, and in 2000, a similar national norm was established in the United Kingdom [8]. However, the implementation of this technology was still underdeveloped in some parts of the country; for example, China begins ECE tests in 1996 [9]. Furthermore, some concerns continue to be addressed, such as the lack of standards and guide books in real engineering applications; the criteria for designers are too high; and some side effects are still present all of this indicates that current ECE research is incomplete, and more studies are needed to speed up the application of ECE, so this paper is a review for the previous studies in the field. After the corrosion of reinforced concrete was mentioned, theory of ECE and system of electrochemical chloride extraction were presented in this paper. The factors which effects on The efficiency of the electrochemical chloride extraction on the concrete microstructure, concrete cover, electrolyte type, current intensity, steel rebar cohesion, and concrete performance were discussed, as well as the advantages and the side effects of ECE. Finally, the technology's orientations were introduced in order to direct future studies.

2. Corrosion of reinforced concrete

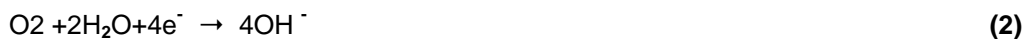
After the passivation is withdrawn, the steel rebar is reactivated [10]. When there is enough water and oxygen, the electrochemical reaction will begin. It also involves four basic procedures, which are described below:

(i) Anode reaction: The iron atoms leave the crystal lattice to become the adhesive atoms on the surface. And the atoms leave the double electric layer to form ion 2Fe , with the following equation:



(ii) Electron transmission: From the steel rebar, the ions produced in the anode transfer to the cathode.

(iii) Cathode reaction: By penetrating, diffusion, and adhesion, oxygen enters the surface of steel rebar, where it absorbs the electron emitted by the anode, yielding the equation:

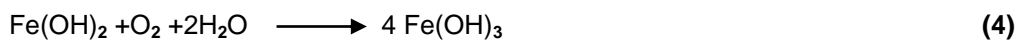


(iv) Forming of the corrosive product

Through diffusion and penetration, the ion Fe^{2+} produced in the anode moves into the deeper zone of surrounding concrete. In the meantime, the ion OH^- formed in the cathode travels to the anode through the concrete pore and the contact surface of concrete and steel rebar, where it combines with the ion Fe^{2+} to form $\text{Fe}(\text{OH})_2$. And the final product is dependent on the availability of oxygen, as shown by the equations (3,4 and 5).



When there is enough oxygen, the $\text{Fe}(\text{OH})_2$ will be further oxidised to $\text{Fe}(\text{OH})_3$, and the $\text{Fe}(\text{OH})_3$ will degrade into soft and porous Fe_2O_3 after dehydration, as:



When there isn't enough oxygen, the $\text{Fe}(\text{OH})_2$ will turn black Fe_3O_4 , as shown in Fig. (6):



Although depolarization agents are not limited to oxygen, hydrogen, for example, may be used as a depolarization agent. However, since reinforced concrete is often put in a medium or alkaline solution environment with dissolved oxygen, the final product was subjected to oxygen richness in general. G.S.duffo and W.Moris scanned the corrosive materials in depth[10].

3. Theory of electrochemical chloride extraction

External anodes and a direct current power supply are used in the ECE treatment to produce a steady current or potential [11]. In addition to the reaction represented by Equation 2 [12], the corrosion products are electrochemically reduced at the steel rebar (cathode) during the ECE treatment. Additionally, hydrogen gas is evolved at the reinforced steel due to the low potential caused by the high current density, as shown in the equation (7) [13]:



The following two equations (8&9) describe the electrochemical reactions that occur at the external anode:



The reaction represented by Equation 9 can be suppressed by keeping the electrolyte's PH (power of hydrogen value) above approximately 9 [14].

According to Equation 8, oxygen is ingested first, followed by the passage of the hydroxyl ion OH^- and chloride Cl^- to the external anode through the pores and holes of concrete. When an electric field is applied to the concrete, the chloride is emitted as a gas, as shown in Equation 9. As a result, the chloride Cl^- is gradually extracted as the process progresses. According to the information given above, three major materials were used in the ECE process: The direct current, the electrolyte solution, and the external anode. Saturated $\text{Ca}(\text{OH})_2$ solutions, 0.1 mole NaOH solutions, and other electrolyte solutions are commonly used [15]. The anode may be iron mesh, stainless steel mesh, or even titanium mesh. And studies show that stainless and titanium wires are the most widely used meshes nowadays [16]. For the ECE technology, the current density was critical; if the current density was too high, the concrete would be ruined [17].

4. System of electrochemical chloride extraction (ECE):

The chlorides extraction technique consists of applying an electric field between the reinforcement inside the concrete and an electrode constituted by a metal mesh fixed externally to the surface of the material. With the application of electric current negatively, charged ions such as :

chloride ions, are attracted to the anode placed on the external surface of the concrete. Also, cations (Na^+) migrate to the reinforcement and there is production of hydroxyl ions (OH^-) on the reinforcement surface, as a consequence of cathodic reactions, these ions raise the alkalinity of the surrounding concrete and restore rebar's protective [18 to 21]. Figs. (1 to 6) show the schematic diagrams of the chloride extraction techniques.

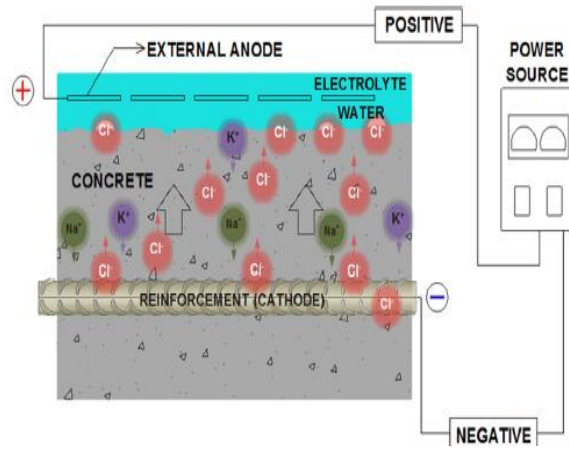


Fig. (1): Schematic diagram of of the samples used for the ECE tests [18].

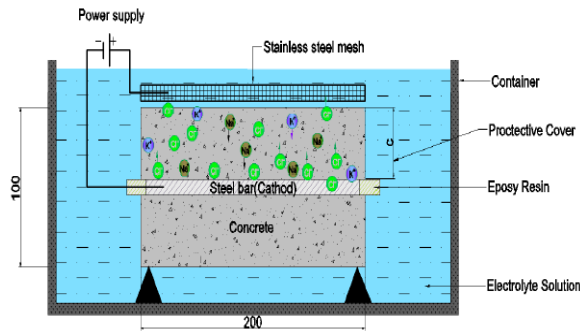


Fig. (2): Schematic design of chloride extraction technique [19].

The electrochemical extraction of chlorides and the electric potential difference between the anode and the cathode cause the following reactions in Eqs.(10,11 and12).



At the same time, hydroxyl ions are produced around the reinforcement by electrolysis as shown in Eqs. (13,14)



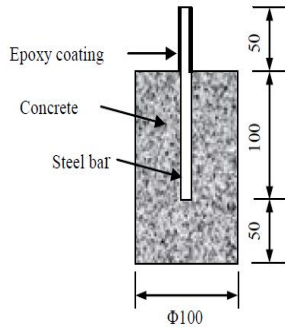


Fig. (3): Schematic diagram of reinforced concrete specimen [20].

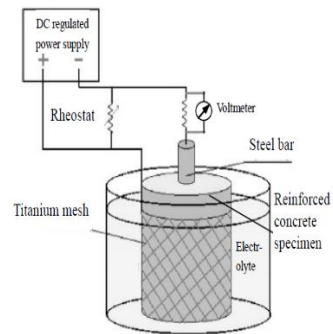


Fig. (4): Schematic diagram of electrochemical chloride extraction equipment [20]

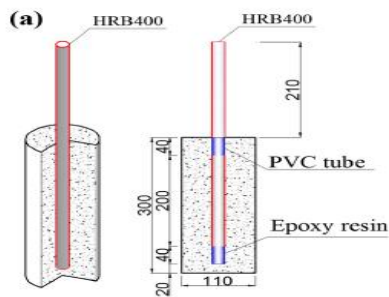


Fig. (5): Schematic diagram of reinforced concrete specimen [21].

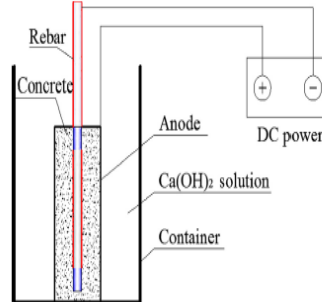


Fig. (6): Schematic diagram of reinforced concrete specimen [21].

5. Factors affecting the electrochemical chloride extraction (ECE)

There are many factors influencing the extraction of chloride from reinforced concrete. These factors are presented and discussed as following:

5.1. Concrete composition

Composition of concrete and its component affects the ECE. Two different Portland cement were investigated [22], the specimen were Reinforced concrete beam , fly ash and GGBS were employed to partly replace Portland cement with approximately 17% and 32%, respectively, sand with fineness modulus of 2.6 was used as fine aggregate, super plastizer was used. The investigated mixes were 1:3 cement : aggregate with $w/c=0.43$ and 1:5 cement : aggregate with $w/c=0.59$. The specimen was Nine kinds of concrete mixes were made by changing the water-cement ratio (W/c) ratio and the proportion of the silica fume (S.F), fly ash (FA), the slag (SL) [23]. The Impact on the concrete microstructure according to study, after ECE treatment, the content of $Ca(OH)_2$ increased, and the new materials were produced near the steel rebar and were rich in Na, Ca, and Fe. Before the ECE treatment, the concrete had a higher porosity and more disperse [24]. The compressive strength of concrete before and after treatment . The strength loss of C35 and C35FS was approximately 2 MPa, while the compressive strength of L50 and LF50 increased by 0.5 MPa to 1 MPa after ECE treatment. Herein, the influence of ECE treatment on the mechanical properties of the concrete could be ignored as shown in Fig. (7).

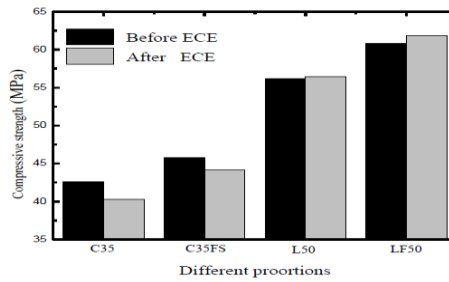


Fig. (7): Compressive strength of concrete before and after ECE [19].

5.2. Covers

Several studies tested the effect of the cover thickness of reinforced concrete on the efficiency of ECE with concrete covers: 1,3 cm [25]. Moreover concrete covers of 25,35 mm were investigated [26]. The thickness of the concrete would hinder chloride extraction [27]. increase in the residual chloride ion content in the surface zone of the reinforced concrete. Therefore, the ECE treatment efficiency also decreased with the increasing cover thickness in Fig. (8) shows the results for each cover, before and after chloride extraction. Samples from two depths of 1,3 cm were analyzed, representing the reinforcement concrete cover for two different mix proportions ($w/c = 0.43$ and 0.59). Percentage of initial chloride was determined in spot test (without layer samplings), since chloride was added to the mixing water during the molding of concrete samples, therefore, having theoretically the same amount of chloride at any depth. The efficiency of ECE is inversely proportion to the concrete cover as shown in Fig. (8).

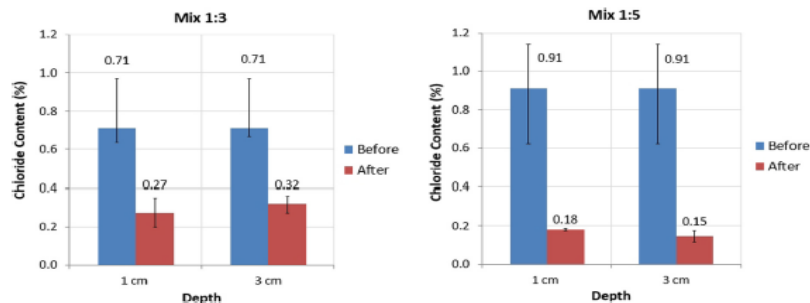


Fig. (8): Chloride content before and after ECE for both mix proportions and for both concrete covers [18].

Corrosion potential (E_{corr}) was read before, during and after chlorides extraction. Results presented in Fig. (9) show gradual increasing of corrosion potential. At the starting point (day 0, still contaminated by chlorides), test indicates 90% probability of corrosion, according to ASTM C 87 . After extraction, the potential decreased to values close to the zone of uncertainty. It is possible that for smaller cover thicknesses a shorter time is required for chlorides extraction when compared to concretes with larger concrete [18]. In concrete with lower w/c ratio (0.43), the thickness of the concrete cover influences corrosion potential. After ECE the corrosion potential remains on the uncertainty zone. On the other hand, for the higher w/c ratio (0.59), the thickness of the concrete cover had no significant influence, resulting in the same level of corrosion potential at the end of chloride extraction. Fig. (10) shows results comparing the differences between water/cement [18].

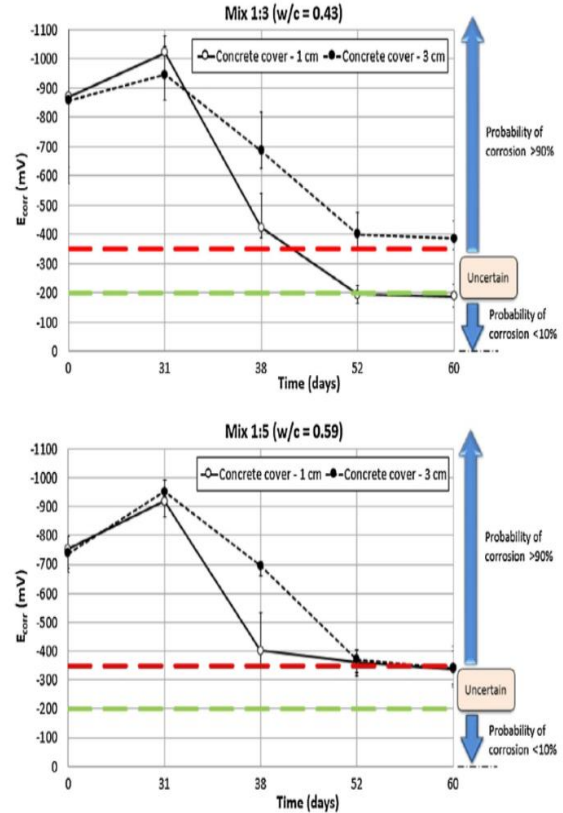
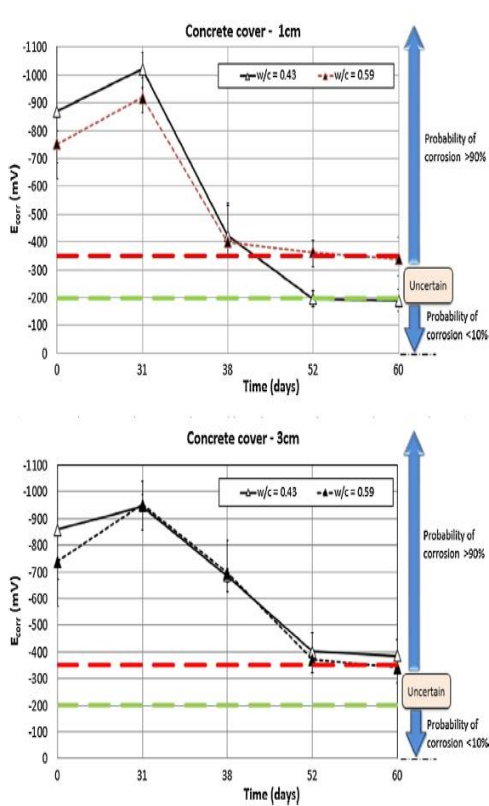


Fig. (9): Evolution of corrosion potential for concrete covers with thickness of 1,3 cm [18].

Fig. (10). Evolution of corrosion potential by comparing different w/c ratio[18].

5.3. Electrolyte

The electrochemical chloride extraction was carried out with distilled water, saturated Ca(OH)₂ solution and saturated LiOH solution as the electrolyte solution concrete with initial chloride ion concentration of 0.29%. From the previous researches [28]. Li⁺ has some superiority in the inhibition in the alkali-aggregate reaction (AAR) of concrete expansion since the ECE tend to accelerate AAR. The current density was constant at 2 A/m². The chloride ion content in the solution was measured by chemical titration, and shown in Fig. (11). It is obvious that extracted chloride ions content from contaminated reinforced concrete decreased with time, and after 12 days of ECE treatment, the chloride ions content migration from concrete to electrolyte solution kept stable. The extracted chloride ion content in the saturated LiOH solution was slightly higher than that in the saturated Ca(OH)₂ solution, while the chlorine removal efficiency of ECE with distilled water as the electrolyte solution continuously remained undesirable and was only approximately 53% of that with the alkali solution. Chang [29] indicated that less bond loss was observed using the Ca(OH)₂ solution than with the NaOH solution. Therefore, using a saturated Ca(OH)₂ electrolyte solution was recommended when reinforced concrete was mixed with a non-active aggregate. The chloride ion content extracted from the concrete with the saturated Ca(OH)₂ electrolyte solution and current densities of 1 A/m², 2 A/m², and 3 A/m² is shown in Figure (11).

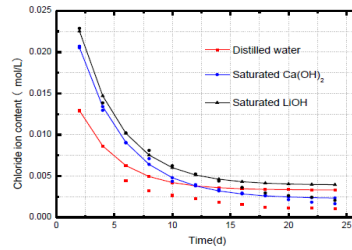


Figure (11). Content and fitting results of chloride extracted from different electrolyte solutions [19].

5.4. current intensity

There is used many current densities 1 A/m^2 [30], 2 A/m^2 [31], 60 volt [32] Rasheeduzzafar [33] found that after applying external current of 538 milliampere per square metre for 14 months, there was considerable movement between the rebar and concrete; and the higher the current or the initial chloride material, the greater the loss of that cohesive power, [34]. electrochemical chloride extraction increases as the voltage applied and the amount of steel rebar increases [35]. Just 50% of the chloride, however, could be extracted [36]. In addition, a novel ultrasonic-electrochemical chloride extraction method was suggested, with an efficiency of approximately 19% higher than conventional ECE treatment [37]. More chloride ions were transported from the contaminated reinforced concrete to the electrolyte solution with the higher ECE current density than with the lower current density. However, the relationship between the extracted chloride ion content and the ECE time was fundamentally identical when the current density varied from 1 A/m^2 to 3 A/m^2 as shown in Figure (12).

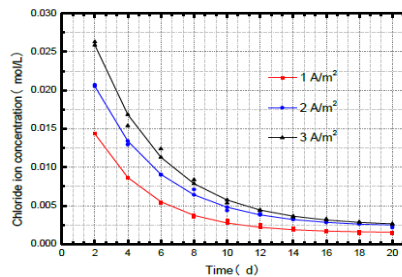


Figure (12). Chloride content and fitting results in electrolyte solution after different current densities [19].

Where, E is the chloride ions removal efficiency, C is the distance from steel bar to the surface (mm), f is the chloride ion distribution function in concrete cover of steel bar, and C_0 is the initial chloride ion content relative to the concrete mass. The calculated chloride removal efficiency of ECE treatment with different current densities of 1, 2 and 3 A/m^2 were 34.98%, 46.81% and 50.48% respectively. The removal efficiencies increased with increasing current density. Previous studies [18] verified that higher current density leads to more efficient ECE treatment is shown in Fig. (13).

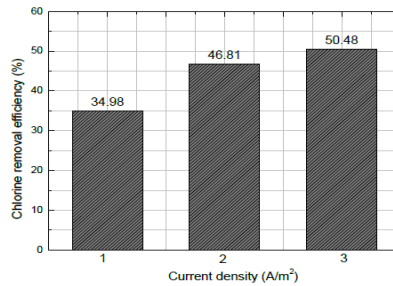


Figure (13). Effect of different current densited on chloride removal efficiency [19].

6. Advantages:

ECE process entails extracting a portion of the contaminating chloride ions from the structure without removing the concrete [38]. It has many advantages over conventional methods, including low environmental impact and high performance [63]. It is still the cheapest method to control the corrosion activity Compared to other methods . It has high durability and efficiency [39].

7.Disadvantage:

the porosity of the concrete increases with the application of electrochemical chloride extraction (ECE) [18]. as shown in Fig. (15) the samples were divided into two groups: samples taken from the face from which chlorides were extracted named (C-EC) and samples taken from the opposite face, named

(S-EC) without the effect of chloride extraction and It reduce the bond between steel and concrete [40].

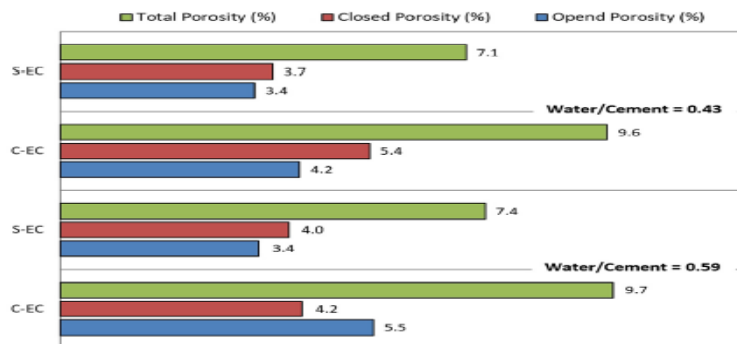


Fig. (14): Porosity by micrography, before and after chloride extraction [18].

8.CONCLUSION

The following are the keys from this paper's study of electrochemical chloride extraction:

- (1) Efficiency of chloride extraction increases with the time of extraction up to 8 weeks. After which the concentration of chloride in the investigated concrete remains without much reduction.

- (2) The current intensity influences the efficiency of ECE, as increasing the intensity enhances the process. Moreover, 1:2 A/m², found to be the most efficient current.
- (3) A thicker concrete cover and more compacted concrete reduced the effectiveness of chloride ion removal.
- (4) Electrochemical chloride extraction increases the Porosity of the investigated concrete which reduce the bond between steel and concrete. Advanced research studies are needed to overcome such defect.
- (5) Future research should concentrate on electrochemical parameter determination, steel rebar-concrete interface mechanism, special applications, field test and numerical simulation strengthening, and the development of new materials and techniques, among other items.

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