A Study of Selecting an Efficient Procedure for Intermittent Electrochemical Chloride Extraction

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Abstract

In this eight specimens were prepared in laboratory. Four of the specimens were with w/c ratio (0.4) and the other four specimens were with w/c ratio (0.5). All of the specimens were intentionally contaminated with 3% (by cement weight) of chlorides during the mixing process in order to study the effect of various parameters, like (current density, intermitting the current in different periods, and the w/c ratio), on the total efficiency of the ECE treatment. A titanium net, immersed in calcium hydroxide electrolyte solution, was used in this work, and the current densities were (0.7 and 1.0) A/m^2 by steel surface. Two different current-on intervals (12 and 5) days were used as well, while the current-off interval was 2 day in all cases of treatment. The plexiglass-spacers, which used between the anode net and the concrete surface in order to reduce the acidification of the concrete surface, result in lower efficiency of the ECE in the adjacent concrete surface above it. Keeping the concrete surface immersed in the electrolyte solution during all the treatment's period led to diffusing a considerable amount of chlorides in these areas out of the concrete.

According to the overall results of the chloride measurement; the 12 days of current-on treatment was most efficient in the early stage of the intermittent treatment, while the 5 days of current-on treatment was most efficient in the advanced stages of the intermittent treatment. Therefore, it can be beneficial to apply the ECE with gradient current-on intervals that starts with long intervals and ends with short intervals. Due to the low current densities that used, the total duration of the treatment was rather long (90 days) and the ECE treatment was most efficient in the specimens that treated with 1.0 A/m^2 by steel surface.

The variation between the two types of w/c ratios that used in this work was low and therefore, the influence of the w/c ratio on the ECE's efficiency was difficult to be noticed.

At the end of the treatment, the rates of extracted chlorides were generally between (80 and 86)% in all the specimens excepting two of them which had two parameters in common (current density 0.7 A/m^2 and 5 days of current-on intervals). These two specimens gave worst result and only about 66% of chlorides were extracted at the end of the treatment.

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Abbreviations

C_{cr} : Critical Chloride Content, or Chloride threshold level (by weight of cement).

ECE: Electrochemical Chloride Extraction.

ECR: Electrochemical Chloride Removal.

RC : Reinforced Concrete.

S-0.4: Specimens with w/c ratio 0.4.

S-0.5: Specimens with w/c ratio 0.5.

w/c : Water to cement ratio.

Wt. percent: by weight of cement in percent.

Definitions

Diffusion: transporting ions (e.g. chloride ions) due to concentration difference, and it takes place in fully or partly water filled pores. In stationary cases, the mechanism of diffusion can be described by Fick's law:

$$J = -D \cdot \frac{dC}{dx} \qquad (1)$$

Where: J is the flux$[kg/m^2.s]$, C is the concentration and x is the distance. D is the diffusion coefficient $[m^2/s]$.

The rate of diffusion depends on many factors like w/c ratio, cement type, porosity in the cement paste, temperature, type of cation (Na^+ or Ca^{2+}) and chloride concentration in the environment [1]. The diffusion follows Fick's laws and the diffusion from the surface inward in a structure is described as function of the diffusion coefficient (depended on the mentioned factors) and the outer chloride concentration[2].

Electromigration: the negative ions (like chloride ions) move towards the positive electrode (the anode), and the positively charged ions (like calcium and sodium ions) move toward the negatively charged electrode (the cathode). The transport current through the concrete is as shown in Figure 1. Other ions than those in the figure are also possible to be affected by the field[2].

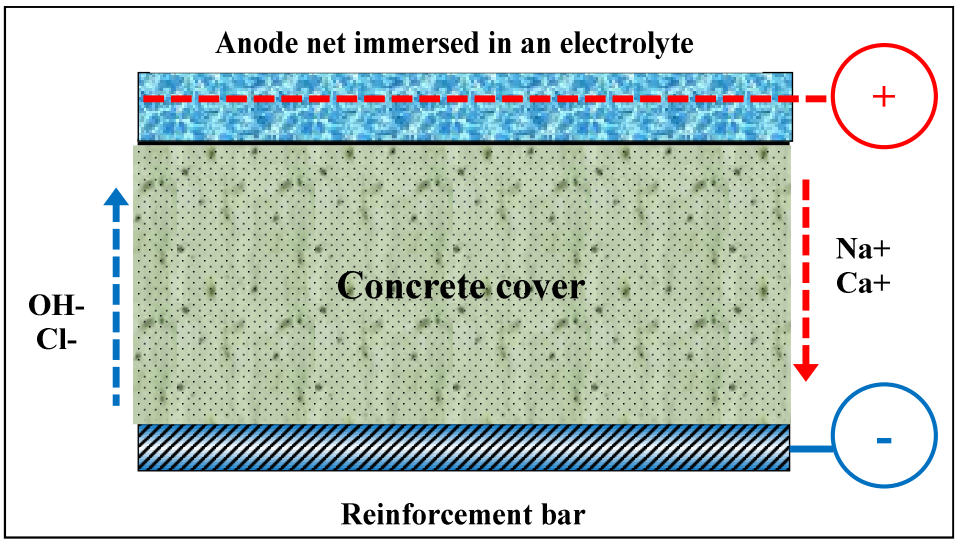

Figure 1: Electromigration in an electrical field in the concrete.

Electro-osmosis: is transporting of mass in liquid filled pores in porous materials due to an electrical field. When ions are accelerated in an electric field they move, and by the viscous forces drag the liquid with them. This viscous drag on the solvent induces convection of the solution. The transport velocity depends on the properties of liquid, solid materials, and the potential difference[2, 3].

Sorption: refers to the action of both absorption and adsorption taking place simultaneously. As such it is the effect of gases or liquids being incorporated into a material of a different state *and* adhering to the surface of another molecule. Absorption is the incorporation of a substance in one state into another of a different state (e.g., liquids being absorbed by a solid or gases being absorbed by a liquid). Adsorption is the physical adherence or bonding of ions and molecules onto the surface of another molecule [4].

Wick action: is the transport of water and any species it may contain through a concrete element from a face in contact with water to a drying face [5].

Pitting corrosion: this type of corrosion is always induced by chlorides. The attacks are characterized by pits. Where the local attack is deeper and much more serious than situation the corrosion is evenly distributed over the whole surface. Inside the pit the liquid may be acidic as a consequence of acid production as shown in Figure 2.

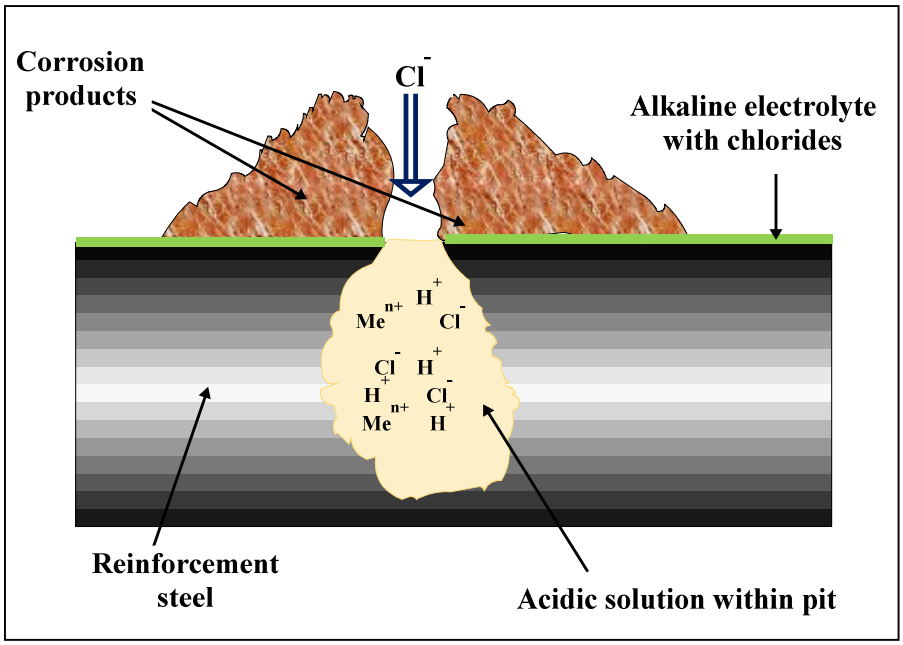

Figure 2: Pitting corrosion.

This happens because of hydrolysis of $FeCl_2$, formed inside the pit according to Eq.(2):

$$Fe^{2+} + 2Cl^{-} = FeCl_2 \qquad (2)$$

$FeCl_2$ reacts with water (somewhat simplified) as in Eq.(3):

$$FeCl_2 + H_2O = Fe(OH)_2 + 2HCl \qquad (3)$$

Consequently hydrochloric (HCl) acid is formed [2].

1-Introduction

It is widely known that contaminating concrete structures with chlorides causes severe damages to the reinforcing steel. There are many ways of chloride ingress into RC structures. It can be added during mixing process by using inadequately washed sea-dredged aggregates, and (in the past) by using accelerating additives that contain high rate of chlorides; or the source of the chloride can be external from the sea-water for marine structures, and may attack the structures subjected to the de-icing salts such as bridges and parking houses [6, 7].

The most important factor that can limit the initiation of chloride-induced corrosion of steel is the ability of hydrated cement to bind the free chlorides in the pore solution in the concrete. That is because only the free chlorides in the pore solution near the steel surface contribute in the initiation of steel corrosion. When the chloride content in the pore solution exceeds the threshold chloride level, the passive film around the steel surface will break down. The bound chlorides don't play a role in corrosion initiation in normal conditions; therefore the chloride binding capacity is an important property of concrete for maintaining the service life. The chloride binding capacity affects by many factors like type of the cement, additives, w/c ratio, age of the concrete at chloride attack, duration of the chloride exposure and so on.

It was proved that is possible to remove the chlorides from the RC by using an electric current after the investigations that were carried out in the USA during 1970s [8]. They used very high current densities and voltages. Later, many investigations proved that using high current densities in ECE cause severe damages on the bond between the reinforcement bars and the concrete, in addition hydrogen embrittlement of prestressed steel bars [9-12]. The principle of electrochemical extraction ECE, or sometimes called desalination of concrete, or electrochemical chloride removal ECR, is to pass a DC current through the reinforcement as cathode to the anode net which is placed temporary on the concrete surface. The anode net is surrounded by water or alkali solution like calcium hydroxide. Chlorides, as negatively charged ions, will be pushed toward the positive anode, and thereby large amounts of chlorides can be removed from the concrete in a relatively short time, often between 6 to 10 weeks.

In later stages, after inventing the ECE technique, it is noticed that the concentration of chlorides in the pore solution begins to increase again considerably after a short time from the end of ECE. The reason of this phenomenon can be explained by the equilibrium between bound and free chlorides. Afterward, an intermittent ECE treatment is used to extract the released bound chlorides from the concrete by interrupting the treatment with periods of current off. In the current free period, the concentration of chlorides in the pore solution is very low comparing with the concentration of bound chlorides in concrete. Then the bound chlorides begin to release into the pore solution until equilibrium between free and bound chlorides occurs. The new released bound chlorides can be extracted out of the concrete

during the next period of current-on treatment, and thus the procedure will be repeated until sufficient results are obtained. The current density plays an important role in the efficiency of the ECE treatment. Applying high current densities in ECE treatment may shortens the duration of the treatment, but on the other hand, causes negative impacts on the concrete and reinforcement especially in prestressed concrete structures. This work contains documentations about the drawbacks of the ECE treatment and overview on current densities that used without subsequent reverse impact on the reinforced concrete.

The aim of this work is study some parameters that may lead to more advantageous results of the ECE treatment. These parameters are w/c ratio, different current density and current on/off intervals. The ECE treatment is applied with these different parameters, and the reduction of chloride contents is monitored by analyzing the concrete powders collected from different depths in the concrete cover. In addition, the work includes useful information about related documentation about ECE treatment, and its side effects on RC. The side effects are not examined in the work due to limiting the current densities within the safe level that don't affect the concrete and reinforcement in general. In brief, the work is aimed to specify the parameters (current density, periods of current on/0ff and w/c ratio) that give most efficient results in ECE treatment.

2-Chloride Ingress into Concrete

In normal situations the reinforcement is highly protected from corrosion by the concrete, because of the high alkalinity (PH>13.5) of the pore solution. Under this high alkalinity steel will remain in passive state. In addition the concrete that well-cured and hydrated with low w/c ratio has low permeability, and thereby prevent in high grade penetrating the corrosion induced agents like chloride, carbon dioxide, moisture, etc. The desirable durability requirement cannot be achieved in practice due to deterioration that caused by the reinforcement corrosion, and in many cases the corrosion is induced by chlorides. The quality of concrete, especially the permeability, presence of cracks, and cover thickness, play a great role in resisting the environmental aggressions that cause the reinforcement corrosion. At once the corrosion initiated, it propagates almost in a steady rate and reduces the service life of the structure[13].

For many decades, investigations have been made for finding clearer understanding of the circumstances that increase the breakdown of the passive state of steel in the concrete, with particular interest directed toward situations where chloride ions, contaminated concrete either through internal additives or through external environment exposure, are the main cause of depassivation. The internal source of chloride is not likely to happen in now days and have been largely resolved as a result of the imposition of increasingly restrictive chloride limits in the standards for concrete materials adopted by most countries. The major problem still in the external source of chlorides, associated with deicing salt or marine splash, which is the spot of concern in worldwide; and the reason of this belongs to the variation, that observed widely, in the threshold chloride level corresponding to the initiation of significant rates of corrosion of reinforcement steel in concrete under different circumstances [14, 15].

The process of chloride ingress start when the chloride ions flow through the concrete cover and then reach certain concentration which is enough to trigger the corrosion of the steel reinforcement[16]. This means the passive- or protection alkali layer of the steel has been destroyed, and the initiation period of corrosion can be described as chemical reaction between the various substances in the concrete. Many of investigation studied the transport of chloride in concrete, based on Fick's diffusion law for water vapor transport [17], chloride ion and thermal diffusion in water [18]. The law relates diffusion process to difference in concentration of chlorides.

If the pores in concrete are partly on completely empty, chloride ions may ingress into concrete by capillary suction. This transport process can be more sufficient than diffusion alone. In porous material like concrete may permeation occurs in presence of pressure gradient, and the flow of solutions through the pores can be expressed by Darcy's law.

David Conciatori *et al* [16] reported that the Fick's diffusion law Eq.(1) represents vapor diffusion well, but it does not describe capillary suction of water. The author showed that chloride ion concentration increases quickly in concrete cover when structural elements are exposed to deicing salts and salty water splashes. Chloride ingress depends on the climatic

condition and salt concentration in the aggressive solutions. While permeability of concrete considered as insignificant parameter when the concrete is in direct and splash water contact.

Chlorides may be transported into concrete either together with water through the micro-pore space, driven by differences in the pore water pressure, or chloride can diffuse through the pore water, driven by the differences in the chloride concentration. The diffusivity of chloride through concrete is characterized by a large variation, which depends in high grade on the w/c ratio [19].

The hardened Portland cement paste consist of cement gel and pores [20]. The spaces between C-S-H particles that are filled with cement gel are called gel pores, while the spaces that are not filled with the cement gel are called capillary pores. Transport properties depend on the size of the capillary pores and its continuity, i.e. the flow of substances, is higher in present of large and continuous capillary pores. If the capillary pores were scattered and non-continuous, then the transport properties will be dominated by the much smaller gel pores [21]. Since the chloride ions is considerably smaller than the diameter of capillary- or gel-pores, a diffusive transport of chloride ions through these pores, when saturated, is allowable [19]. Transporting chlorides through aggregates is unlikely to happen because of low permeability of aggregates. Hence, the transport in a concrete is mainly dependent on the properties of the cement paste, like binder type, porosity and pore size distribution, which primarily affected by the w/c ratio. There are many mechanisms that contribute in chloride ingression into concrete: diffusion, sorption, capillary suction, migration and wick action. The diffusion takes place in present of concentration gradient, which mainly drives the transport of chloride ions in concrete exposed to a direct contact to seawater, as submerged, tidal and splash zones in offshore concrete structures where the moisture condition in the concrete is stable. Fick's 2nd law is commonly used to describe chloride ion diffusion in concrete as given in Eq. (4), as it considered modeling the diffusion of un-reactive species (i.e. chloride ions) into a semi-infinite medium (i.e. concrete).

$$\boldsymbol{C_{(x,t)} = C_s(1 - erf\frac{X}{2\sqrt{Dt}})} \qquad \textbf{\textit{(4)}}$$

Where ($C_{(x,t)}$) is the concentration of chloride ions at the depth (x) and the exposure duration t, (C_s) is the surface chloride concentration, which actually is dependent on concrete mix proportion and degree; (D) is the diffusion coefficient.

3-Chlorides in the Concrete

There are two types of chlorides in the chloride contaminated concretes; the first type is free chlorides which, normally, are dissolved in the pore solution, and the second type is bound chlorides which are chemically and physically bound by the cement paste. In addition it may exist as chemically bound chloride with the minerals of the aggregate's composition. When the pH of the pore solution is above (12.5) only the free chlorides in the pore solution induce the corrosion of the reinforcing bars and the bound chlorides don't contribute in the corrosion process. Otherwise, as the pH value of the pore solution drops from (12.5) the bound chlorides will be released rapidly and dissolve in the pore solution as free chlorides and subsequently cause corrosion of the reinforcement[22, 23]. In other word, there is equilibrium condition between free and bound chlorides in contaminated concretes, and this equilibrium depends on the pH level of the pore solution. The carbonation of concrete accuses decrease in the pH and thereby most of the bound chlorides will be released into the pore solution. Therefore the chloride content in practice is limited to the threshold level. The critical chloride thresholds are mostly expressed a critical total chloride contents, as it is much easier to determine than determining the concentration of free chlorides[7].

Physically, the chlorides in the concrete can be absorbed into the inner surface of the pores in cement paste, and chemically can be bound by the hydration products. Tricalcium silicate (C_3S) has capacity to bound about (0.3 to 0.5) % of chlorides by mass of C_3S; aluminates also can bind chlorides (the hydrate phases of Tricalcium aluminate C_3A), and tetracalcium aluminate (C_4AF) integrate chlorides usually as $CaCl_2$ [7]. The cement types that have low content of C_4AF in its composition such as sulphate-resistant cements have low capacity to bind chlorides, and thereby the risk of chloride induced corrosion will be higher compared to an ordinary Portland cement[24]. Furthermore, cement pastes with high calcium fly ash have more capacity for binding chlorides than cement pastes with low calcium fly ash; that's due to the some cementitious components in the high calcium fly ash which can hydrate to bind chlorides[6].

4-Chloride threshold in the concrete

The chloride threshold (or critical chloride content) is the limit of chloride concentration by weight of cement (in percent) where chloride contents below it don't cause corrosion of the reinforcing steel bars. Unfortunately, the threshold level is not constant for all types of concrete. For instance, the corrosion may occur at chloride concentration of 0.1 wt.-percent while chloride concentrations as high as 1.4 wt.-percent don't initiate corrosion in concretes with high alkaline environments. In addition, some types of cement have high capacity for binding chlorides chemically, and thereby, reduce the chloride concentration in the concrete's pore solution that can contribute to corrosion[25]. The combination of increased alkalinity and alkali ion content around the reinforcing bars (cathode) leads to increase the critical threshold level; Therefore, the conclusion of ECE's efficiency should be based on the results of the chloride analysis together with the alkali ion content[26].

In many studies, the critical threshold level expressed as free chlorides or$[Cl^-]/[OH^-]$. These expressions has drawbacks of poor accuracy and repeatability as it fails to consider the participation of bound chlorides in sustained corrosion and the buffering capacity of the cement matrix. The most common way to represent the critical threshold level is by total chloride content relative to the cement weight, as it take in consideration the inhibiting effect of the cement and the aggressive nature of chloride. The values of threshold in total chloride content are relatively narrow range comparing with those expressed in free chloride or $[Cl^-]/[OH^-]$. it is proposed that the mole ratio of total chloride to the acid neutralization capacity of cement (as the mole concentration of H^+) is a better method of capturing the inhibiting effect[27].

Ki Yong Ann *et al*[27]; reported that the air voids content at the concrete-steel interface leads to a lower critical threshold level due to absence of cement hydration products there. The author pointed also to the side effects of calcium-nitrate based corrosion inhibitors which are remarkably raising the critical threshold level in early stages; but, as long term perspective, presenting nitrite ions in concrete allow external chlorides to penetrate into the concrete more easily and thereby degrade the effect of increased critical threshold level.

Ueli Angst *et. al.*[28] investigated the critical chloride content in concrete, and unfortunately their attempts for limiting the chloride threshold values in a reliable range were to no avail. Thereby, the service life design couldn't be improved and related decisions will remain based on long-term experience from existing structures.

G. Markeset [29] studied the relation between the critical chloride content and the predictions of service life. The author described the C_{cr} as a very sensitive input parameter in the service life calculation, and this parameter is difficult to measure. The work based on installing corrosion sensors in an existing marine structure, and from probabilistic service life calculation, the author found that it is possible to increase the service life in a considerable rate by increasing the characteristic value of C_{cr} (Figure 3). For instance, the service life time increases from 50 years to 100 years as the C_{cr} increases from 0.34 to 0.67 %.

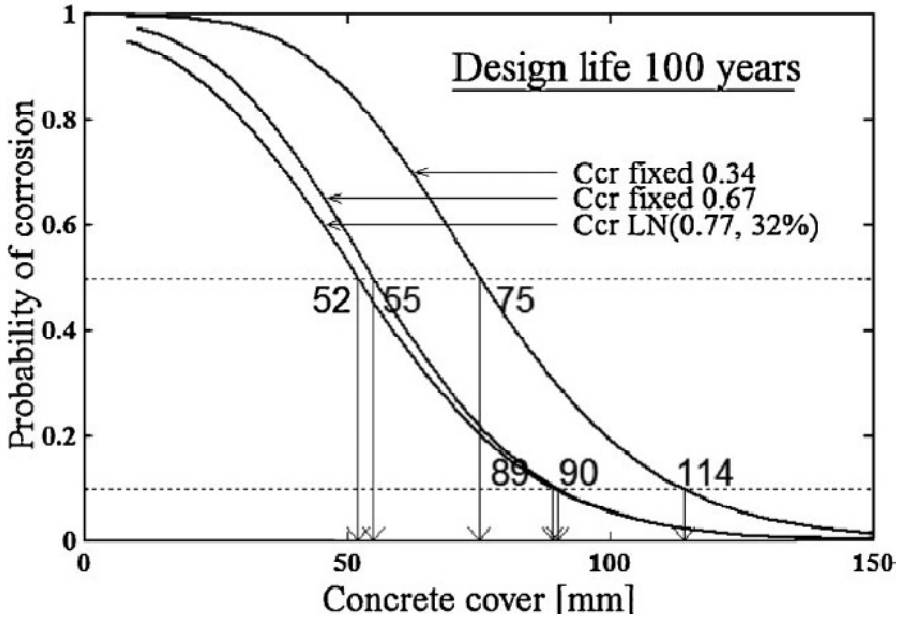

Figure 3:Effect of Ccr on required concrete cover for design service life of 100 years (Ccr given in % Cl_ of weight of cement)[29].

5-Pore Structure of Concrete

There are three types of pores in the concrete: macrospores, capillary pores and gel pores. The hydration process of the cement paste leads to forming calcium silica hydrate (C-S-H); which has a layer structure that gains strength to the concrete. The space between these layers called gel pores, and its dimensions can reach up to several nanometers. While the voids that are not filled with hydration products, due to inhomogeneous distribution of the concrete mixture particles, are called capillary pores. The dimension of capillary pores is various and depends on the w/c ratio, but in general they have dimensions of 10 to 50 mm. Macrospores can be formed as air entraps into the concrete as result of insufficient compaction during the mixing process of the fresh concrete. Sometime macrospores are formed by adding certain admixtures. More details about the dimension ranges of the different types of pores in concrete are showed in (Table 1).

In a fully saturated concrete, as in subsea structures or rain exposed concrete surfaces, the pores are interconnected with each other and filled with water, while the atmosphere exposed concrete may have dry pores and the water content in the pores depends on the relative humidity of the environment. The water in the pores of the concrete is called pore solution.

Many of ions that are produced by the hydration process may dissolve in the pore water, mainly NaOH and KOH which make the pore solution high alkaline with pH between 13 and 14 [7].

Type	Gel Pores	Capillary Pores	Macrospores
Dimensions of the pores	1-10 nm	0-100nm	0,1-a few mm

Table 1: Dimensions of pores in hydrated cement paste[7].

6-Chloride induced corrosion of reinforcing steel in the concrete

When the concentration of chlorides at the surface of the reinforcing steel exceeds the threshold limit, the protective passive film around the reinforcing bar at that area will breaks down, and thereby pitting corrosion may occur. The attacked area by chlorides acts as anodes, and the rest non-damaged areas, that still are passive, acts as cathodes. Afterwards, the H^+ ions generates inside the pits due to corrosion reactions. This will lead to acidification of the environment in that area. Moreover, the chlorides as negatively charged ions will be moved toward the anodic region, and therefore an increase of the chloride content occurs inside the pits. Thereby, corrosion is accelerated and leads to quick reduction in the cross section of the reinforcing bars in these areas[7].

The corrosion of reinforcement steel is an electrochemical process, where the surface of the corroded steel functions as a mixed electrode that is a composite of anodes and cathodes, and electrically connected through the body of steel itself. Thus coupled anodic and cathodic reaction takes place. The pore water in concrete acts as an aqueous medium, i.e. a complex electrolyte. Therefore a reinforcement corrosion cell is formed as shown in (Figure 4) [13].

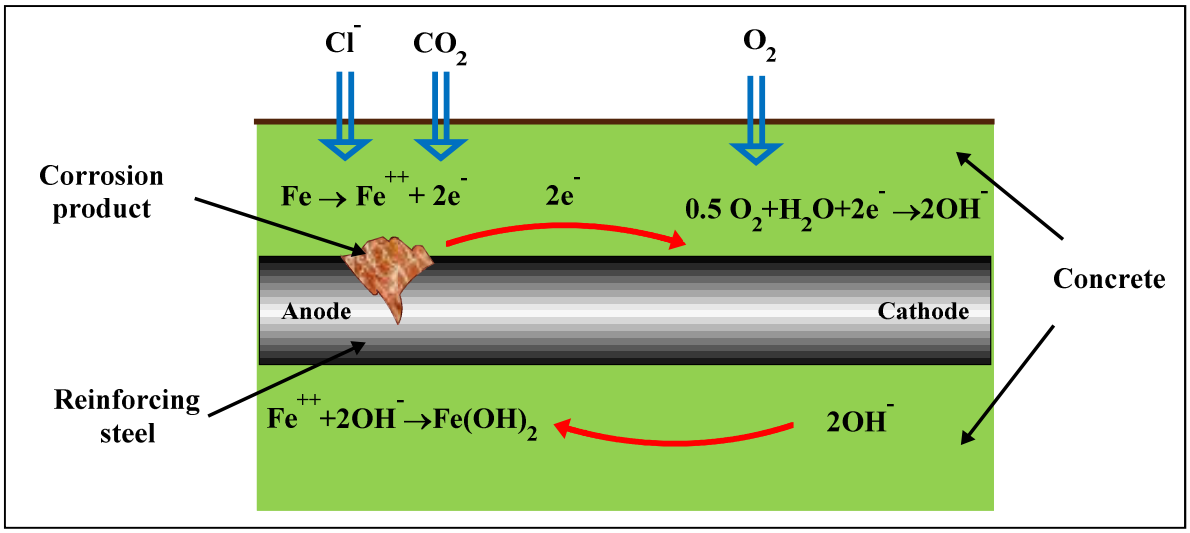

Figure 4: Schematic illustration of the corrosion of reinforcement steel in concrete (as an electrochemical process).

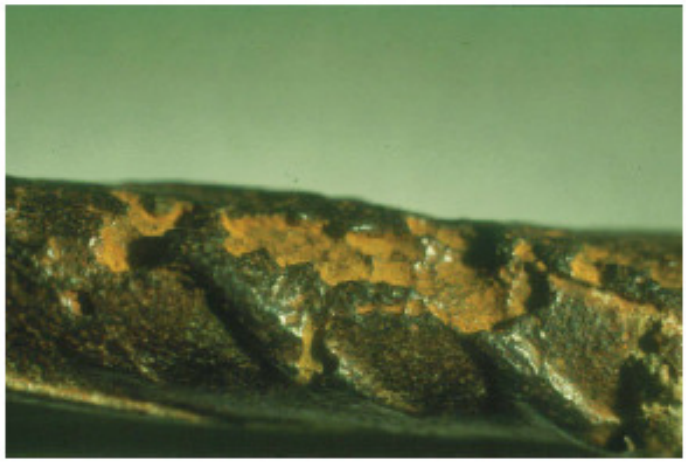

Figure 5: Chloride-induced steel corrosion[30].

Reactions at the anodes and cathodes are widely described as half-cell reactions. The anodic reaction is an oxidation process, which results in dissolution or loss of metal; while the cathodic reaction is a reduction process which results in reduction of dissolved oxygen forming hydroxyl ions. For a steel bar embedded in concrete, following anodic reactions are likely to occur:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 8H^+ + 8e^- \qquad (5)$$

$$2Fe + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 6e^- \qquad (6)$$

$$Fe + 2H_2O \rightarrow HFeO_2^- + 3H^+ + 2e^- \qquad (7)$$

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (8)$$

These reactions above depends on the pH of interstitial electrolyte, presence of aggressive anions, and the existence of an appropriate electrochemical potential at the steel surface[13].

The availability of O_2, and the level of pH in the vicinity of the reinforcement surface, are the driving force of the possible cathodic reactions[13]. The most likely reactions can be described as follows:

$$\mathbf{2H_2O + O_2 + 4e^- \rightarrow 4OH^-} \qquad \textit{(9)}$$

Or:

$$\mathbf{2H^+ + 2e^- \rightarrow H_2} \qquad \textit{(10)}$$

The report of C.L.[15] confirmed the relation between the nature of the steel-concrete interfacial zone and the resistivity of the reinforcing steel against the depassivation that results from chloride ions. It considered as one of the significant factors that affect the threshold chloride levels which initiate a significant corrosion when the concrete structures are exposed to chloride ingress. The role have been explained by buffering action of the solid hydration products deposited in the vicinity of the reinforcing steel, and particularly, the presence of a substantial proportion of portlandite within the hydrated material proportion which this prevents the pH value from falling below 12.6. It reported also that this buffering action gains the resistivity to the pore solution against leaching the hydroxyl ions, and also hindering the consumption of these ions by the anodic reaction products which formed inside the incipient pits on the steel surface. In microscopic examination, the author reported that gross disruption of the steel and concrete interfacial zone is one of the destructive effects that can cause large water-filled voids beneath the reinforcing bars as result of accumulating excessive bleed water at the steel- concrete interface, and subsequently leads to provoke the initiation of corrosion in presence of chloride ions[15].

7-Electrochemical Chloride Extraction (ECE)

In nowadays premixed chloride in concrete is no longer expected, but as long as concrete is a porous material, penetrating harmful ions, like chloride ions, is likely to happen at structures exposed to chloride contaminated environment. There are many factors which govern the ingress of harmful substances into concrete structure such as type of the cement, permeability, additives, temperature, relative humidity etc…

It is very important to treat the chloride contaminated concretes in the early stage of aggression, because in severe damaged reinforcement, as result of chloride induced corrosion,

even removing the chlorides from concrete will not regain the passivity of the reinforcing bars[31].

Before inventing ECE method, the mechanical full- or patch repair was common method for removing the chlorides from the chloride contaminated structures. The mechanical repair was accomplished by chiseling the contaminated concrete cover to different depths depending on the concentration and extent of the chlorides. In worse cases it chisels until the reinforcing bars. Then the reinforcing bar treats by sand blast to remove the corrosion products from it, afterwards, the chiseled areas fills with new concrete or only mortar for small patches. There are many drawbacks of using the conventional mechanical repair such as the high cost, noise, pollution, requiring time and labor, and achieving problems in some parts of structure.

In 1970s, investigations carried out in USA and proved that it is possible to remove chloride ions from concrete by applying an anode electrolyte to the concrete surface and passing direct current (DC) between the anode and the reinforcing steel, which acts as a cathode. Thereby the chloride ions which are negatively charged will be repelled by the cathode and migrate toward the anode. Other ions in the pore solution, like sodium, potassium and hydroxyl ions may move in this electrical field as well[32, 33]. This invention confirmed by numerous other studies [34-37]. The technique majorly take advantage of the fact that migration of ions under an electrical field in concrete is much faster than diffusion[38]. The method developed afterward by Norcure to facilitate the treatment of vertical surfaces[39]. The technique inherited various names like: electrochemical chloride removal ECR, desalination, and electrochemical chloride extraction ECE.

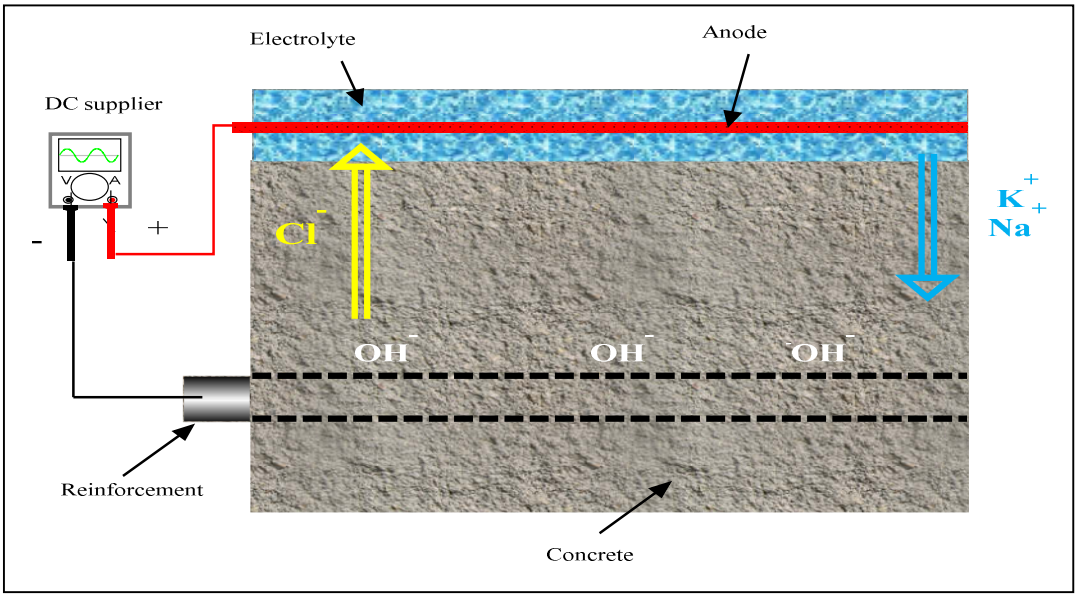

Figure 6: Mechanism of electrochemical Chloride Extraction

As shown in Figure 6, the anode system consists of an anode metal (usually titanium net), installed on the surface of the concrete, and embedded in a wet paper pulp or only an electrolyte solution, depends on execution facilities. Tap water can be used as electrolyte, but

usually enriched with alkali chemicals, like calcium hydroxide, to prevent acidity of the solution and evolution of chlorine gas during the ECE process.

As mentioned earlier, the chloride ions are pushed away from the reinforcement by the applied current and moving towards the anode. Once ions reach the concrete surface, passes into the anolyte and thus will be removed from the concrete. The chemical reactions that take place at the cathode can be expressed as follows[40]:

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \qquad (11)$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \qquad (12)$$

While the anodic reactions are expressed as:

$$4OH^- \rightarrow 2H_2O + O_2 + 4e^- \qquad (13)$$

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \qquad (14)$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad (15)$$

The ECE is particularly suited for structures in which active corrosion is occurring, and the damages in concrete are little[33]. The main benefit of ECE that it is a short-term process (3-5 weeks). Thereby, long-term monitoring costs and mechanical efforts are saved. Furthermore, it is non- intrusive and can be used without interrupting the traffic flow, when applied on bridges or parking housed. In prestressed concrete structures, the ECE is not desirable and should be used very carefully regarding the current density to avoid hydrogen embrittlment. The ECE may sometimes lead to evoking the alkali-silica reactivity, and the remedy for that issue is putting lithium ions into the electrolyte[41].

7.1-The anode system

The most popular anode material that uses in ECE treatment is coated titanium mesh[23]. This metal has the highest strength-to-weight ratio of any other metal, and in its unalloyed condition, titanium is as strong as some types steels, but 45% lighter in weight[42]. Furthermore, titanium is an inert metal, and under suitable conditions cannot corrode, but it may require the use of a buffered electrolyte or regular replacement of electrolyte since chlorides will be accumulates in the electrolyte during ECE process causing acidification of the electrolyte. Another alternate of anode material is steel mesh. The drawbacks of this type of anode are so many enough to limit the use of it. The steel is not an inert material, and a large amount of it can be reduced by corrosion at the advanced stages of the ECE process. Furthermore, the rust products will stain the concrete surface and then an aesthetic surface treatment will be required after the ECE process[43].

The most common electrolytes that have been used in various ECE projects are: water, calcium hydroxide (lime) solution, and lithium borate solution. The water has no buffering

property, and electrolyte acidification will occur if it used with an inert anode. Therefore, the water electrolyte needs regular replacement. Calcium hydroxide has a very low solubility in the water and as solution can provide a limited buffering capability. While the lithium borate electrolyte, which is consisting of a mixture of lithium hydroxide and boric acid. This type of electrolyte can provide a highly buffered solution which is suitable for the closed system applications, or treating concrete structures with alkali reactive aggregates[43]. The solution of lithium borate is most expensive among these other two commonly used solutions[44].

In the ECE process, the anode system is installed temporarily on the concrete surface unlike the cathodic protection where the anode is embedded permanently. A proprietary system developed in Norway where wet shredded papers are sprayed onto the concrete surface to form a wet layer of paper. Then the anode mesh is fixed to the surface by wooden batons, and finally another layer of wet shredded papers are applied. The anode system maintained wet during all the period of treatment. This method makes it possible to apply ECE on vertical surfaces and other surfaces that are difficult to use a bare electrolyte solution[23]. Another alternate used in USA by SHRP project on bridge decks where "blankets" are used on vertical surfaces provided with a circulating system of electrolyte solution[45].

During the ECE treatment, it is very important to maintain a good contact between the electrolyte and the concrete surface in order to minimize the circuit resistance[46]. This can be accomplished by three methods: sprayed shredded paper, synthetic felt mats, and surface-mounted tanks [43, 44, 47-49].

7.2-Current density and the efficiency of intermittent current in ECE

Many investigations carried out in the 1970s for studying the ECE treatment [50, 51]. Very high current densities were used in order to get shorter treatment periods. Consequently, these high current densities, led to prompting many drawbacks like cracking due to the high temperatures of the concrete, increasing the permeability, and loss of the bonding strength between steel and concrete.

The SHRP's report number S-657[8] recommended current densities below 5 A/m^2 and total charge below 1500 $A.h/m^2$ by concrete surface. These limits are based on laboratory and field results regarding chloride removal efficiency and damages to the concrete or the reinforcement. As well, the voltage is also limited to less than 50 volts for safety reasons.

In many researches, based on Eq.(16), showed that the chloride extraction efficiency decreases over time during the treatment, and it is most efficient in the early stages of the treatment[52-54]. Therefore, any prolongation of ECE treatment to more than 1500 $A.h/m^2$ is reported to be inefficient as nearly all of the current flow is transported by hydroxyl ions[55]. By other word, the increase in OH^- content and the decrease in Cl^- content leads to a marked reduction of the chloride transference number (t_{cl}) according to Eq.(16) [52-54, 56].

$$t_{cl} = \frac{I_{cl}}{I_{tot.}} \qquad (16)$$

Where: (t_{cl}) is the chloride transference number;

(I_{cl}) is the amount of DC current carried by the chloride ions.

(I_{tot}) is the total current.

The ECE treatment removes only the free chlorides present in the pore solution of the concrete. With continuous ECE treatment the concentration of chlorides will decrease over time, and thereby the efficiency of the treatment will decrease as well according to Eq.(16). The current is gradually transported by the hydroxide ions and at the end of the treatment only the bound chlorides will be remained in the concrete[55]. By interrupting the current, equilibrium between free and bound chlorides will take place in the concrete. This equilibrium leads to release the bound chlorides into the pore solution until reaching an overall balance of chloride concentrations in the concrete. Thus, a restart of the current can increase the efficiency of the treatment by extracting more new released chlorides. According to the origin of the hypothesis [52, 57], it is confirmed that a period of current interruption is beneficial and increases the efficiency.

In 1989 in Switzerland, an ECE treatment applied on an abutment with 26 m length at one side of an underpass under a highway as a rehabilitation technique[55]. The cover depths of the concrete varied between 25 and 35 mm, and the concrete quality reported as good. Previous investigation revealed a high chloride content in the vicinity of the reinforcing bars due to intensive deicing salt exposure. A commercial activated titanium mesh was used in that work. The treatment applied in two stages. The first treatment applied with continuous current densities in range (0.3 to 0.75) A/m^2 by concrete surface for about two months. The second treatment applied six months later in order to retreat the areas with chloride content more than 1% of the cement weight. In the second time an intermitted ECE technique was used with (2 weeks current on/ 1week off), and the current densities were in range (1 to 0.7) A/m^2 by concrete surface for about two months. The aim of using an intermittent ECE treatment was to enhance the extraction's efficiency due to rebalancing of the chloride ions in the concrete. More procedure details reported in the references [55, 57, 58].

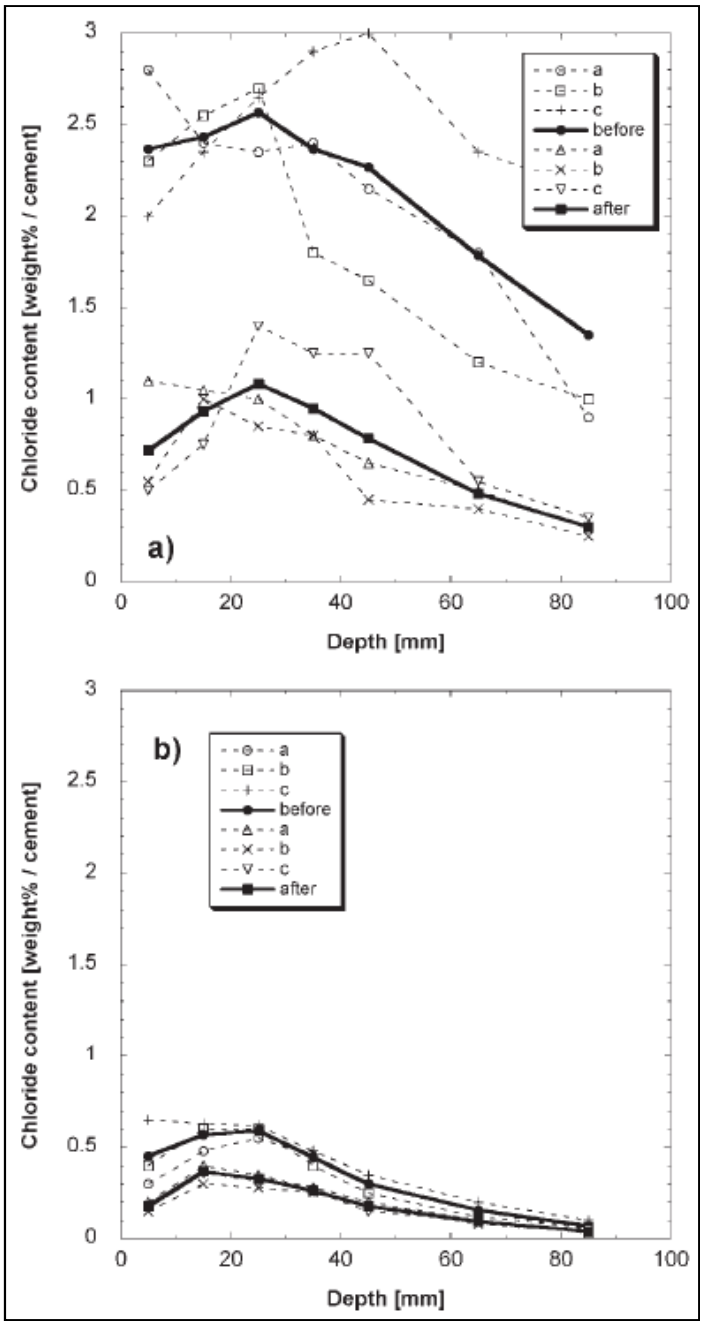

Figure 7:Total chloride depth profiles before and after the second ECE treatment in areas with (a) high and (b) low initial chloride concentration[55].

As it reported, in each of the treatments about 50% of the total chloride ions were extracted from the concrete. The intermitted ECE was more effective in the areas with the highest chloride content (Figure 7a). The authors deduced that the intermittent ECE treatment was more sufficient than the first continuous ECE relating to ability of the intermittent treatment to extract the bound chlorides from the concrete.

In another work, carried out by Ueli Angst[7], where an intermittent ECE treatment was used on two concrete specimens with dimensions (320 × 245 × 70) mm and (0.5 and 0.6) w/c ratio. The specimens were contaminated with chlorides and (chloride/resistivity) sensors were embedded in different depths of the concrete specimens. The cover thickness in the referred

specimens was 25 mm; more details about the concrete composition and reinforcement detail are reported in the associated reference. A perforated Cr-Ni-steel plate was used as anode. The anode embedded in two layer of 1 cm thick plastic foam, and a Plexiglass sheet was used in order to firm the contact of anode system with the concrete surface. Tap water was used as electrolyte by dropping continuously on the sponge layers through a sprinkling hose. An intermittent ECE treatment was applied with current density 2 A/m^2 by the steel surface. As shown in (Figure 8 and Figure 9), the ECE treatment was most effective in the beginning of the ECE process, and after about 5 days the efficiency dropped considerably. The currents switched off for 12 days after one week of continuous treatment. As shown in the referred figures, the release of bound chlorides occurred in the first 2 days of the current-off treatment, and after that no significant changes happened to the free chloride contents. The author accomplished the intermittent ECE treatment in three phases. The total charge used in this work was 860 A.h/m^2 by the steel surface. By this treatment, (63% and 68.9%) of chlorides are removed from the concrete for the specimen with (w/c 0.5 and w/c 0.6) respectively. There were no significant negative impacts of the method on the concrete after the treatment. Only a slight increase of porosity of the concrete in the vicinity of reinforcement and the pore sizes became smaller during the treatment. Thereby, the loss of bond between the concrete and reinforcement was neglishable comparing to the high bond strength that already was gained by the ribbing in the reinforcing bars.

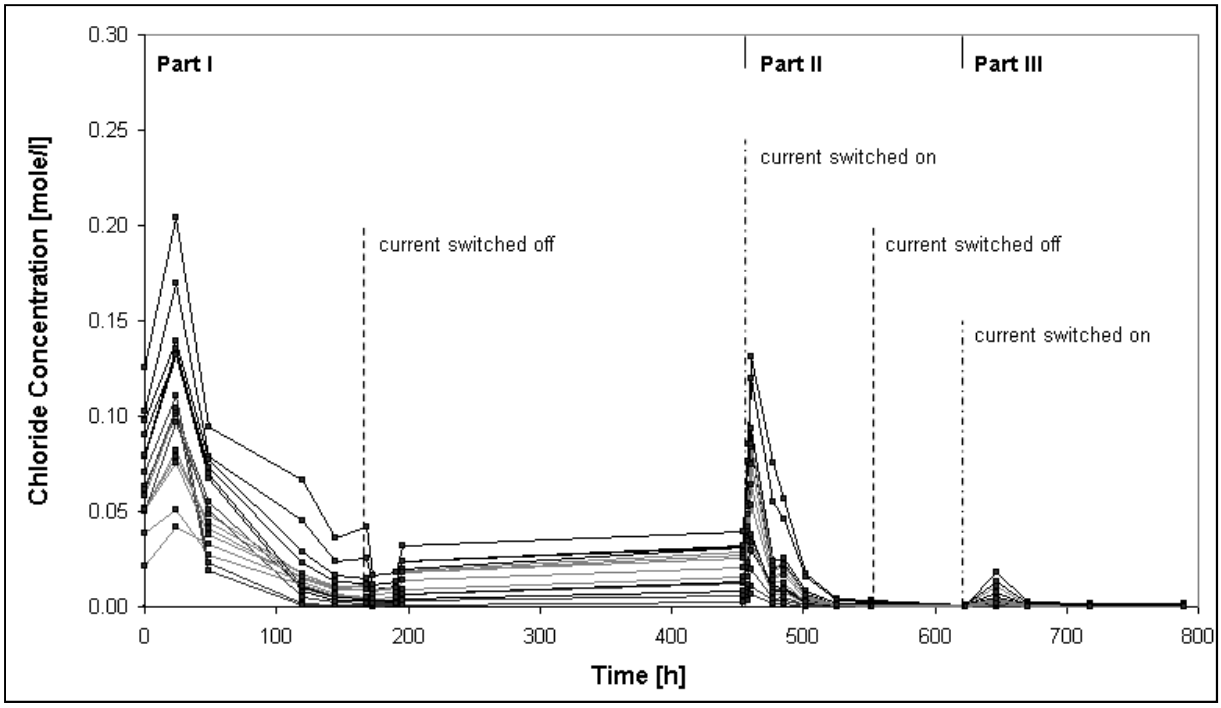

Figure 8: Chloride concentrations during ECE for the specimen with w/c ratio 0.5, (Part I–III)[7].

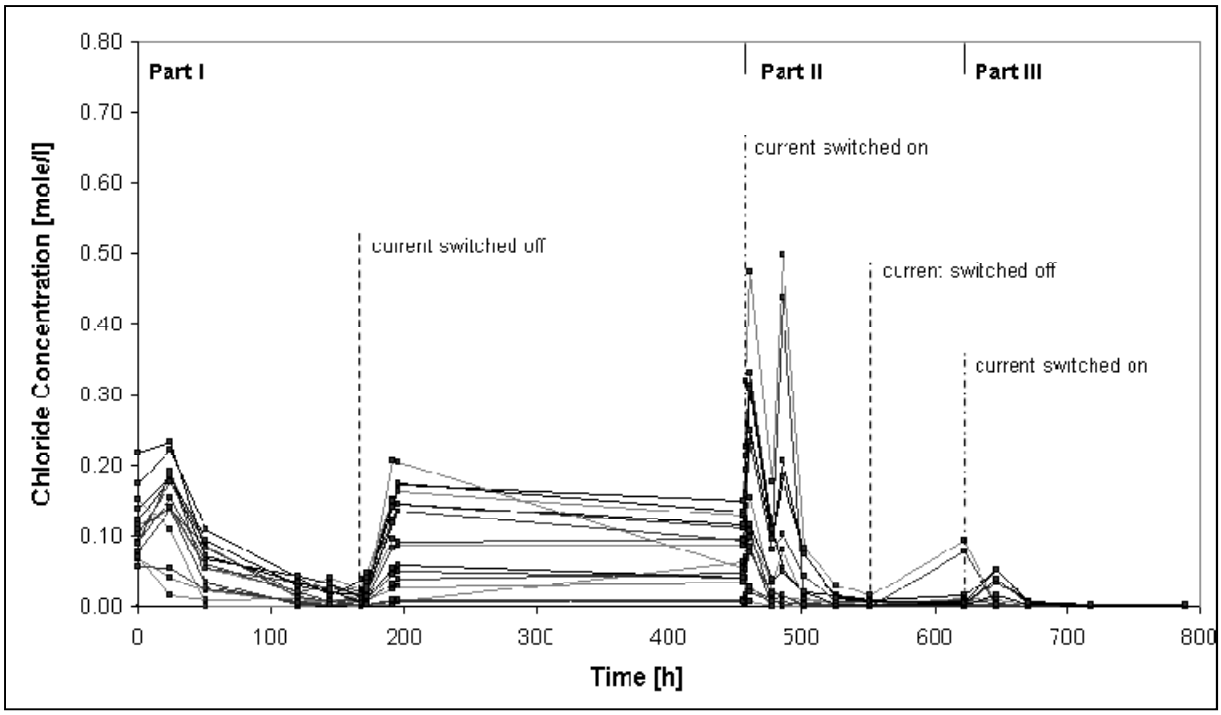

Figure 9: Chloride concentrations during ECE for the specimen with w/c ratio 0.6, (Part I–III)[7].

Fajardo, G. *et al.* [59] used an intermittent current in their ECE research in order to study the efficiency of the intermittent ECE treatment in comparison with the continuous ECE treatment. In that research, cylindrical concrete specimens, with 50 and 110 mm diameters, were used. Both types of the specimens were with length 110 mm, and steel rods with diameter 10 mm were cleaned chemically and centrally embedded into each specimen. An ordinary Portland cement was used in that work with w/c ratio (0.6). The specimens were cured for 28 days at room temperature and 100% RH. Then chlorides was allowed to penetrate the specimens by subjecting them to an artificial sea-water over a period of a 300 days with cycles of three days immersing and four days drying at 40° C. Afterwards, the electrochemical chloride extraction was applied on sixteen specimens placed in PVC containers where titanium mesh anodes were been fixed on their surfaces in each container. The specimens were partially immersed with distilled water as an anolyte. A constant current of 1 A/m^2 by steel surface was applied for 90 days in two application techniques: one with continuous current over the whole period of the treatment, and the other with intermitted current of 5 days on followed by 2 days off in repeated cycles over the mentioned treatment's period. In the intermitted current case, the anolyte was renewed each time before starting the current. In addition, specimens with current-free are also placed in anolyte as reference specimens (these specimens are referred with "0A" or "control" in the associated figures). The authors observed less efficiency of ECE treatment in the specimens with large cover thickness. The percentage reduction of the chloride contents at the steel surface was 75% for specimens with 20 mm cover thickness, and 30% for the specimens with 50 mm cover thickness (Figure 10 , Figure 11 and Figure 12). Furthermore, an accumulation of chlorides

were observed between depths 16mm to 32 mm in the specimens with cover thickness 50 mm. The authors didn't observe any influence of the intermittent treatment on the global efficiency of the technique as shown in (Figure 12). The polarization of steel remained effective during the interruption of current contradictorily to the expected ionic rebalancing.

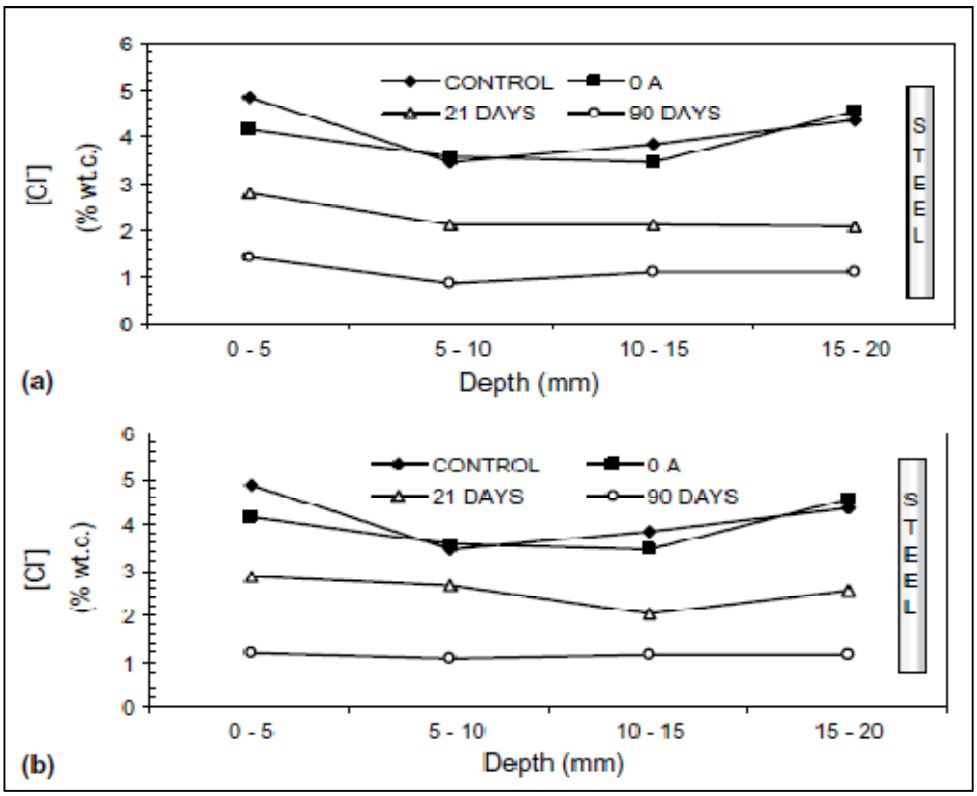

Figure 10: Chloride concentration versus cover depth for 20 mm of cover depth: (a) no renewal of anolyte, and (b) with interruption and renewal of anolyte[59].

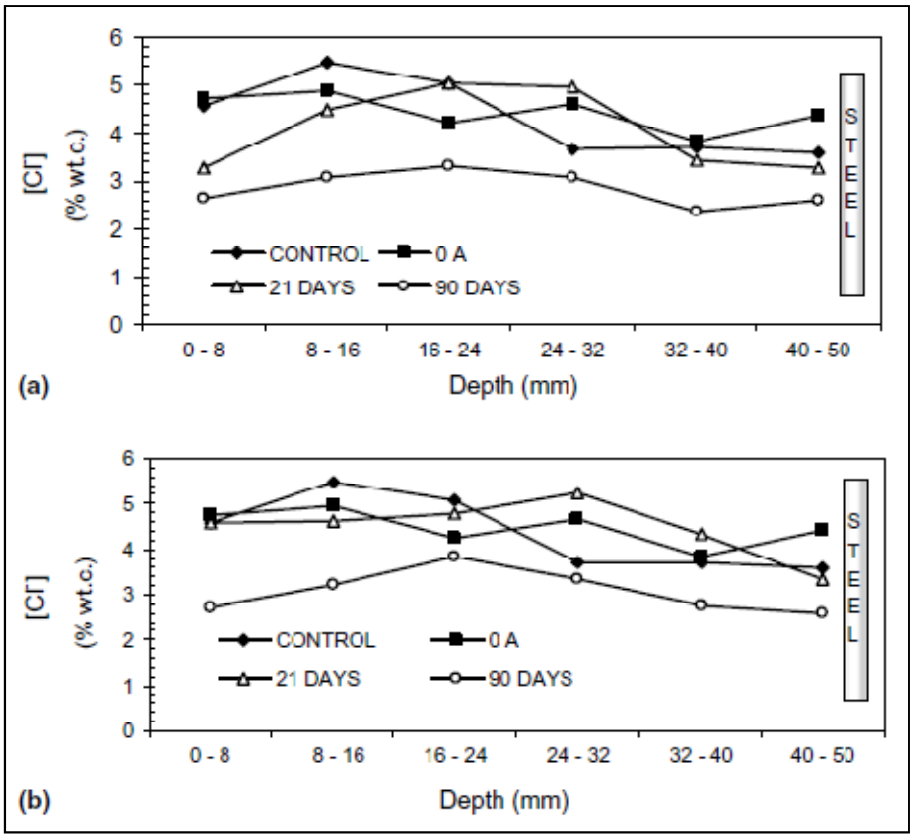

Figure 11: Chloride concentration versus cover depth for 50 mm of cover depth: (a) no renewal of anolyte and(b) with interruption and renewal of anolyte.

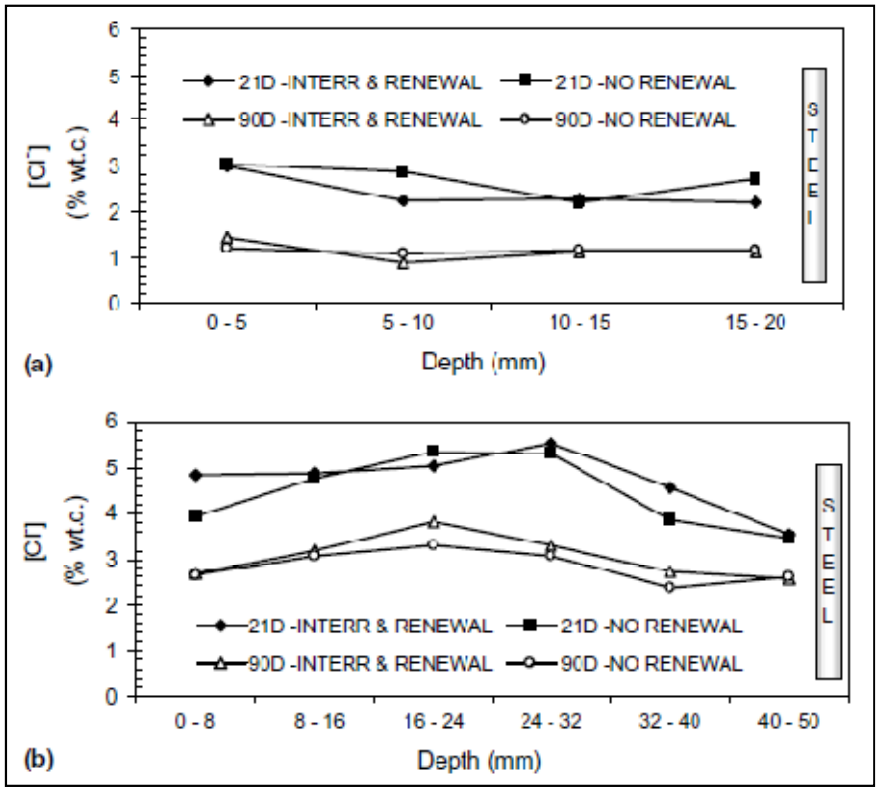

Figure 12: Comparison for 21 and 90 days, different treatments: (a) 20 mm cover depth and (b) 50 mm cover depth (INTERR & RENEWAL = with interruption of current and renewal of anolyte, NO RENEWAL = without interruption and no renewal of anolyte)[59].

Fajardo, G. *et al.* [59], studied also the movement and concentration's distribution of alkali ions in the treated specimens. The concentration of Na^+ ions, at the vicinity of the reinforcement, was increased with 40 % and 20% for the specimens with cover thicknesses 50 mm and 20 mm respectively, and the authors explained that by the higher initial chloride concentration in the 50 mm cover specimens, which also have more quantity of pore solution that normally include a lot of Na^+ ions. While the concentration of the K^+ ions in the same area was increased with 42% and 30% for the specimens with cover depth 20 mm and 50 mm respectively (Figure 13). The increasing percentage was almost similar for specimens with 20 mm cover in both (Na^+ and K^+) states; although the quantity of K^+ ions in the concrete is not high relating to Na^+ ions. That is, as authors reported, due to conductivity of the concrete, which it depends on the velocity and the concentration of the ions that were present in the pore solution. Since, in this case, the initial K^+ ions in the concrete were low, then the velocity, which depends on the cover thickness, was the dominant factor for ion movements. The authors concluded that the K^+ ions moves more quickly towards the reinforcement than the other cations that they analyzed, and the different alternatives that were been used in their work, regarding the interruption and continuity of the current, did not influence the total efficiency of the technique. The chlorides removed from the concrete specimens with rates 30% (5 cm cover) and 75% (2 cm cover).

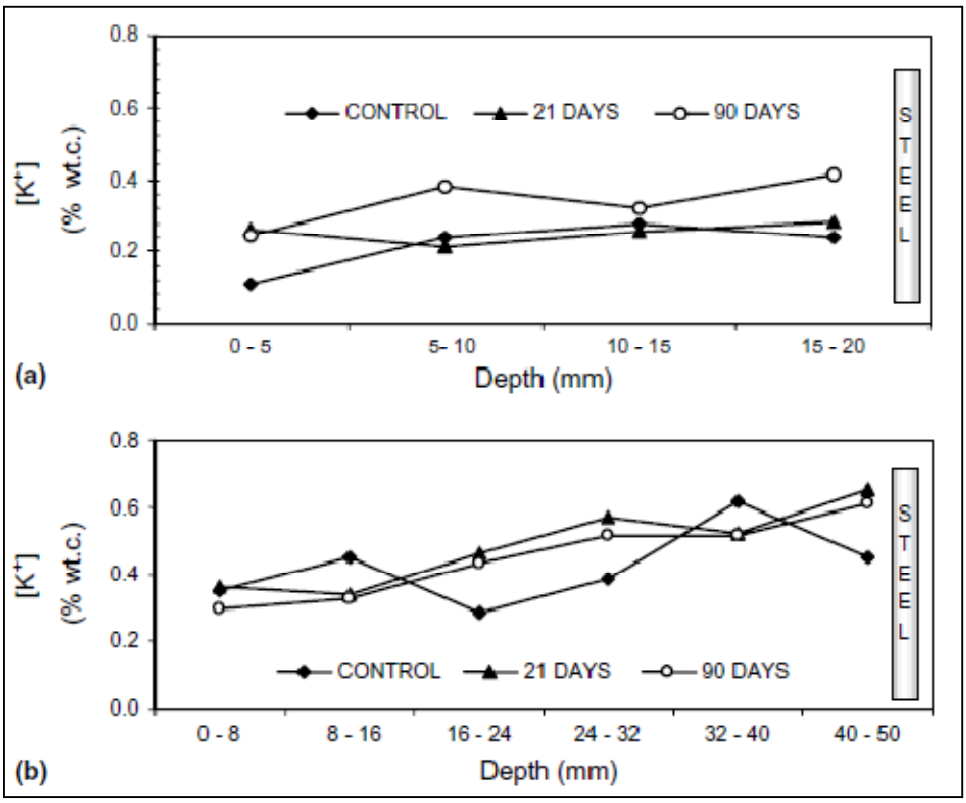

Figure 13: Concentration of K_+ as a function of the cover depth: (a) 20 mm cover depth and (b) 50 mm cover depth[59].

Another investigation in Japan, carried out by UEDA TAKAO *et al* [12], studied the influence of ECE treatment on prestressed concrete structures. The authors observed more severe hydrogen embrittlement behavior in the specimens that treated at current density of 5 A/m^2 by steel surface than those treated with current density of 10 or 15 A/m^2.

UEDA TAKAO *et al*, in another work [60], investigated the influence of the intermitted ECE treatment on hydrogen embrittlement in prestressed concretes. The authors reported that treatments with continuous current more than 2 weeks accuse evolution the diffusible hydrogen that can be absorbed into the steel bars.

The efficiency of ECE to extract chlorides depends on the applied current i.e. higher current density leads to more transport of ions. It is not recommended to apply a very high current density as that will cause dramatic consequences on the concrete and the reinforcement. The current density is usually kept in range 1 to 2 A/m^2 by the steel surface. since the potential is related with the current, values above 40 V_{DC} are undesirable due to subsequent negative impacts on the concrete[26].

Finally, basing on these researches, it can be deduced that a current density in range 1-2 (A/m^2) of steel surface is adequate to avoid any considerable reverse impacts on the concrete generally, and an intermittent ECE treatment should enhance the efficiency of the chloride extraction with current-on duration less than 2 weeks followed by a period of current-off not more than 2 days. The duration less than 2 weeks of current-on is still questionable and requires further studies in order to find most efficient procedure of ECE treatment. Therefore, this work was planned in order to go some steps forward in that way.

8-Efficiency of ECE

The total charge passed through the concrete is the dominant factor of the ECEs efficiency. In an electric field, the charged ions move by migration along the current flow lines with various velocities depending on the strength of the electric field and the charge of the ions. During the ECE, large amounts of negatively charged chloride ions are flowed by the current toward the anode, and the concentration of the chlorides in the pore solution decreases over time. Subsequently, the concentration of OH^- increases at the reinforcement. Thus, at later stages of ECE treatment, the efficiency decreases as the current carry less chloride ions and mainly transport the OH^- ions[7, 32]. Since the chloride removal efficiency is most effective in the areas with high concentration of chlorides. This will give advantageous consequence by distributing the chloride concentrations evenly within the concrete. As shown in the (Figure 14) the acting force on the ions is stronger for the shorter field lines, i.e. the efficiency of chloride removal is highest in areas with shortest distance between the reinforcing bars (the cathode) and the anode, while the efficiency is lower in the areas between reinforcement. However, the electric field in the concrete can't be homogeneous due to the geometry of the reinforcement and instability of the temporarily installed anode. In brief, the treatment efficiency depends on the initial concentration of chlorides, distribution of chlorides in the concrete and the electric field[7]. As well as, there are some secondary parameters like w/c ratio and adequate periods of current on/off that may contribute in improving the efficiency of the ECE treatment. These secondary parameters were investigated in this work in order to get more efficient procedure than those generally used in previous related works.

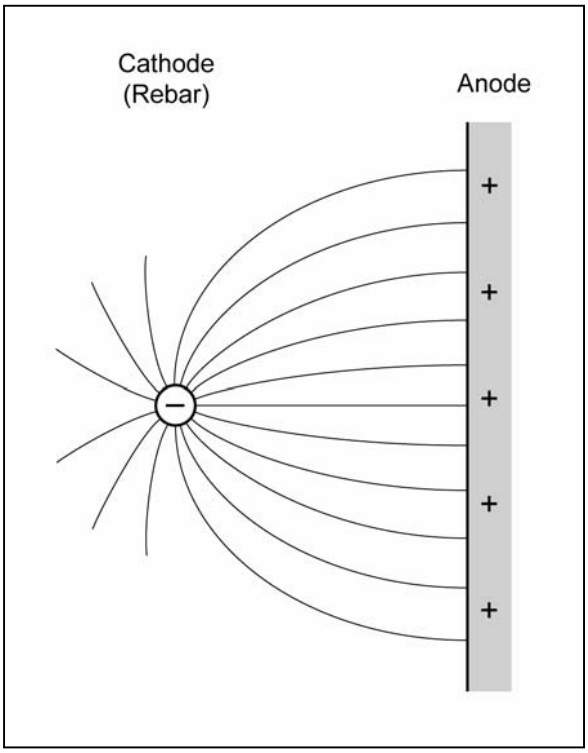

Figure 14: Streamlines in a homogeneous concrete[7].

9-Drawbacks of ECE Treatment

During ECE process, many of side effects may occur in various rates depending on the duration of the treatment and the current density. These side effects are:

- Changes in the cement matrix.
- Damage of the concrete surface.
- Possible alkali-silica reaction (ASR).
- Reduced bond strength between steel and concrete.
- Hydrogen embrittlement.

9.1-Changes in the cement matrix

In the past, it was known that the migration of ions in concrete takes place through its pores, but in fact the constituents of cement are not electro-neutral. They carry charge and are involved in the migration process[26]. The circulation of the applied current, between the external anode and the cathode (reinforcement), not only affect the chloride ions (Cl^-), it also repels hydroxide ions (OH^-) toward the anode. In contrast, positively charged ions like sodium (Na^+), potassium (K^+) and calcium (Ca^{2+}) will be moved toward the cathode and accumulate in the vicinity of reinforcement. Many of cement constituents contains these ions, and thereby, the structure of the cement matrix will be changed during ECE. These changes will don't affect the strength of materials as *Bertolini, et. al*. [61] showed in the results of Vickers hardness test of treated and non-treated concretes.

9.2-Damages of the concrete surface

As result of electrode reactions, the electrolyte close to the anode will turn acidic in the ECE treatment. The concrete is not an acid resistant material, and thereby, the exposed concrete surface will be etched and weakened during the ECE. This issue can be avoided by adding a buffer such as lithium borate to the electrolyte, but in same time, this will reduce the efficiency of extraction due to distributing the charge over more ions than in case of using pure tap water electrolyte[62]. The acidification, as reported, is not dangerous, and occurs shortly after starting ECE treatment. This will not affect the structure's integrity. It can be retarded or completely suppressed by constant exchanging the electrolyte (i.e. running water). When the concrete etches, it's color changes from grey to red, and the pore structure becomes open. It can easily be removed and replaced by suitable coating material[26].

In this work no surface damage noticed in the first weeks, but after 5 weeks of ECE treatment, the outer edges of the specimens adjacent to the electrolyte were crumbled during drilling the specimens for collecting samples. Such damages didn't prompt in the previous sample-taking processes. These damages were insignificant and it can be related to acidification of the concrete surface. The amount of electrolyte solution that used in this work was relatively large comparing with the concrete surface, where about 12 liter of electrolyte solution used for only concrete surface (250x350 mm^2). In addition the pH level of the electrolyte solution was regularly monitored and maintained over 12. Therefore, no considerable surface acidification was observed in this work.

9.3-Alkali-Silica reaction

In ECE treatment, the alkali ions (which are positively charged) accumulate around the cathode (i.e. the reinforcement), where the hydroxyl ions are generated. The alkali-silica reaction can take place if the alkali concentration exceeded 3 kg/m^3 and in presence of reactive aggregates. The alkali-silica reaction leads to form an expansive ettringite gel that causes cracking with typical map pattern[7, 63]. In nowadays this side effect considered being less important in many countries due to standards that limit the use of reactive aggregates and therefore this topic is not discussed with details in this work.

9.4-Reduced bond strength between steel and concrete

Due to ions exchange that occurs during the ECE treatment; the cement matrix in the vicinity of reinforcement will be weakened, and subsequently the bond between steel and concrete will be reduced. This effect increases with increase of the current density or treatment duration, and it is very critical in the concrete structures that constructed in the fifth decade of 19th century, where plain bars are used as reinforcement. The bond in plain bars, unlike ribbed bars, depends only on the strength of reaction products between the reinforcement and the concrete[26].

Vennesland *et al* [32], in a related investigation, used concrete prisms with w/c ratio 0.7 and containing 2% of chlorides by cement weight. The applied currents were 1.6, 4 and 8 A/m^2 by steel surface, in treatment durations of 7, 4, 26 and 56 days. The results of pull-out test showed significant reduction in the bond stress within the charge range 600-5000 Ah/m^2 of steel surface, and the bond stress increased extremely at higher charges. As reported, the bond stress continued to decrease at the period between 7 and 17 days of treatment, and afterwards increased to the level of the reference specimens after 28 days.

In another investigation carried out by Buenfeld *et al* [64], explained the temporary reduction of bond strength by disappearing the corrosion products in the vicinity of the reinforcement,

and this reduction of strength doesn't fall below the design strength. The authors expected worse consequences in case of premixed chloride concretes where the corrosion starts at early stages and leads to creeping away the surrounding concrete. Since the concrete is not a flexible material to creep back, then a permanent reduction in the bond strength may occur.

Related investigation made in 2003 by Chang[65], where a pull-out test performed on cylindrical concrete specimens with w/c ratio 0.66, and a longitudinal reinforcing bar. 3% chlorides were premixed in the specimens whilst some of them prepared without chlorides to be used as references. The specimens cured in lime-saturated water for 28 days, afterwards ECE applied on them for periods 1 to 6 weeks with constant voltages (5, 10, 20, 30 V). In addition; two constant current densities (1.88 and 18.8 A/m^2) and specimens without ECE treatment were used for comparison. The results showed an increase of the bond strength in the chloride contaminated specimens that left without electrochemical treatment. The reason explained by the expansive corrosion products which leads to prestress the concrete around the corroded reinforcing bars[23]. Whilst the results for specimens, that treated at considerably high current density (18.8 A/m^2), showed 40% loss in bond after two weeks and 50% after six weeks. Basing on these results, the author concluded that the loss of bond strength occurs primarily in the first two weeks. The specimens that treated at low current density (1.88 A/m^2) showed an insignificant loss of bond strength during the period of treatment.

Another investigation carried out by Takaw Ueda *et al* [66], where the chlorides premixed with the concrete by rates (0, 4, 6, 8, and 10) $kg/m^3$of concrete. These amounts of chlorides added as a replacement for equivalent weight of fine aggregates. The specimens cured in moist air for 28 days in polyethylene bags. The ECE treatment applied with intermittent direct current densities (2.5 and 5 A/m^2 by steel surface) and various power-on intervals. The investigation consisted of chemical analysis, half-cell potential measurement, micro-hardness distribution measurements, pull-out test, and flexural test of reinforced concrete beams in order to examine the interface between concrete and reinforcing steel. After 8 weeks of treatment with both 2.5 A/m^2 (total charge 3360 $A.h/m^2$) and 5 A/m^2 (total charge 6720 $A.h/m^2$) for the specimens with premixed 8 kg/m^3 chloride. The micro-hardness test showed forming a soft layer around the steel bar in both of the treating states, but the range of the softened cement was wider in the specimen with current density 5 A/m^2 due to larger current density. The authors pointed to this phenomenon as reason for degrading the bond strength between concrete and steel bar, and the cause of cement paste softening is referred to transforming silicates in the C-S-H of cement paste into soluble silicates with concentrations of NaOH and KOH which brought with the alkali products that accumulated around the reinforcement during passing the electric current. The result of the pull-out test was consistent with the author's consideration about softening the adjacent cement to the reinforcing bars, where results showed reduction of the bond strength in the treated specimens comparing with non-treated specimens. The authors concluded that the amount of accumulated alkali around the reinforcement depends on the amount of the premixed chlorides, duration of the treatment and the current density applied in the ECE treatment.

9.5-Hydrogen embrittlement

Applying high voltages during the ECE treatment leads to generation of nascent hydrogen at the cathode [23]. Then hydrogen embrittlement occurs if the generated hydrogen in the (Eq.17) is absorbed into the reinforcing steel bars, and thereby the fracture toughness of the steel will be reduced[35, 48]. Producing hydrogen gas (Eq.18) leads to increase the local pressure and subsequently promote cracking in the concrete [35, 48, 67].

$$H_2O + e^- \rightarrow H^* + OH^- \qquad (17)$$

Where (H^*) is adsorbed hydrogen.

$$H^* + H^* \rightarrow H_2 \qquad (18)$$

Latterly, many investigations reported that if the current density limited to 1A/m^2 by steel surface or less, the hydrogen evolution will not adversely affect the structure [23, 49, 68]. Furthermore the high-strength steel is more susceptible to hydrogen embrittlement than the lower strength steel. This feature makes the ECE undesirable for prestressed concrete structures where the steel is already prestressed up to 75 % of its ultimate tensile strength during the prestressing process, and will be liable to catastrophic failure [23, 68, 69]. It is possible to control the problems of hydrogen embrittlement and evolution of hydrogen gas by limiting the potential of the steel below the hydrogen's evolution potential[23].

An investigation in Japan, carried out by *UEDA TAKAO et al,* studied the effect of desalination (ECE) on prestressed concrete. The experiment consisted of specimens with dimensions (150X150X400) mm of concrete prisms with w/c ratio 0.39 and prestressing steel bars (Ø13 mm) at the center of specimen's cross section. The prestressing force was 50 and 60 % of tensile strength, sustained by a steel mold and the prestressing force wasn't introduced to the concrete to avoid any stress loss in the steel due to creep and drying shrinkage in the concrete. The chlorides in this investigation were premixed with rate (8 kg/m^3) of concrete, and the prestressing steel bars were intentionally notched at the center point of each bar in depths (0.5, 1, 1.5, and 2 mm), and salt water was sprayed to the notch part for accelerating the corrosion. Then concrete was cast around the prestressed bars and cured in 4 weeks before applying current density of 5 A/m^2 by steel surface for periods of (1, 2, 4, 6, and 8) weeks. One direction of current flow was maintained by insulating the sides with epoxy resin. After ECE treatment, the prestressing bars were taken out for conduction slow strain rate tensile tests and hydrogen thermal analysis by using a chromatograph gas. The authors concluded that applying intermitted treatment with continuous current less than 2 weeks is adequate to avoid the evolution of diffusible hydrogen. The authors didn't found any effect of notched prestressed bars on the ECE's efficiency comparing with the results of normal reinforced concrete, and there were no effects of the notch depth on the degree of hydrogen embrittlement, but the depths itself had greater negative influence than the hydrogen embrittlement[60].

The hydrogen embrittlement, as mentioned earlier, is most concerned in prestressed concretes where steels with high strength are used. There are no documents on adverse impacts of the ECE treatment on ordinary reinforced concretes. *Bennett et al* [8] found only a modest loss in ductility for ordinary reinforcement steel which had ability to recover in a short time after the end of treatment.

In this work, no prestressing concrete were used. So the examination of hydrogen evolution and hydrogen embrittlement is not in the plan.

10-Experimental Scheme

In order to investigate the influence of different parameters on the ECE's efficiency, 3% by the cement weight of chlorides premixed with the mortar in form of sodium chloride. This has undesirable effect on hydration process and causes altered C-S-H hydration products[70], but due to the limited time for this work; it was impossible to obtain contaminated specimens with external chloride sources.

10.1-The Specimens

In this work eight prisms of reinforced concrete specimens, with dimensions (350x250x85) mm, were used. Four specimens were with w/c ratio 0.4 (S-0.4), and the other four specimens were with w/c ratio 0.5 (S-0.5). Standard Portland cement and non-reactive aggregates were used. Sika ViscoCrete FB-2 was used as plasticizer additive for enhancing the mixing process. Detail rates of the concrete compositions are presented in (Table 2).

Specimens	Water	Cement	Aggregate			Super-plasticizer
			0-8mm	8-11mm	11-16mm	
S-0.4	161	402.5	1027.1	387.4	387.4	1.6
S-0.5	176.7	353.4	1027.1	387.4	387.4	1.4

Table 2: the concrete compositions in (Kg/m^3).

In addition, chlorides are intentionally premixed with rate 3% of the cement weight which is quite enough to cause severe chloride corrosion of steel. The chlorides added as sodium chloride salt (NaCl), and to secure adding the mentioned rate of pure chloride content into the concrete mixture; following calculation in the (Table 3) are prepared in order to determine the equivalent amount of NaCl that gives aimed rate of chlorides in both of S-0.4 and S-0.5.

Cl- density (gr/mol)[1]	35.45
Na+ density (gr/mol)[2]	22.99
Total density of NaCl (gr/mol)	58.44
Cl % (Cl/NaCl)	60.66
Required NaCl (kg/m^3) for S-0.4	$(0.03 \times 402.5 \div 0.6066) = 19.90$
Required NaCl (kg/m^3) for S-0.5	$(0.03 \times 353.4 \div 0.6066) = 17.48$

Table 3: Calculating equivalent rate of NaCl that secure 3% Cl in the specimens.

Same amount of reinforcement have been used for all the specimens. In each specimen, the reinforcement accomplished by distributing 10 bars with diameter 8mm in two crossed layers and 50 mm spacing center to center between the bars of same layer to form a quadratic net as shown in the (Figure 15). The upper layer consist of 6 bars (4bars with length 21mm and 2 bars with length 25 mm that stuck out about 20mm from the concrete and the outer cross section was bored for enhancing the cathode connection).While the lower layer consist of 4 bars with length of 31mm. The crossing points of the bars welded in order to ensure the conductivity over all the reinforcing net. A normal construction steel type (B500NC)[3] was used. It is planned to apply the ECE treatment on one surface of the specimen. Therefore, the main concrete cover, that will be subjected to the ECE treatment, was 50 mm (as it is common in practice), while the concrete cover on the opposite site, was 19 mm which is enough to cover and isolate the reinforcement from the external environment during the treatment.

The specimens were cast in wooden forms, as shown in (Photo 1,page 65); then stored in a room maintained at 20^oC and 100% of relative humidity for one month in order to gain enough compressive strength before starting with the ECE process.

[1],[2]: Obtained from the product's label.

[3] : According to the Norwegian standard NS 3576.

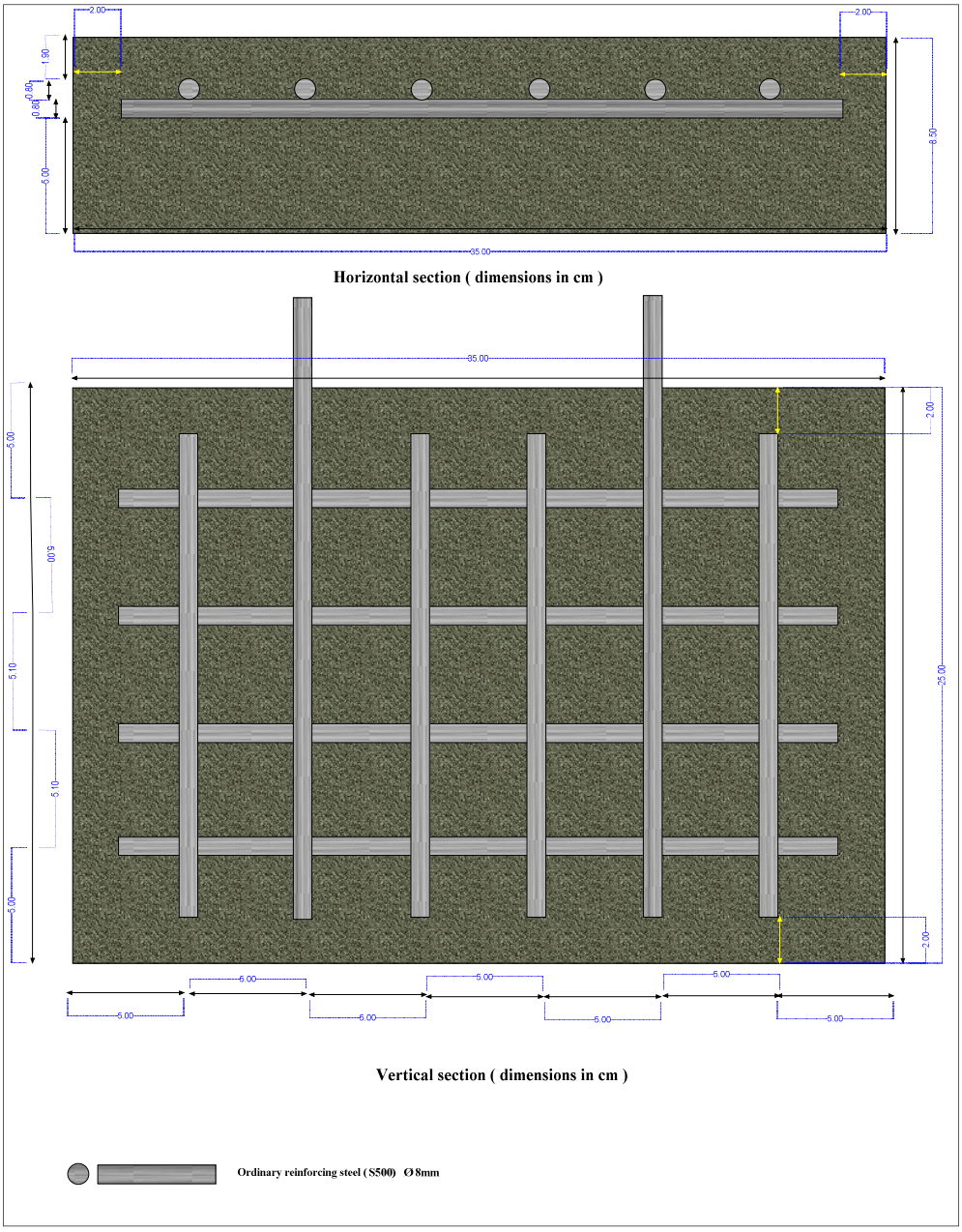

Figure 15: Vertical and horizontal sections of the specimens.

10.2-Electrochemical Chloride Extraction

There are different ways for applying ECE treatment regarding the selection of the anode material, the electrolyte media, and details about the current connection. In order to starts with ECE treatment in this work, the following setup was chosen:

10.2.1-Setup for the Electrochemical Treatment

As mentioned earlier in (section 7, page 17), the electrochemical chloride extraction technique requires an external anode in an electrolyte, and a DC-source. In this work, each specimen was treated individually in PVC-containers with dimensions (56x36x14) mm. Titanium-net (or -mesh) was used as anode metal, and installed inside the PVC- containers between two crossed layers of plexiglass spacers as shown in (Figure 16 and Photo 5). Then, the specimens placed in the PVC-containers and electrolyte of hydroxide calcium solution $Ca(OH)_2$ added into the containers up to level where about 10 mm of the specimens were immersed in order to secure the electrical conductivity of the system. A liquid electrolyte gives better conductivity between the anode and the concrete surface than other electrolytes like wet shredded papers where gaps between the shredded papers and concrete surface are likely to happen during the ECE treatment; but liquid electrolytes can't be used on sloped or vertical surfaces. More details and photos about the set-up of ECE are presented in the appendix (Section 15.2, page 68).

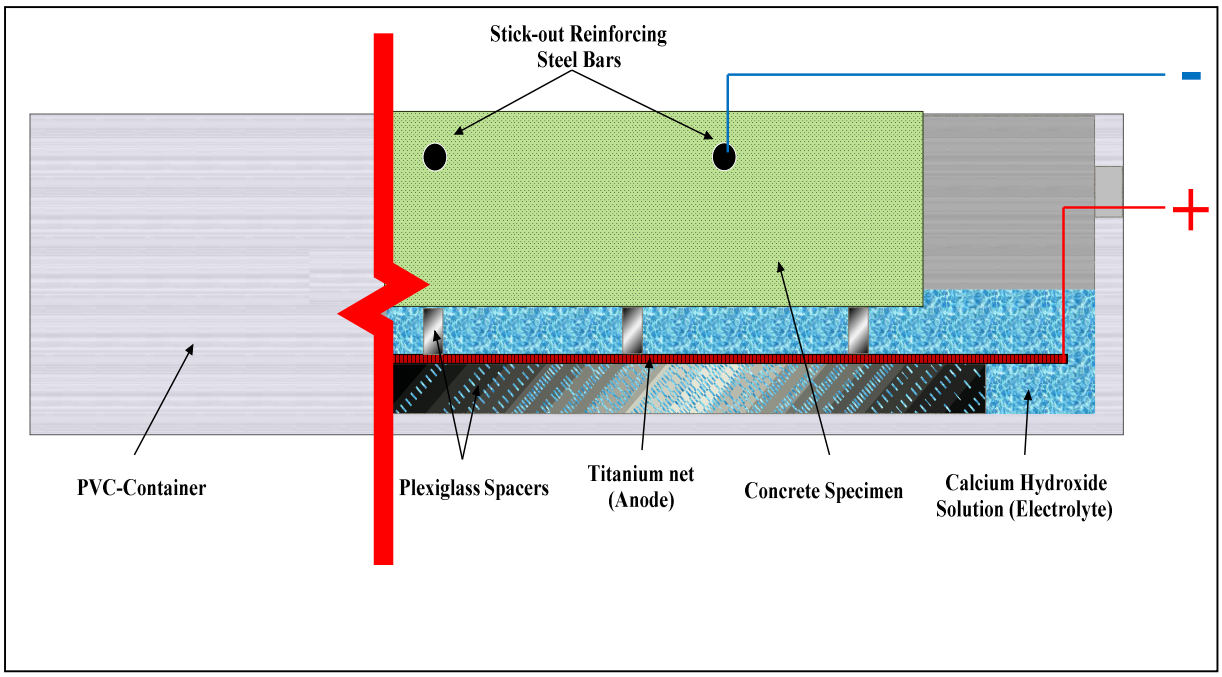

Figure 16: The set-up of the ECE treatment.

For starting the ECE treatment on the 8 specimens, four laboratory DC-suppliers (with a voltage range of 0-30 V and a current range of 0-3.2 A) were used. Every two specimens were connected serially to a DC-supplier as depicted in the (Figure 17).

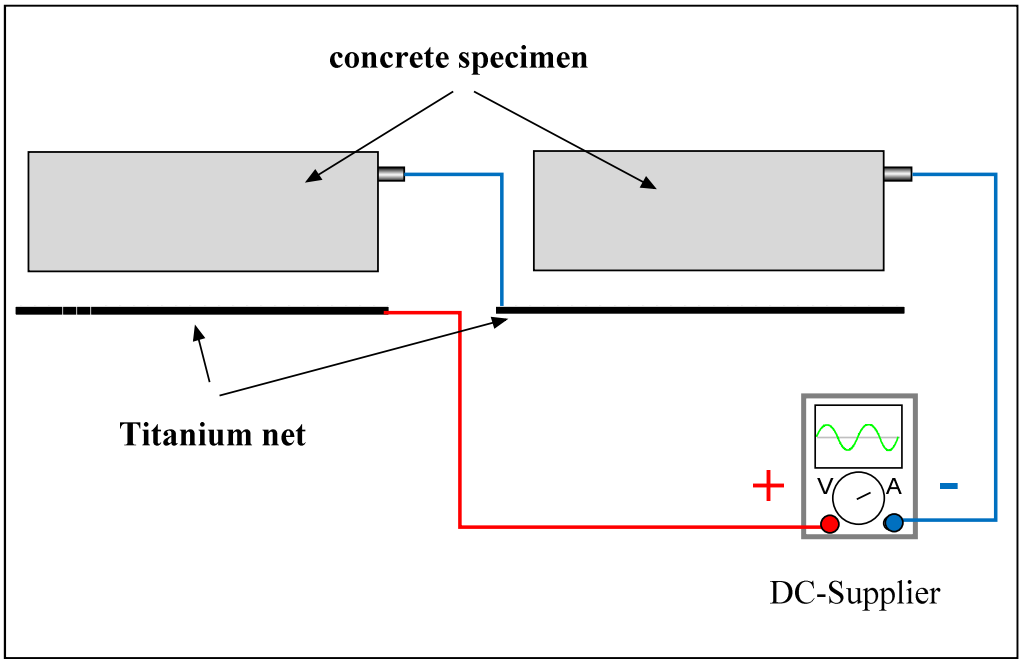

Figure 17: Connecting two specimens serially to the DC-supplier.

10.2.2-Applying the ECE treatment

The main aim of this work is to study the efficiency of ECE treatment due to different parameters like current density, current interruption, and w/c ratio. The current densities that used in this work were (1.0 and 0.7) A/m^2 by steel surface, which are within the safe range that don't result in severe reverse impacts on the concrete and steel bars as mentioned earlier in (section 7.2 page 20, section 9.4 page 31, and section 9.5 page 32). Therefore, no side effects of the ECE treatment on the reinforced concrete are discussed in this work.

Basing on the researches reported in the (section 7.2, page 20), it can be deduced that the ECE is most effective where the concentration of free chlorides in the pore solution is highest, and the treatment will be less effective after prolonging the continuous current-on treatment more than two weeks . As showed in the (Figure 9 from reference[7]), there are significant variation in the efficiency of chloride extraction even within two weeks, especially in the second and third intervals of treatment in the referred work. Therefore, in order to study the efficiency of ECE regarding the period of current-on treatment, durations of (5 and 12) days had been chosen for this work.

The periods of current-on were interrupted by intervals of current-off treatment in order to release the bound chlorides by the theory of rebalancing the chloride concentrations. As it is obvious in (Figure 9), this equilibrium completed almost within the first 2 days after the DC-power was switched off and after that the progress of releasing bound chlorides was

insignificant. Thus, periods of 2 day current-off is decided for all types of treatment that used in this work. The schematic procedure of applying ECE treatment on the specimens is presented in (Table 4).

Specimens	W/C	Current-density (A/m^2) by steel surface	Current intervals	
			Duration of current on (days)	Duration of current-off (days)
Specimen 1 (S 1)	0.5	0.7	12	2
Specimen 2 (S 2)	0.4	0.7	12	2
Specimen 3 (S 3)	0.5	1.0	12	2
Specimen 4 (S 4)	0.4	1.0	12	2
Specimen 5 (S 5)	0.5	0.7	5	2
Specimen 6 (S 6)	0.4	0.7	5	2
Specimen 7 (S 7)	0.5	1.0	5	2
Specimen 8 (S 8)	0.4	1.0	5	2

Table 4: Schedule of the different types of intermittent ECE treatment that used in this work.

In order to secure passing the planned current density through the specimens, the DC-supplier must be adjusted to the equivalent total current. This can be obtained by multiplying the planned current density with the steel- or concrete area as showed in (Table 5). Then, the current was set by connecting a multimeter in series with the described system. The current was controlled regularly, as well as the level of electrolyte solution. The DC- suppliers that used in this work was provided with a LED indicator which lit red at good electric conductivity and lit green at corruption in the electric field. The level of electrolyte maintained at a level where about 10 mm of the specimens were immersed and thereby the conductivity between the electric poles was secured.

Steel area (m^2)	Concrete area (m^2)	Current Density (A/m^2)		Total current required at the DC-supplier	
		By steel area	By concrete area	(mA)	(V)
0.0640	0.0875	1	0.73	64.00	10
		0.7	0.51	44.80	8

Table 5: Specifications of the current density used in this ECE treatment[4].

[4] : More calculation details are presented in the appendix page 69.

11-Results

The progress of the ECE treatment was followed by measuring the chloride content (by cement weight) prior- and during the treatment every two weeks. The treating cover depth was 50 mm in all the specimens. The chloride measurements were accomplished by drilling the specimens with 16mm tip hammer-drill and powder samples of each 10 mm depth of the concrete cover were collected separately as illustrated in (Figure 18). Afterwards, the holes were refilled by a rapid repairing cement mortar in order to maintain same concrete cover thickness over the entire treating period, and samples will not be collected again from these areas again in further chloride measurements. In order to get most possible accurate results in the chloride analysis process, the samples were dried in an oven at temperature 100°C for minimum 6 hours. Presenting moisture in the samples increases the weight of the powder, and subsequently affects the chloride results. In addition, it is deduced in advanced stages of the treatment that collecting samples from one place in the specimen will don't give a good picture of the actual chloride contents in the entire specimen. That's due to locating stones in some depths result in lower chloride measurements in these depths since the aggregates normally are free of chlorides in its composition. In this work, samples until the third week of treatment were been taken from only one place. The chloride analysis of these samples showed somewhat large deviation between the results of neighboring depths. Therefore, in further sample collecting processes, it decided to take samples from two different places in each specimen. As more places you drill for collecting samples as more accurate chloride results will be, but as long as the specimens in this work were rather small, collecting samples was limited to only two places in each specimen.

As mentioned earlier in the (section 8, page 28) the ECE treatment is most effective at the areas that are located vertically under the reinforcing steel bars (the cathode) where the current field paths are shortest; therefore, the powders were collected from the areas directly under the reinforcing bars. It was easy to speculate these areas with help of the stick-out steel bars and the data of 50 mm spacing between the steel bars.

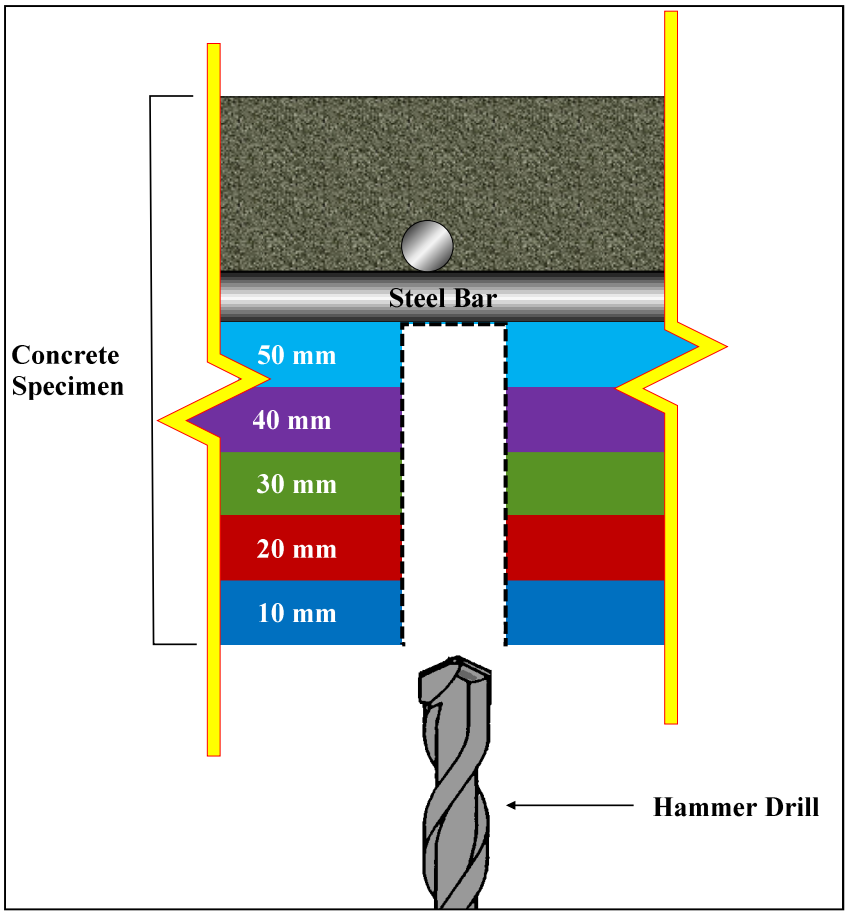

Figure 18: Illustration of collecting the powder samples from different depths in the concrete cover.

The chloride analysis test was accomplished by using (MillChlor RCD) chloride analyzing kit.

11.1-Initial chloride measurements

The initial chloride content that planned in the mixture receipt was 3% by cement weight for all the specimens, but in order to ensure that the chlorides distributed homogeneously during the mixing process, two specimens of each w/c value were been selected (S 2, S 3, S 6, and S 7), for measuring chlorides in them. Powders collected by drilling 10 mm of the upper cover (total thickness of the upper cover is about 20 mm) which is not active in the ECE treatment, and thus, no repairing was necessary as long as the reinforcing bars were still not exposed to the outer environment.

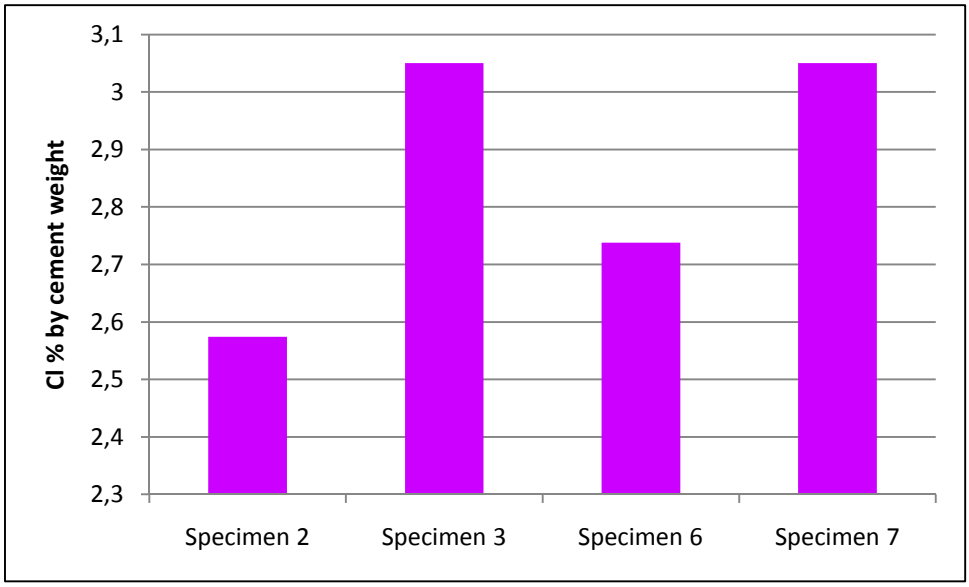

Figure 19: Chloride content in the selected specimens prior to applying ECE treatment.

The results of chloride analysis, as shown in (Figure 19), were consistent with the data in the mixture receipts as average chloride contents were about 3 % by cement weight. Lower rates of chlorides in the specimens (2 and 6) can be explained by locating stone in the depths where the powder samples are collected, and thereby the chloride results will be lower as discussed earlier.

11.2-Chloride measurements after applying ECE treatment

The chloride contents were measured in the periods of current-off treatment in order to secure passing the planned current density during the planned current-on treatment.

11.2.1-Chloride measurements after 5 days of treatment

The first measurements of chloride were for the specimens (5, 6, 7 and 8) as their current were switched off for the first time after 5 days of current-on treatment. These specimens, at that point in time, were charged with 84 Ah/m^2 by steel surface. As shown in (Figure 20) there is no significant difference between the results of chloride contents in these specimens excepting the (specimen 5) where the high chlorides at vicinity of the reinforcement was rather strange. This may explained by low current field in that spot during the ECE treatment resulted by bad contact between the concrete surface and the anode system due to evaporating the electrolyte solution to a level below the level of the concrete surface. The powder samples collected from only one place in the first three chloride measurements (i.e. until the chloride measurements of day 40 of ECE treatment), and this can't give a good picture of the actual chloride content in the whole specimens. The samples after the referred time have been collected from 2 places for each depth in the specimens and the results were considerably smother between the neighboring depths than those in the previous measurements.

An average percent of the extracted chlorides in the specimens were calculated by comparing the average chloride content of the all depths in the specimen with the initial chloride content which is (3 % by cement weight) as presented in the equations (19 and 20):

$$\textit{Average chloride content}\,(Avg.Cl) = \frac{\sum \textit{the chloride contents in the all 5 depth zones}}{5} \qquad (19)$$

$$\textit{Average percent of the extracted chlorides in the specimen} = \left(1 - \frac{Avg.Cl}{3}\right) * 100\% \qquad (20)$$

During these 5 days of treatment about 40 % of chlorides were extracted in the specimens (6, 7 and 8), while this rate was only 27 % in the (specimen 5) as shown in (Figure 21). Anyway, the results so far don't show a considerable effect of the different parameters that used in the ECE treatment for mentioned specimens.

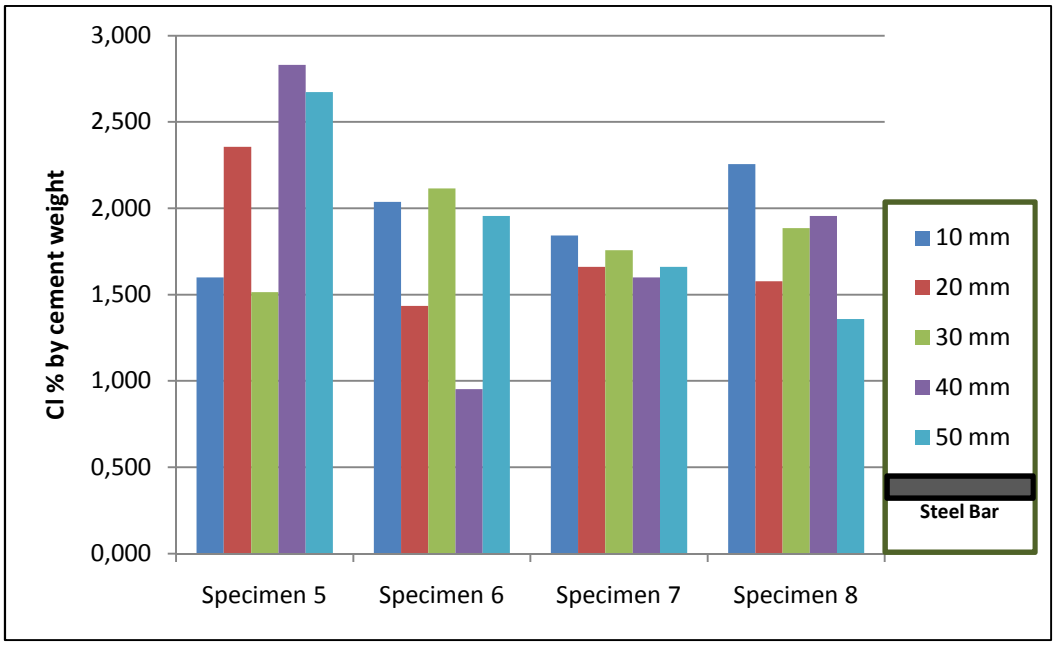

Figure 20: Chloride content in specimens (5-8) after 5 days of ECE treatment.

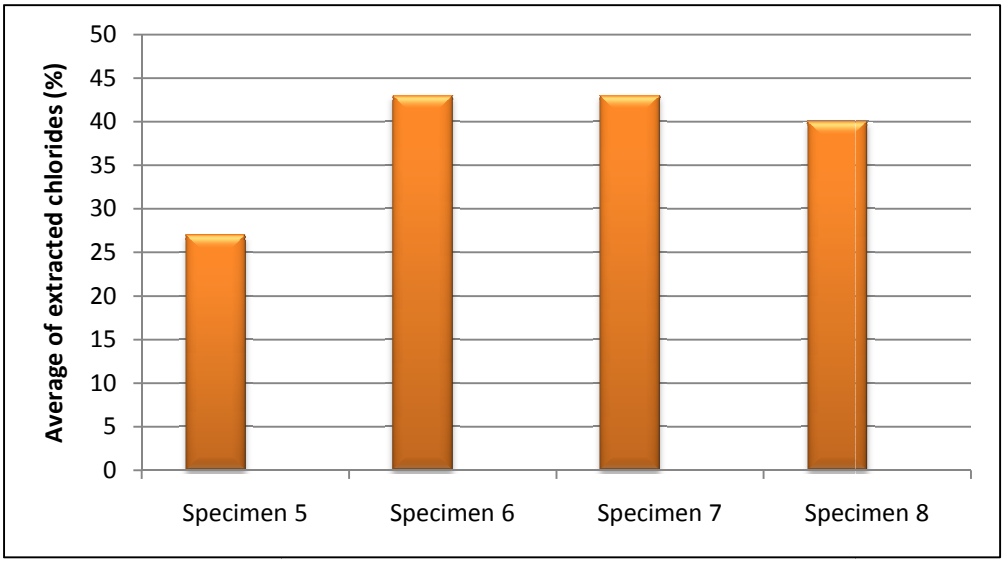

Figure 21: Average rate of the extracted chlorides in the specimens (5-8) after 5 days of ECE treatment.

11.2.2-Chloride measurements after 19 days of treatment

Another powder samples were collected from the specimens and the results were as shown in (Figure 22). At that point in time, the total charge was 252 Ah/m^2 by steel surface for specimens (1, 2, 5 and 6) and 360 Ah/m^2 by steel surface for specimens (3, 4, 7 and 8). The chlorides in the surface depths of all the specimens were generally lower than chloride contents in the other depths.

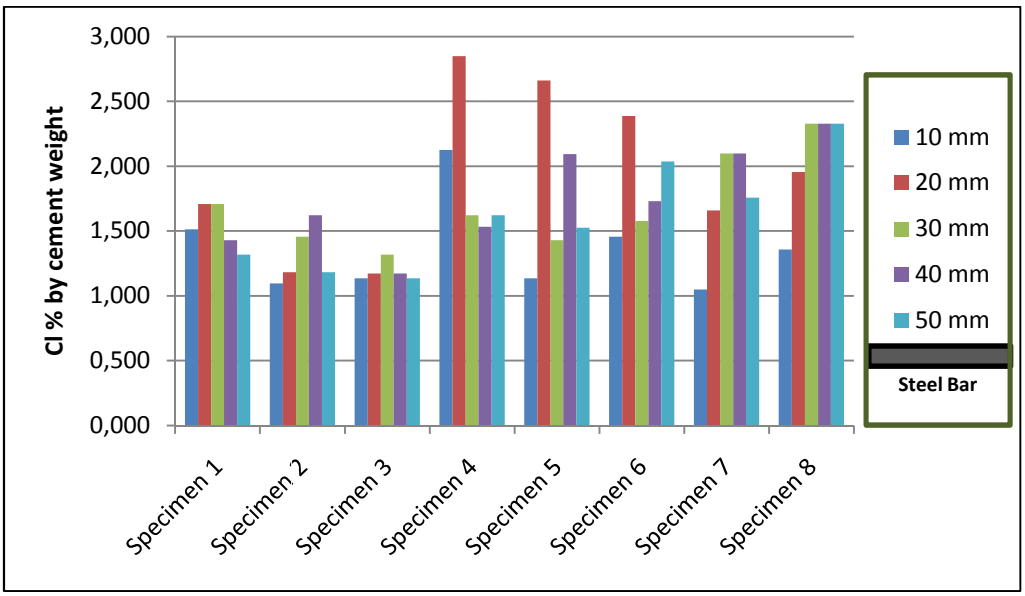

Figure 22: Chloride content in the specimens after 19 days of intermittent ECE treatment.

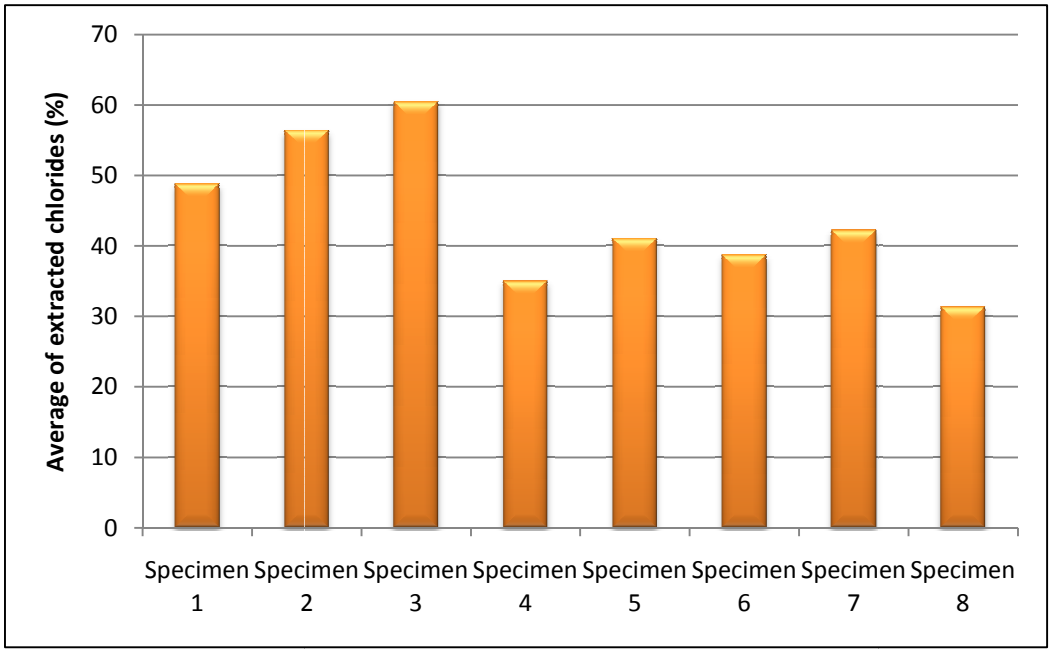

Figure 23: Average rate of the extracted chlorides in the specimens after 19 days of ECE treatment.

Furthermore, the chloride contents in the specimens that treated with 12 days current-on intervals (specimens 1, 2, 3 and 4) were lower than chloride contents in the specimens that treated with 5 days current-on intervals (specimens 5, 6, 7 and 8), and among the specimens with 12 days current-on intervals the specimen 3, which combine two other parameters (0.5 w/c ratio and 1.0 A/m^2 by steel surface current density), had lowest chloride content and about 60 % of initial chlorides were extracted at that time (Figure 23). This was consistent with theoretical facts that imply increasing the efficiency of ECE treatment with increasing the current density and the permeability (higher w/c ratio). The chloride results in specimen 4 (Figure 22) were rather strange. It supposed to be lower than what obtained, as long as the specimen 2 had lower chloride contents which has same w/c ratio as specimen 4 and treated at lower current density (0.7 A/m^2 by steel surface) than that used with the specimen 4 (1.0 A/m^2 by steel surface). In the experimenter's opinion, the reason of this phenomenon was due to collecting powder samples exactly from the area where the plexiglass-spacers were located under the concrete surface as shown in (Figure 24). The plexiglass is a non-conductive material electrically, and thus the electric field between the cathode and anode were distorted as depicted in the (Figure 24). This distortion of the electric field paths resulted an area with low electric field in the surface depths over the plexiglass-spacer, and thereby it was impossible to extract the chlorides by the shortest electric field paths (which are most effective for extracting chlorides as mentioned earlier in the section 8 page 28). In addition, the plexiglass-spacers blocked the direct contact between the pore solutions at the referred area and the electrolyte solution. Subsequently, the diffusion of chlorides from the pore solution in adjacent depths couldn't occur through the shortcut distance to the electrolyte

solution, and thus the diffusion rates reduced at those surface depths. In the depths near the reinforcement of the same specimen; the electric field paths were available (Figure 24), but due to that distortion in the electric field the electric field paths became longer than in case without obstacles between the anode system and the concrete surface. Therefore, the efficiency of the ECE treatment in these depths in the specimen 4 was lower than that in the corresponding depths in the specimen 2 which has same w/c ratio as specimen 4 and even treated at lower current density. Thereby, It can be deduced that the electric field paths in the ECE treatment (which is depending mainly on the concrete thickness between the electric poles) plays an important rule that can be, in some situations like this, more important than the current density. Anyway, this issue could be avoided if the plexiglass spacers were fixed inside the PVC-containers and the specimens were marked at the contact areas with the spacers in order to not collecting samples from these areas.

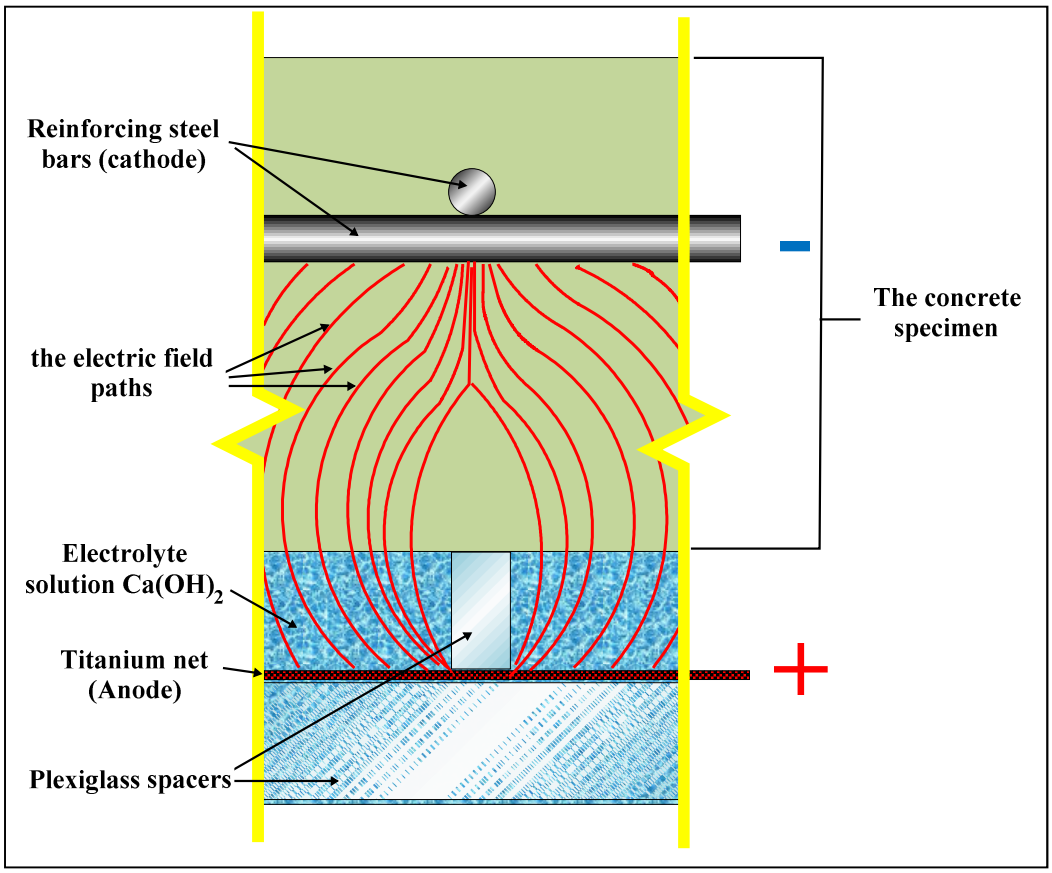

Figure 24: Distorting the electric field paths by the plexiglass spacers.

11.2.3-Chloride measurements after 40 days of treatment

The total charge that passed through the specimens, at that point in time, was 500 Ah/m^2 by steel surface for specimens (1, 2, 5 and 6) and 837 Ah/m^2 by steel surface for specimens (3, 4, 7 and 8). The results of chloride contents that obtained from chloride analysis were as shown in (Figure 25). The results of specimens that treated with 5 days current-on intervals (i.e. S5, S6, S7 and S8) began to be even with results of the specimens that treated with the 12 days of current-on intervals; although the total charge of the specimens (1, 2, 5 and 6) was considerably lower than the total charge of (3, 4, 7 and 8); but, at that time, the first group of specimens experienced 10 days of current-off treatment and the second group experienced just 4 days of current-off treatment. As observed earlier (in section 7.2 page 20) the ECE is most efficient at the early stage of the treatment and the efficiency of the treatment reduces with reduction of the free chlorides in the pore solution. This means that the amount of released bound chlorides was higher in the specimens (1, 2, 5 and 6) than in the specimens (3, 4, 7 and 8). According to the results in the (Figure 9 from ref.[7]) the ECE treatment is most efficient at the early period of treatment and after each time the current switches on at the phases of intermittent ECE treatment. Therefore, at advanced stages of treatment in this work, the long duration of current-on treatment became less efficient.

Regarding the overall progress of chloride extraction, the efficiency was still higher in the specimens that treated with 12 days of current-on treatment (specimens 1, 2, 3 and 4) as shown in (Figure 26), but the differences were not significant. This overall progression of the mentioned specimens thanks to the high efficiency of the treatment with 12 days of current-on at the earlier stages of the ECE process, but it seems that this parameter will be less efficient in the further stages of the ECE treatment, and the specimens with 5 days of current-on treatment is tending to be more efficient.

An overview on the results (Figure 25) gives an impression that samples, in most of the specimens, have been collected from the areas where the plexiglass-spacers are located due to somewhat higher chloride contents at the surface depths in the referred specimens. The probability of the cause of this phenomenon has already explained and depicted in (Figure 24). While in the other specimens the surface depths had always lower chloride contents comparing with those in the middle depths. The reason of that is explained in the next measurement of the chlorides.

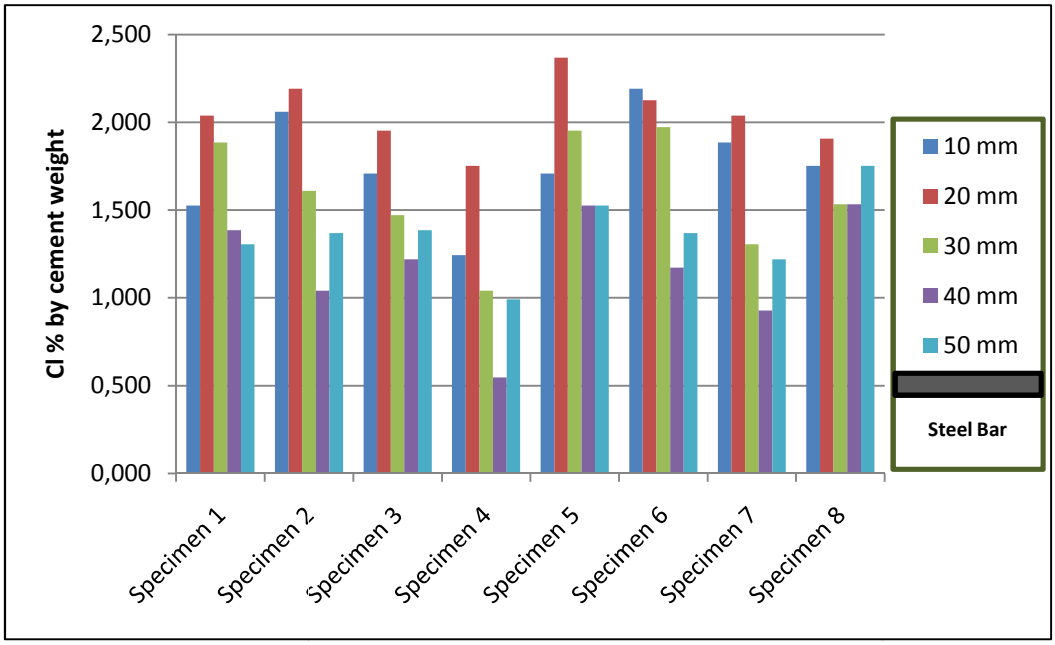

Figure 25: Chloride content in the specimens after 40 days of intermittent ECE treatment.

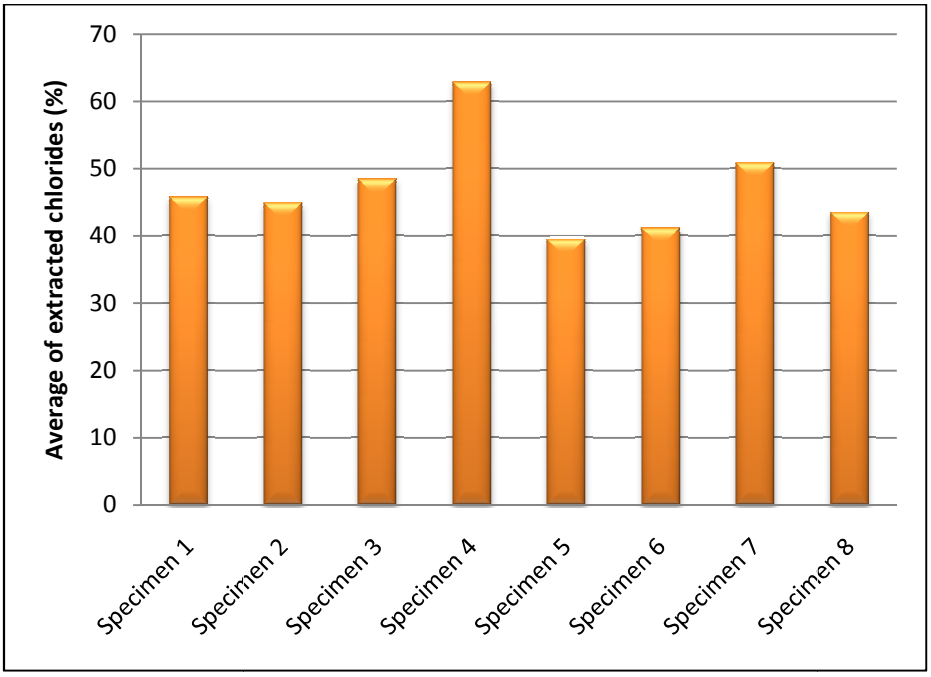

Figure 26: Average rate of the extracted chlorides in the specimens after 40 days of ECE treatment.

11.2.4-Chloride measurements after 54 days of treatment

As usual, the DC powers were switched off and the specimens were removed from the system in order to collect the powder samples. There was a strong smell of chlorine from the electrolyte solution in the PVC-containers which caused also a drop in the pH level in the electrolyte. Therefore, it was necessary to exchange all the electrolyte solutions with a fresh calcium hydroxide solution.

At this point in time, the total charge was 668 Ah/m^2 by steel surface for specimens (1, 2, 5 and 6) and 1125 Ah/m^2 by steel surface for specimens (3, 4, 7 and 8). The results of chloride measurement showed a lowest chloride contents in the specimens (3 and 4) than those in the other specimens (Figure 27 and Figure 28). This imply that the specimens, that treated with the combined parameters (12 days of current-on and 1 A/m^2), are still most efficient than the other specimens; but on the other hand, the progress in the specimens that treated with (5 days of current-on) is higher than the other specimens that treated with (12 days of current-on) comparing with the progress in the referred specimens in the earlier stages of ECE process although the specimens with (5 days current-on) intervals were charged with half amounts of currents that the specimens with (12 days of current-on) were charged with. This implies the useless of long duration of continuous current-on treatment at the advanced stages of the ECE process, and this is consistent with results in (Figure 7 and Figure 8) from previous works that discussed in (section 7.2, page 20) where showed a regress in the ECE's efficiencies at the advanced stages of the process where the chloride concentrations became lower.

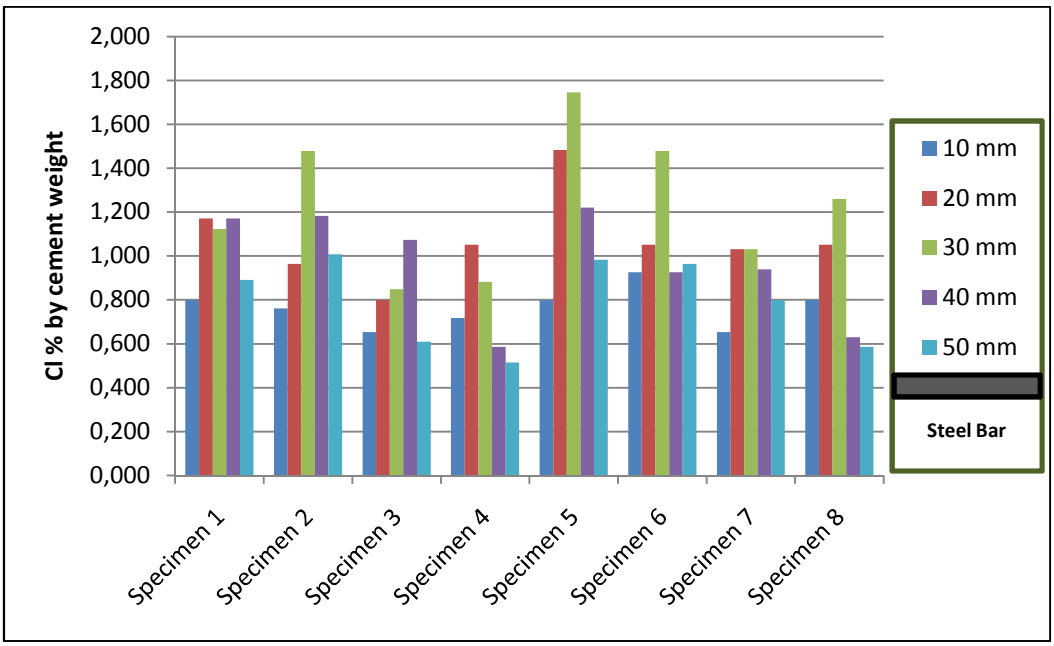

Figure 27: Chloride content in the specimens after 54 days of intermittent ECE treatment.

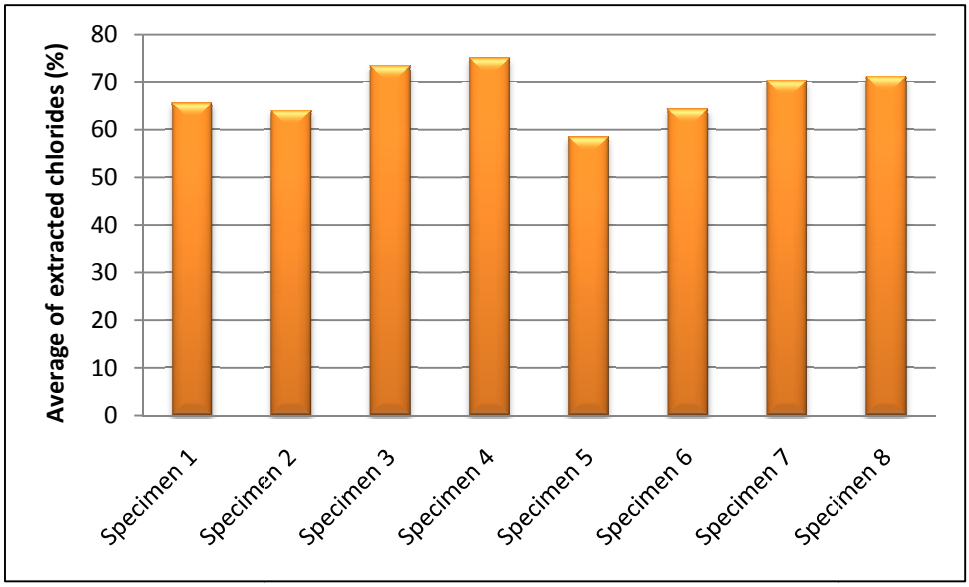

Figure 28: Average rate of the extracted chlorides in the specimens after 54 days of ECE treatment.

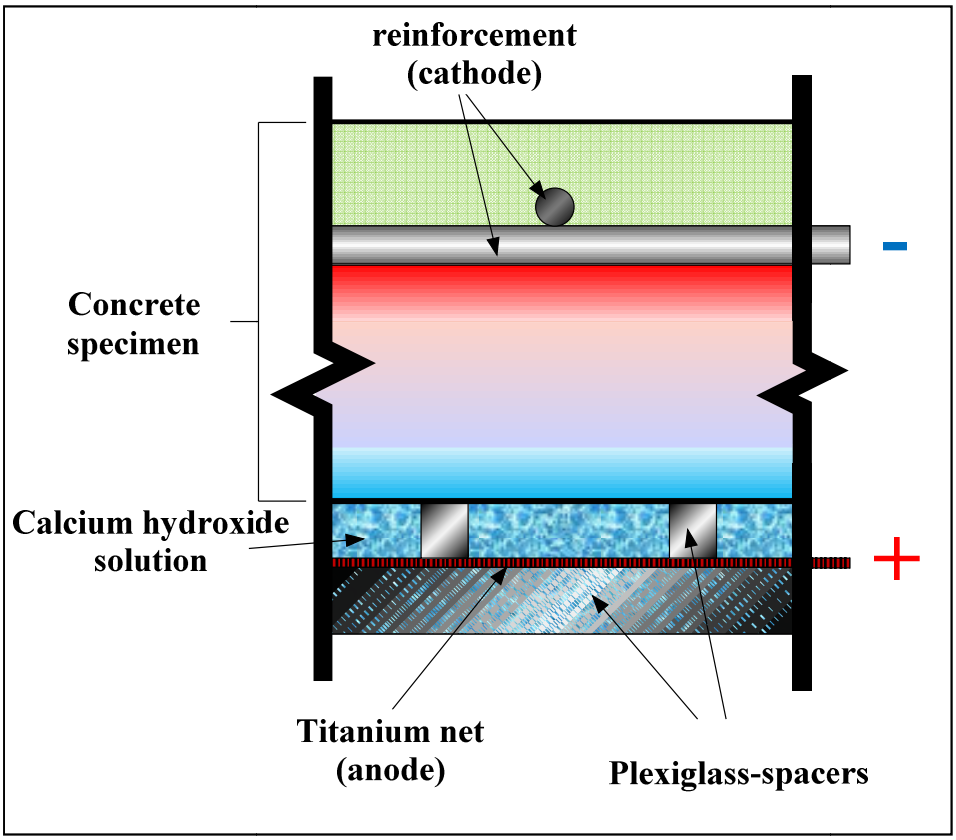

Figure 29: Illustration of descending the effect of current density and degree of saturation in the cover depths.

In this results also, the concentrations of chlorides in the middle depths are generally higher than the other depths. The experimenter explained this phenomenon with following steps:

1- The reason of low chloride density at vicinity of the reinforcement is due to high strength of the cathode pole at that point and this strength is relating reversely with the distance of the current path through the concrete cover due to electric resistivity of the concrete. The current strength is depicted in the (Figure 29) by a fading red color (where dark contrast refers to high current strength and light contrast refers to low current strength). Therefore, the efficiency of the ECE were most effective in the depths near the reinforcing bars. This explains the low chloride contents at the vicinity of the reinforcement.

2- at the depths near the concrete surface where the strength of the negative electrons is lower due the long path through the concrete, and thereby, the chlorides that removed by the electric field were lowest comparing with the other depths is lowest; but in addition, there are another parameter that contribute in reducing the chloride concentration in these depths. As long as the concrete surface was in direct contact with electrolyte solution, the surface depths of the concrete were fully saturated by the electrolyte solution. As it known, the capillary suction reduces with increasing the depth of the media. Therefore, the higher depths were less or not saturated due to density of the used concrete and concrete cover was rather thick. The degree of saturation in different depths as depicted in the (Figure 29) by a fading blue color (where dark contrast refers to a fully saturated concrete and light contrast refers to a dry concrete).

At the surface depths, which are fully saturated, the pore solution in these depths will be in a continuous direct contact with the electrolyte solution and diffusion of chlorides takes place between the pore solution in the concrete (high concentration of chloride) and the electrolyte (no- or very low- concentration of chlorides). Thus, major rates of chloride concentrations in this zone are removed by the diffusion and lower rates by the electric field. This dual contribution led to the low concentrations of chlorides in the surface depths.

This phenomenon cannot be noticed in the ECE treatments where high current densities are used. As mentioned earlier in the (section 7, page 17), the migration of ions under an electrical field in concrete is much faster than diffusion. The current densities that used in this work were low, besides, the used concretes were rather dense (w/c ratio 0.4 and 0.5).

3- in the intermediate zone where both effects of the current strength and diffusion are low. This zone is representing the depths where the red and blue colors are faded out in the (Figure 29). In this zone the strength of the electric field is lower due to electric resistivity of the concrete that results lower ECE efficiency in this zone comparing with areas near reinforcement. Furthermore, the concrete in this zone is not fully saturated which means that the pore solutions are not in a continuous contact with the electrolyte solution, and therefore no diffusion of chlorides into the electrolyte solution from this zone is likely to happen. These dual weak effects from the electric field and the diffusion led to higher concentration of chlorides in this zone comparing with the other two zones.

11.2.5-Chloride measurements after 68 days of treatment

At this point in time, the total charge was 836 Ah/m^2 by steel surface for specimens (1, 2, 5 and 6) and 1413 Ah/m^2 by steel surface for specimens (3, 4, 7 and 8). As shown in the (Figure 30 and Figure 31), there wasn't considerable development in the chloride extraction process comparing with the previous result. Even results in the specimens with (5 days current-on) intervals showed insignificant change in the rate of extracted chlorides in comparison with the previous result. The percents of extracted chlorides from the specimens were generally (60-70) % of the initial chloride content. The ECE treatment was most efficient in the specimen 4 where about 80% of the chlorides were extracted. It supposed that specimens 3 will give better results than the specimen 4 as long as the first referred specimen has 0.5 w/c ratio and the second specimen has 0.4 w/c ratio. Both of them treated with same parameters of current density and duration of current-on treatment. The specimen 3 is more permeable than the specimen 4, and consequently should the ECE be most efficient in the concretes with highest permeability. This mystery was solved after that the experimenter has checked the results of chloride concentration prior to starting the ECE treatment (Figure 19). The referred figure shows lower initial chloride content in the specimens 2 and 6 than the planned initial chloride content of (3 % by cement weight). All the specimens (2, 4, 6 and 8) made of the same concrete mixture (w/c 0.4). Since the average initial chloride content in the specimens (2 and 6) was about 2.65 % by the cement weight, then it can be deduced that all the specimens (2, 4, 6 and 8) had lower initial chloride contents than the specimens (1, 3, 5 and 7) where their initial chloride results were consistent with the planned initial chloride content. That may happened as result of inhomogeneous distribution of pre-added chlorides during the mixing process of the concrete with (0.4) w/c. Thereby, the lower initial chlorides in the specimen 4 may explain the reason of higher ECE's efficiency in the referred specimen than that in the specimen 3.

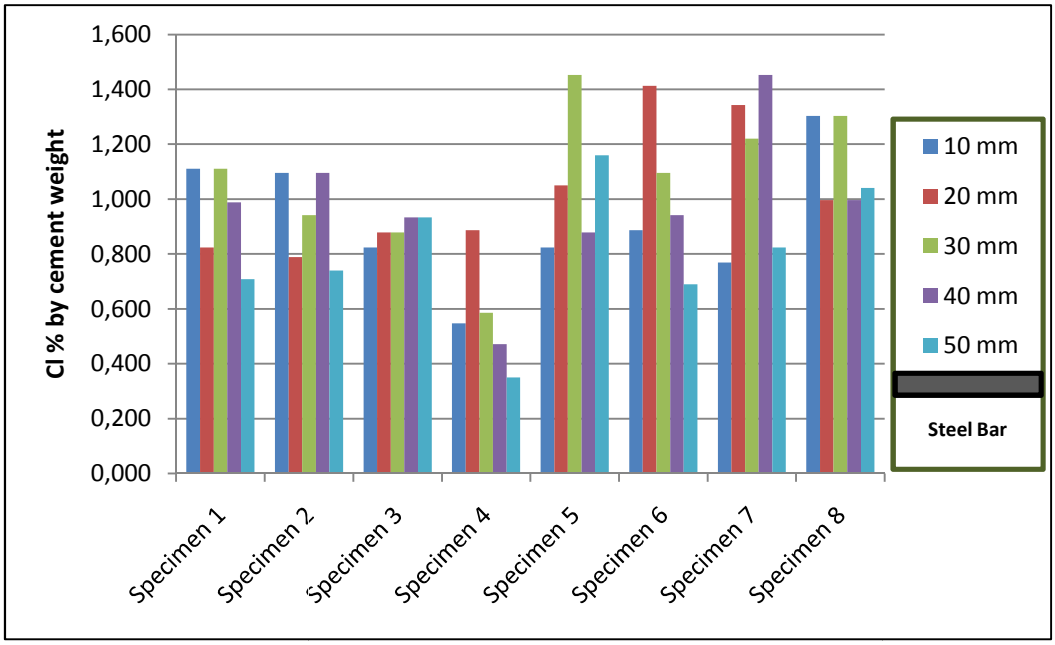

Figure 30: Chloride content in the specimens after 68 days of intermittent ECE treatment.

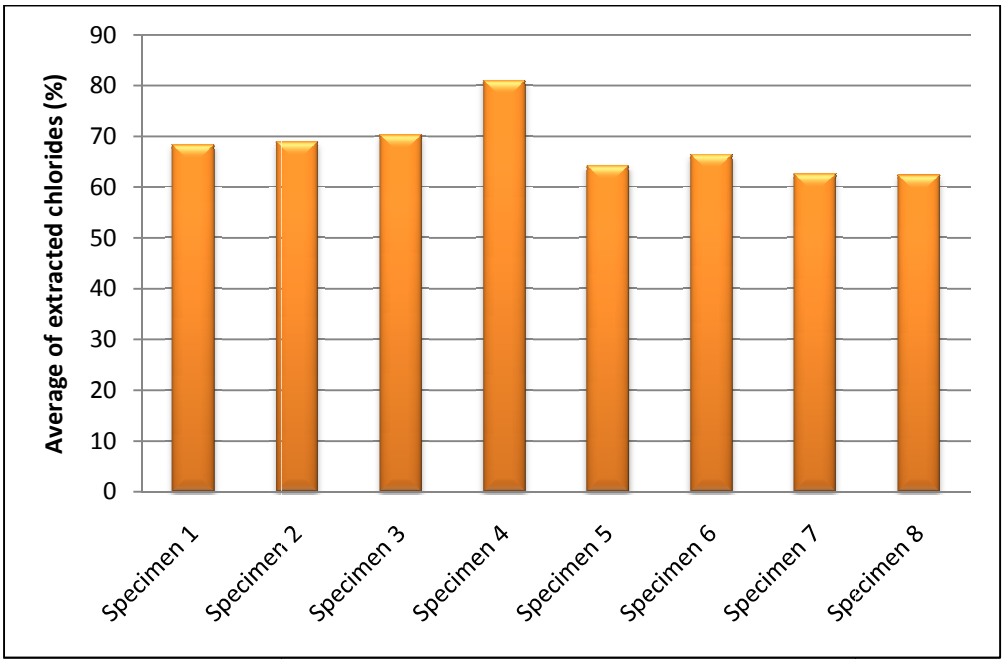

Figure 31: Average rate of the extracted chlorides in the specimens after 68 days of ECE treatment.

11.2.6-Chloride measurements after 90 days of treatment

At this point in time, the total charge was 1105 Ah/m^2 for specimens (1, 2, 5 and 6) and 1845 Ah/m^2 by steel surface for specimens (3, 4, 7 and 8). It decided to stop the treatment at that point due to two reasons:

The first reason was due to the low chloride contents at the vicinity of reinforcing bars in most of the specimens, besides the progress generally was very low or even there were regresses in the results of the specimens (5 and 6) as shown in the (Figure 32 and Figure 33). Generally, the chloride contents at the reinforcement depth were below 0.3% by the cement weight. As discussed earlier in (section 4, page 13) there are not reliable ranges for chloride threshold levels, and this results that obtained in this work are very sufficient if the concrete maintained in a high alkaline environment.

The results at this stage were rather near to each other, therefore the results at this stage of treatment didn't help too much for deducing a most adequate procedure of the ECE treatment since some of specimens may reached this maximal limit of chloride extraction at an earlier point in time and couldn't develop further, and thereby, the other specimens that may were less effective in earlier stages could give the same results at the end of treatment. Therefore, it should be focus on the earlier results for finding a more accurate influence of the different parameters that used in this work.

The second reason was due to exceeding the total charge in the specimens (3, 4, 7 and 8) over 1500 Ah/m^2 by steel surface, and this has negative impacts on the concrete; besides, any prolonging of the ECE treatment more than 1500 Ah/m^2 by steel surface is reported to be inefficient due to transporting all of the current flow by the hydroxyl ions as already discussed in the (section 7.2, page 20).

As final efficiency of the treatment, the approximate percent of the chlorides that extracted out of the specimens was 86 % in the specimen 1, 84% in the specimen 2, 83% in the specimen 3, 85% in the specimen 4, 66% in the specimen 5, 67% in the specimen 6, 87% in the specimen 7 and 82% in the specimen 8 (Figure 33).

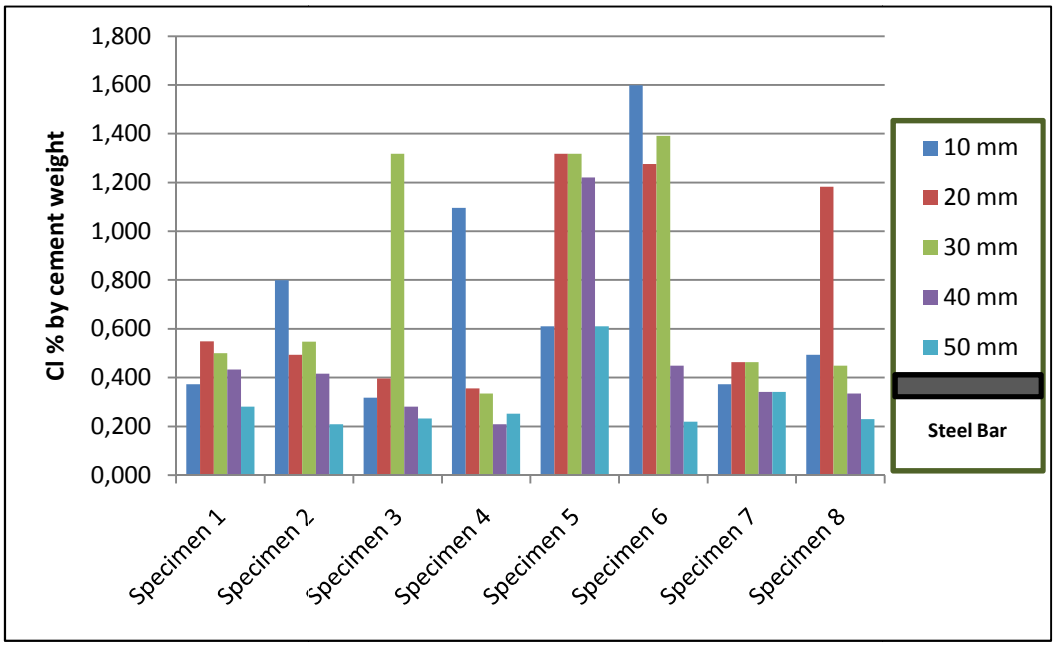

Figure 32: Chloride content in the specimens after 90 days of intermittent ECE treatment.

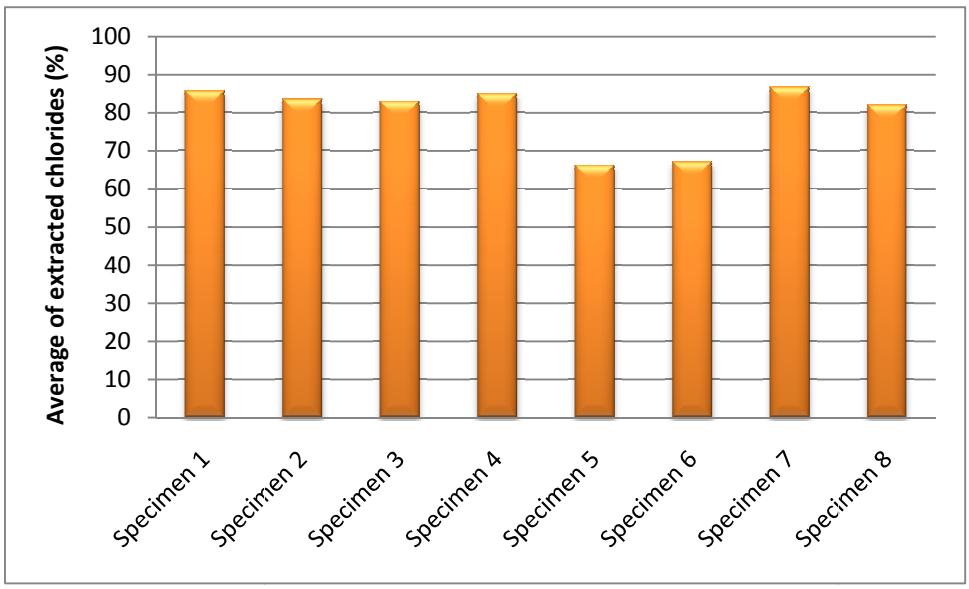

Figure 33: Average rate of extracted chlorides in the specimens after 90 days of ECE treatment.

12-Discussion

In chloride contaminated structures, only the chlorides in the depths near the reinforcement leads to corrosion of the reinforcing steel bars. Therefore, the chlorides at the vicinity of the reinforcement are most necessary to be removed. As presented in the (Figure 34 and Figure 35) the most of the chlorides were extracted during the first 3 weeks of the treatment. This was consistent with the previous works that presented in the (section 7.2, page 20); where the efficiency of ECE was highest when the chloride concentrations were highest. There were considerable lower chlorides at the vicinity of reinforcement in the specimens that treated with (12 days of current-on intervals) than those in the specimens that treated with (5 days of current-on intervals). This implies higher efficiency of the ECE with parameter of (12 days of current-on) at the early stage of the ECE process. Among the four specimens that treated with (12 days of current-on intervals), the specimen 3, that combine two other parameters (0.5 w/c and 1 A/m^2 current density), was most effective. That was expected due to combined advantage of its parameters (higher w/c ratio and current density).

According to the results in the (Figure 34 and Figure 35); there was a significant regress in the efficiency of the ECE after the week 3 in the specimens that treated with the parameter (12 days of current-on). On the other hand, there was an obvious progress in the results of the specimens that treated with parameter (5 days of current-on) at the period between week 3 and week 9. Since most of the chloride concentrations were generally removed from the specimens in the early stage of the treatment; the long periods of current-on treatments were not sufficient. In an intermittent ECE treatment, the total concentration of bound and free chlorides decreases with prolongation of the treatment's duration. Therefore, the amount of the released bound chlorides will be lower in each current-off interval comparing with the one and so on. Basing on obtained results in this work, the periods of current-on treatment should not be constant overall the treatment's duration. The efficiency of the intermittent ECE would be more efficient if it started with (12 days of current-on) treatment and afterwards reduced in each further current-on interval.

The current densities that used in this work were rather low; therefore a slow progress of the treatment was noticed. The current density of (0.7 A/m^2 by steel surface) gave insufficient results in all cases of combination with the other parameters. In contrast, the current density (1 A/m^2 by steel surface) gave most sufficient result in the specimens that combined with the parameter (12 days of current-on). This combination of higher current density and longer period of current-on interval led to higher total charge in these specimens; and as mentioned earlier in the (section 8, page 28), the efficiency of the ECE treatment increases with increase of the total charge passed through the concrete.

The combination effect of the parameters (0.4 w/c, 1A/m^2 current density and 12 days on current-on interval) gave the most linear results during the overall period of the treatment; as presented by the result of the specimen 4 in the (Figure 35), and the efficiency in this combination was better than other cases in most parts of the treatment's duration. In contrast, the combination effect of parameters in the specimens (5 and 6) gave lowest efficiencies

during the overall period of the treatment due to low current density and total current charge in these two specimens.

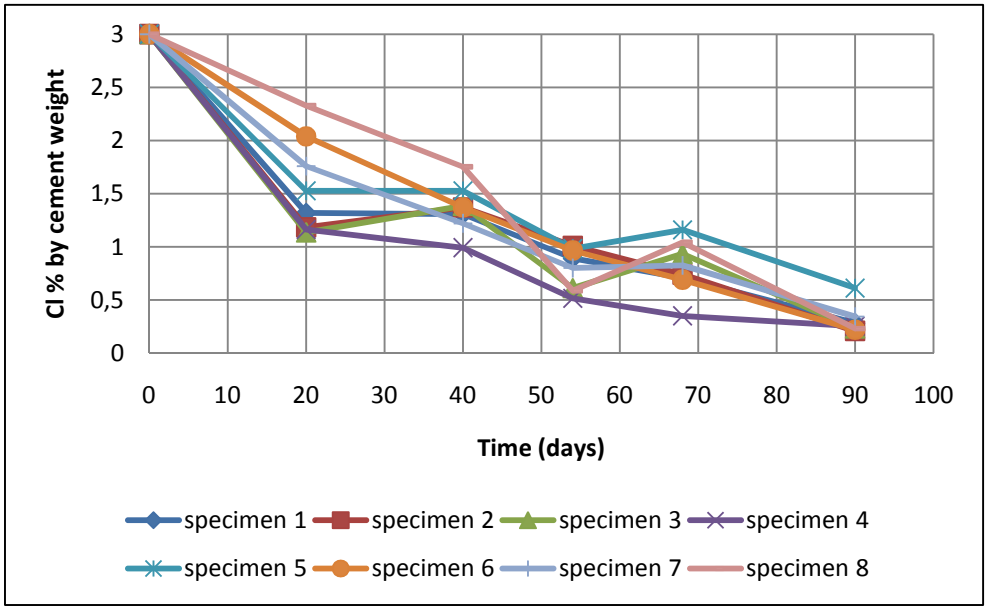

Figure 34: Chloride content at the vicinity of reinforcement bars in the specimens during the intermittent ECE treatment.

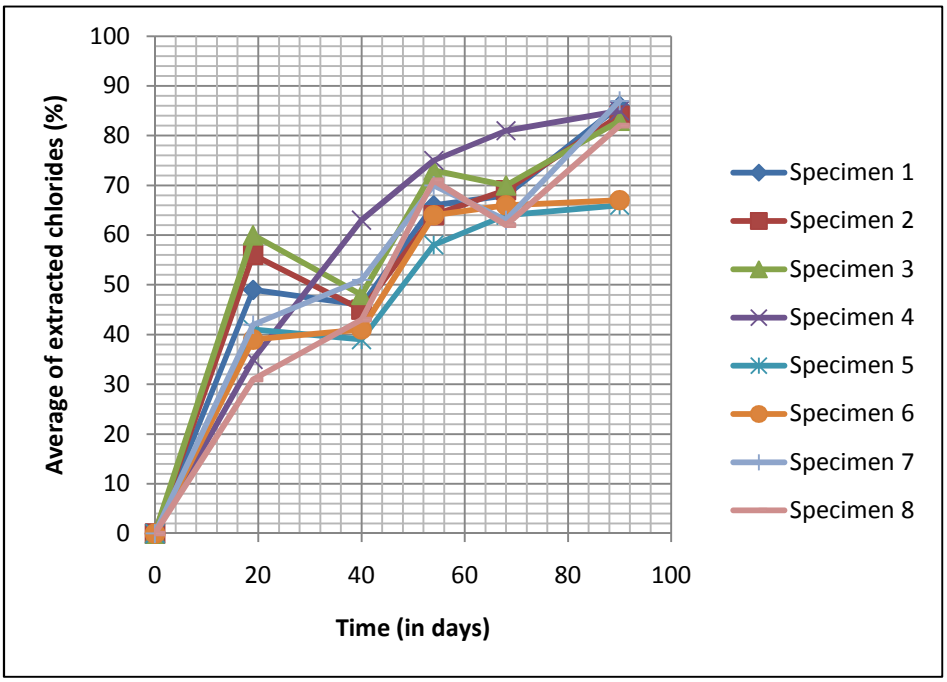

Figure 35: the progress of the ECE process in the specimens during the intermittent ECE treatment.

According to general overview on the results that obtained from this work; it can be deduced that a little higher current densities than those used in this work could gave more sufficient results in shorter treatment duration. For instance, current densities between (1.5-2.0 A/m^2 by steel surface) could be an advantageous alternate; since this range of current density is within the recommendation that reported in the reference [26] (as presented earlier in the section 7.2-page 20). The result that obtained in the reference [7] (which also presented earlier in the same referred section) don't encourage to choose current-on intervals longer than 12 days. Since 12 days of current-on interval gave good results in the early stage of treatment in this work and the 5 days current-on interval was more efficient in the further stages of the treatment; so it can be a benefit to start an ECE with a (12 days of current-on) in the first phase of the intermittent treatment and reducing the current-on treatment period with 2 days in the next phase and so on until the aimed results are reached as presented in (Table 6). The duration of current-off interval that used in this work was 2 days, and it wasn't necessary to investigate another durations of current-off intervals since the results in (Figure 9 from reference [7]) was sufficient enough to deduce that 2 days of current-off is optimal for releasing the most of bound chlorides.

There wasn't significant difference between the w/c ratios in the concretes that have been used in this work and all the specimens were rather dense; therefore it was difficult to observe the influence of the w/c ratio on the ECE's efficiency.

Phases of ECE	Duration of current-on (days)	Duration of current-off (days)
1.Phase	12	
		2
2.Phase	10	
		2
3.Phase	8	
		2
4.Phase	6	
		2
5.Phase	4	
		2
6.Phase	4	
	to be continued with same intervals as in this phase.	2

Table 6: suggestion for most effective ECE procedure.

13-Conclusion

In this work, experimental tests have been carried out in laboratory in order to find most effective procedure for applying the ECE treatment. Based on the overall results of the whole concrete cover depths in general, and the results of depths near the reinforcement in particular; following conclusions are derived:

1- The efficiency of ECE treatment decreases with decreasing the chloride concentration in the concrete. Thereby, the duration of current-on phases in an intermittent ECE process should be reduced with the reduction of ECE's efficiency over time; while it is sufficient to use constant duration of 2 days current-off interval along all the period of intermittent ECE process.
2- Current densities lower than $1A/m^2$ (by steel surface) makes the duration of ECE treatment longer than usual, and current densities in range ($1.5 – 2.0\ A/m^2$) can be optimal choice for treating concretes with normal reinforcing bars (not prestressed concrete) basing on considerations of the treatment's efficiency and negative impacts on the reinforced concrete.
3- Electrically non-conductive solid objects between the anode and the concrete surface leads to weaker electric field in the associated area in the concrete and subsequently the efficiency of ECE in these areas will be lower.
4- The two values of w/c ratio (0.4 and 0.5) that used in this work were too near to each other and therefore no considerable influence of the variation of this parameter was noticed. Since the permeability of the concrete increases with increase of the w/c ratio; there is no doubt that the chlorides can be extracted more easily in the concretes with higher w/c ratio.
5- A significant amount of chlorides can be removed from the surface depths of concrete by diffusion in case if the concrete surface maintained fully saturated during the ECE process.

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15-Appendixes

15.1-Preparing the specimens

A wooden plates with thickness 20 mm, was used to make the forms of the specimens. The positions, where the reinforcing bars will stick out, are bored in advance of mounting the pieces of the form. Then, every 4 forms accomplished on one large piece of wooden plate. After completing the forms, the internal surfaces lubricated with form-oil, and then the reinforcing net installed in the forms. In order to maintain the homogeneity of the concrete cover, no reinforcement chairs are used for supporting the reinforcing bars. The reinforcement chairs (which usually made of plastic materials) could affect the flow of ions in these areas during ECE treatment; furthermore, the electric current field will also be affected due to bad electric-conductivity of plastic materials. As another alternate for adjusting the cover thickness and supporting the reinforcing bars during the casting process, a wooden baton mounted over one of the reinforcement net's end. Then the reinforcement supported to the baton by polyester threads after adjusting the cover thickness. The other end of the reinforcement is already supported by the form via the stick-out part of reinforcing bars (Photo 1). Actually that is why two of reinforcing bars planned to stick out, as this will support the reinforcement firmly during the casting process. For cathode connection only one stick-out is sufficient as all the conductivity over all the reinforcing bars are ensured by welding the crossing points.

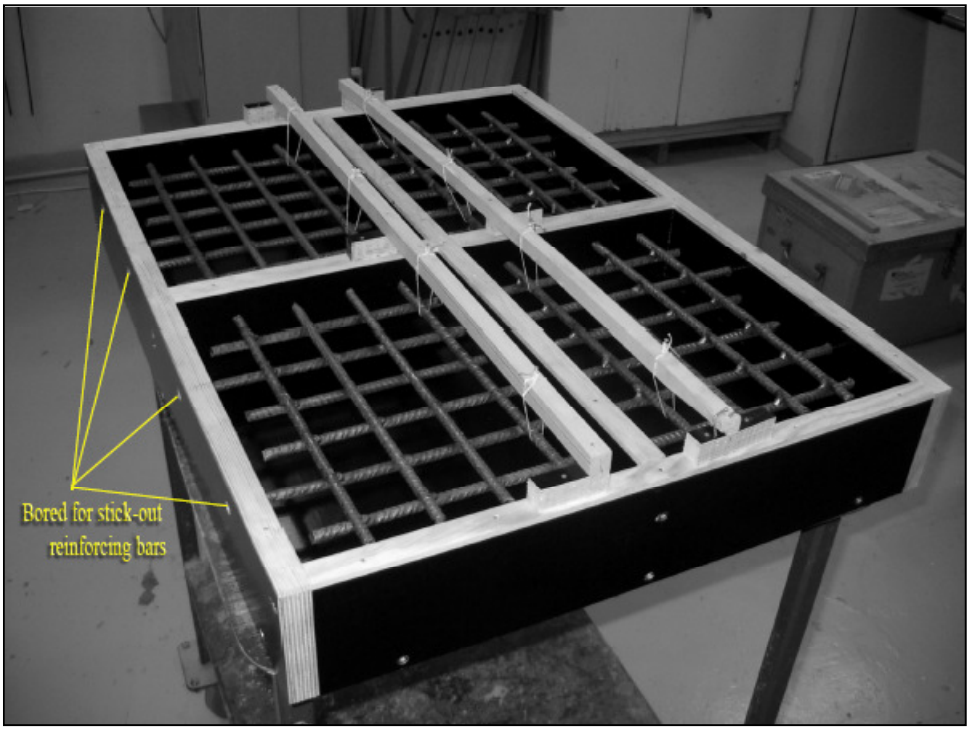

Photo 1: preparing the specimen forms.

As known, the fresh concrete mixture must be vibrated during the casting in order to get a homogenous distribution of the concrete compositions, and driving out the restricted airs. And during the casting and vibrating process; the reinforcement level was maintained by wooden batons and the holes of the stick-out steel bars (Photo 2).

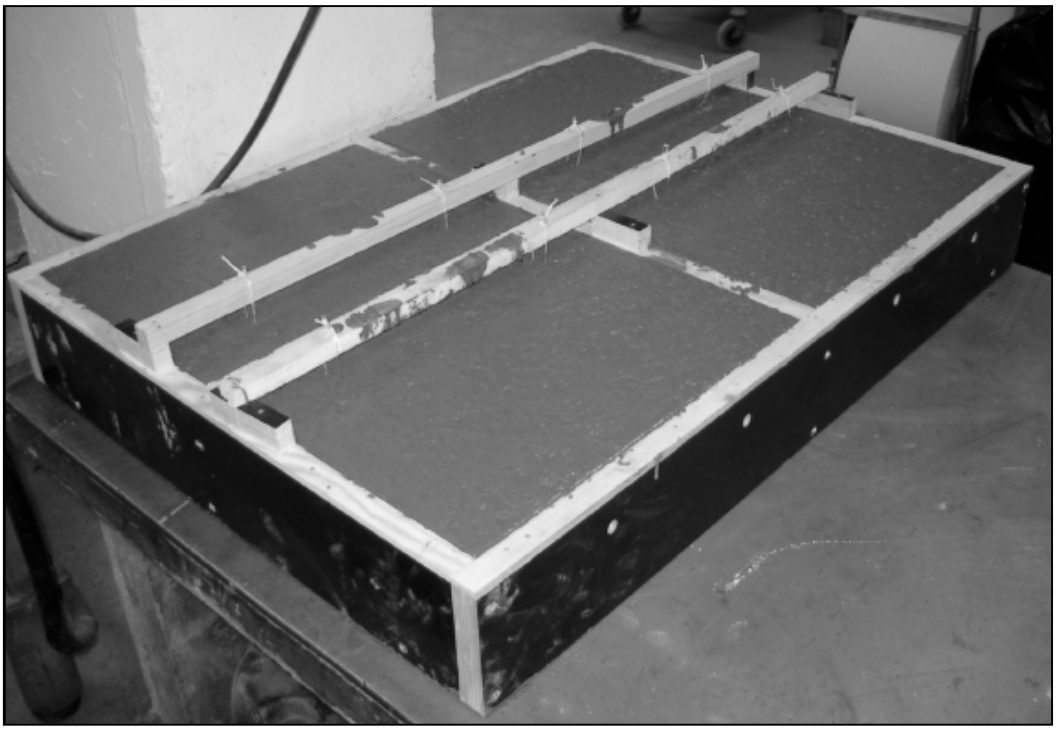

Photo 2: Casting the specimens

After one month of curing, the specimens were demolded carefully. Now, the specimens have enough strength and ready for ECE treatment (Photo 3).

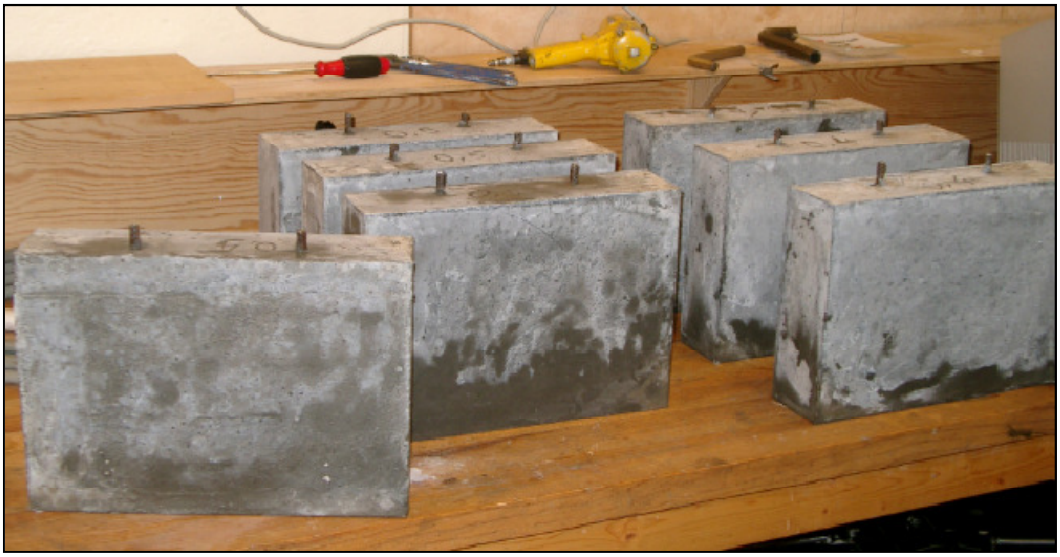

Photo 3: Demolding the specimens after one month of curing at room temperature and 100% RH.

15.2-The set-up of ECE treatment

The titanium net provides from the fabrics in different net-spaces and sheet widths, usually packed in form of rolls (Photo 4). In this work, the titanium mesh was prepared by cutting 8 pieces of it from a titanium roll. The areas of these pieces should, at least, be equal to areas of the concrete surfaces that will be subjected to ECE treatment.

Photo 4: Titanium net as provides from the fabrics.

In order to minimize the acidification of concrete surface during the ECE treatment, plexiglass sheet was cut into sticks with height 20 mm, thickness 10 mm, and in different lengths that suit the dimensions of the PVC-container (Photo 5). The plexiglass sticks will help to support and create efficient spaces among the bottom of PVC-container, titanium net, and the concrete surface. This will give more spaces for the electrolyte, and the concentration of extracted ions in the electrolyte will be minimized. After installing the anode in the PVC-container as shown in (Photo 5), the set-up of electrical connection was arranged in a way that every two specimens will be connected serially to one DC-supplier. Thus 4 DC-suppliers were used in this work for treating the 8 specimens.

Afterwards, it is recommended to put the concrete specimens in the PVC-containers prior to adding the electrolyte solution. That's because the plexiglass spacers have light weights and the solution can make them unstable or float. The type of electrolyte that used in this work was hydroxide calcium solution $Ca(OH)_2$. The electrolyte added to the anode system up to level where about 10 mm of the specimens were immersed.

Photo 5: Installing the titanium net in the PVC-container, and connecting the electric wires.

15.3-Starting ECE treatment

In order to start ECE treatment, the DC-suppliers should be set to total current density that secure passing designed current density the specimens. In this work two values of current densities were used, (0.7 and 1.0) A/m^2 by steel surface, and calculations of required total current densities were made as follows:

1- Calculating surface area of reinforcing steel bars:

Total length of reinforcing bars (L) $= 4 \times 31cm + 4 \times 21cm + 2 \times 23cm = 2.54\ m$

Total surface area of reinforcing bars$= 2\pi \times r \times L = 2\pi \times 0.004 \times 2.54 = 0.064\ m^2$

(r): is the radius of the reinforcing bars.

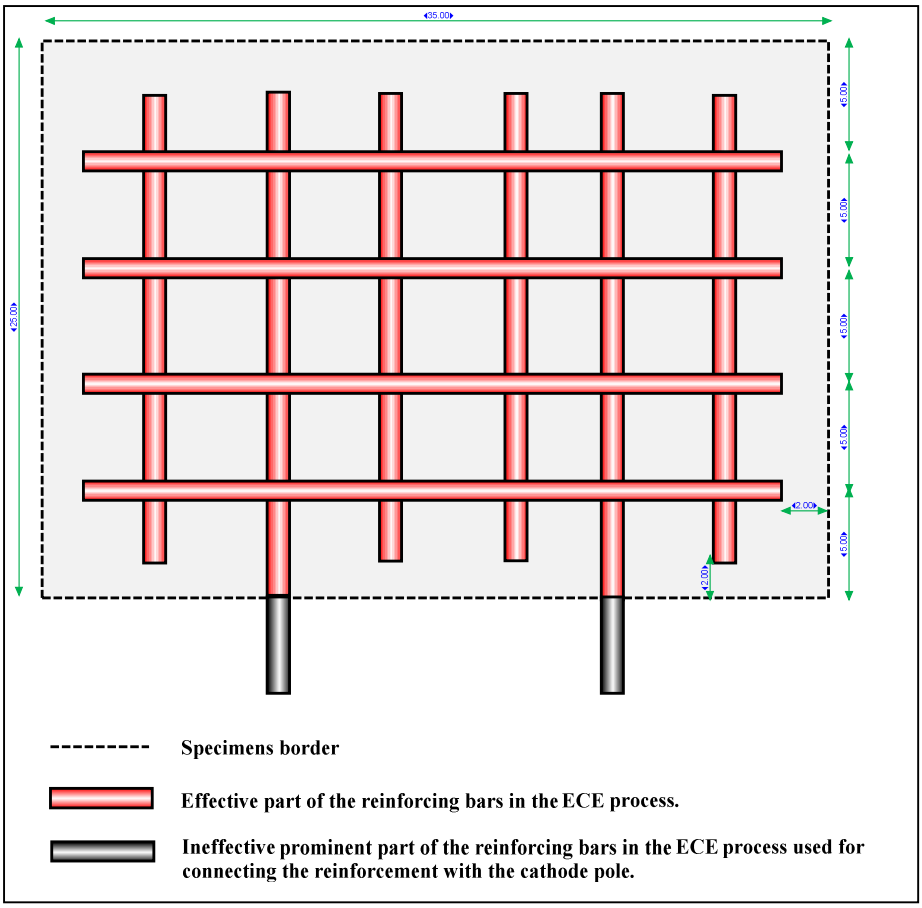

Figure 36: Illustration of distribution of reinforcing bars in the specimens.

2- Required total current density at the DC-supplier (I) Ampere= $i \cdot S$
Where (i) is current density (A/m^2), and (S_s) is surface area(m^2).
Thus, for (i=0.7 A/m^2 by steel area):
$I_{(0.7)}$=0.7 x 0.064 = 44.80 mA.

And for (i=1.0 Amp./m^2 by steel area):

$I_{(1.0)}$= 1.0 x 0.064= 64.00 mA.

3- Converting current density (i) by steel area to (i) by concrete area:
Concrete surface area (S_s)= $0.250m \times 0.350m = 0.0875\ m^2$.
i= I/S_c
$i_{0.7}$= 0.0640 / 0.0875 = 0.51 A/m^2 by concrete area.
$I_{1.0}$= 0.0448 / 0.0875 = 0.73 A/m^2 by concrete area.

Then, the ECE treatment was applied on the specimens as shown in (Photo 6 and Photo 7).

Photo 6: Starting the ECE treatment of specimens S1-S4.

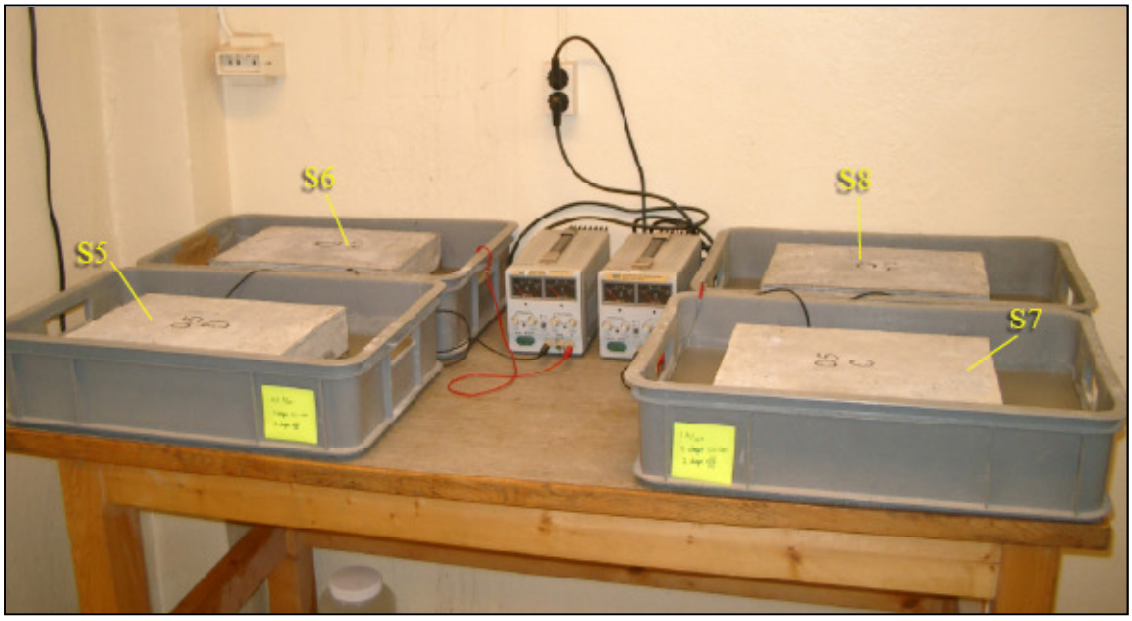

Photo 7: Starting the ECE treatment of specimens S5-S8.

15.4-Tools and devices used in the chloride analyses

1-Hammer drill for collecting powder samples.

2-Laboratory DC power supply (model: GPS-3030) with ampere range (0-3.2) and volt range (0-32).

3-MillChlor RCD chloride analyzing field kit (Photo 8).

4-pH-test strips.

Photo 8: MillChlor RCD chloride analyzing kit.

15.5-Experimental data and calculations

The results chloride content obtained from the chloride analyses are in form chloride percent by concrete weight, and in order to convert it as percent of cement weight, must divide these results by the (cement/concrete) weight rate. This rate can be founded as following:

$$(\text{Cement/Concrete}) = \frac{(cement\ weight)}{(weight\ of\ all\ the\ concrete's\ solid\ compositions)}$$

The data of concrete composition weights are given in (Table 2).

1- **For the (S-0.4) specimens (S2, S4, S6, S8):**

$$(\text{Cement/Concrete})_{0.4} = \frac{402.5\ Kg}{(402.5+1027.1+387.4+387.4)Kg} = 18.26\%$$

2- **For the (S-0.5) specimens (S1, S3, S5, S7):**

$$(\text{Cement/Concrete})_{0.5} = \frac{353.4\ Kg}{(353.4+1027.1+387.4+387.4)Kg} = 16.39\%$$

Following data and calculations are obtained from different stages of chloride analyses process:

Specimens	C % in depth 10 mm from surface	
	by concrete weight	by cement weight
S 2	0.47	2.574
S 3	0.5	3.05
S 6	0.5	2.738
S 7	0.5	3.05

Table 7: Cl % before applying ECE treatment.

Specimens	Cl %	Depths measured from concrete surface (mm)				
		10	20	30	40	50
S 5	A	0,262	0,386	0,248	0,464	0,438
	B	1,599	2,355	1,513	2,831	2,672
S 6	A	0,372	0,262	0,386	0,174	0,357
	B	2,037	1,435	2,114	0,953	1,955
S 7	A	0,302	0,272	0,288	0,262	0,272
	B	1,843	1,660	1,757	1,599	1,660
S 8	A	0,412	0,288	0,344	0,357	0,248
	B	2,256	1,577	1,884	1,955	1,358

A: Cl % by concrete weight; **B**: Cl% by cement weight.

Table 8: Cl % after 5 days of ECE treatment.

Specimens	Cl %	Depths measured from concrete surface (m m)				
		10	20	30	40	50
S 1	A	0,248	0,280	0,280	0,234	0,216
	B	1,513	1,708	1,708	1,428	1,318
S 2	A	0,200	0,216	0,266	0,296	0,216
	B	1,095	1,183	1,457	1,621	1,183
S 3	A	0,186	0,192	0,216	0,192	0,186
	B	1,135	1,171	1,318	1,171	1,135
S 4	A	0,388	0,520	0,296	0,280	0,296
	B	2,125	2,848	1,621	1,533	1,621
S 5	A	0,186	0,436	0,234	0,343	0,250
	B	1,135	2,660	1,428	2,093	1,525
S 6	A	0,266	0,436	0,288	0,316	0,372
	B	1,457	2,388	1,577	1,731	2,037
S 7	A	0,172	0,272	0,344	0,344	0,288
	B	1,049	1,660	2,099	2,099	1,757
S 8	A	0,248	0,357	0,425	0,425	0,425
	B	1,358	1,955	2,327	2,327	2,327

A: Cl % by concrete weight; **B**: Cl% by cement weight.

Table 9: Cl % after 20 days of ECE treatment.

Specimens	Cl %	Depths measured from concrete surface (mm)				
		10	20	30	40	50
S 1	A	0,250	0,334	0,309	0,227	0,214
	B	1,525	2,038	1,885	1,385	1,306
S 2	A	0,376	0,400	0,294	0,190	0,250
	B	2,059	2,191	1,610	1,041	1,369
S 3	A	0,280	0,320	0,241	0,200	0,227
	B	1,708	1,952	1,470	1,220	1,385
S 4	A	0,227	0,320	0,190	0,100	0,181
	B	1,243	1,752	1,041	0,548	0,991
S 5	A	0,280	0,388	0,320	0,250	0,250
	B	1,708	2,367	1,952	1,525	1,525
S 6	A	0,400	0,388	0,360	0,214	0,250
	B	2,191	2,125	1,972	1,172	1,369
S 7	A	0,309	0,334	0,214	0,152	0,200
	B	1,885	2,038	1,306	0,927	1,220
S 8	A	0,320	0,348	0,280	0,280	0,320
	B	1,752	1,906	1,533	1,533	1,752

A: Cl % by concrete weight; **B**: Cl% by cement weight.

Table 10: Cl % after 40 days of ECE treatment.

Specimens	Cl %	Depths measured from concrete surface (mm)				
		10	20	30	40	50
S 1	A	0,131	0,192	0,184	0,192	0,146
	B	0,799	1,171	1,123	1,171	0,891
S 2	A	0,139	0,176	0,270	0,216	0,184
	B	0,761	0,964	1,479	1,183	1,008
S 3	A	0,107	0,131	0,139	0,176	0,100
	B	0,653	0,799	0,848	1,074	0,610
S 4	A	0,131	0,192	0,161	0,107	0,094
	B	0,717	1,051	0,882	0,586	0,515
S 5	A	0,131	0,243	0,286	0,200	0,161
	B	0,799	1,483	1,745	1,220	0,982
S 6	A	0,169	0,192	0,270	0,169	0,176
	B	0,926	1,051	1,479	0,926	0,964
S 7	A	0,107	0,169	0,169	0,154	0,131
	B	0,653	1,031	1,031	0,940	0,799
S 8	A	0,146	0,192	0,230	0,115	0,107
	B	0,800	1,051	1,260	0,630	0,586

A: Cl % by concrete weight; **B**: Cl% by cement weight.

Table 11: Cl % after 54 days of ECE treatment.

Specimens	Cl %	Depths measured from concrete surface (mm)				
		10	20	30	40	50
S 1	A	0,182	0,135	0,182	0,162	0,116
	B	1,110	0,824	1,110	0,988	0,708
S 2	A	0,200	0,144	0,172	0,200	0,135
	B	1,095	0,789	0,942	1,095	0,739
S 3	A	0,135	0,144	0,144	0,153	0,153
	B	0,824	0,879	0,879	0,933	0,933
S 4	A	0,100	0,162	0,107	0,086	0,064
	B	0,548	0,887	0,586	0,471	0,350
S 5	A	0,135	0,172	0,238	0,144	0,190
	B	0,824	1,049	1,452	0,879	1,159
S 6	A	0,162	0,258	0,200	0,172	0,126
	B	0,887	1,413	1,095	0,942	0,690
S 7	A	0,126	0,220	0,200	0,238	0,135
	B	0,769	1,342	1,220	1,452	0,824
S 8	A	0,238	0,182	0,238	0,182	0,190
	B	1,303	0,997	1,303	0,997	1,041

A: Cl % by concrete weight; **B**: Cl% by cement weight.

Table 12: Cl % after 68 days of ECE treatment.

Specimens	Cl %	Depths measured from concrete surface (mm)				
		10	20	30	40	50
S 1	A	0,061	0,090	0,082	0,071	0,046
	B	0,372	0,549	0,500	0,433	0,281
S 2	A	0,146	0,090	0,100	0,076	0,038
	B	0,800	0,493	0,548	0,416	0,208
S 3	A	0,052	0,065	0,216	0,046	0,038
	B	0,317	0,397	1,318	0,281	0,232
S 4	A	0,200	0,065	0,061	0,038	0,046
	B	1,095	0,356	0,334	0,208	0,252
S 5	A	0,100	0,216	0,216	0,200	0,100
	B	0,610	1,318	1,318	1,220	0,610
S 6	A	0,292	0,233	0,254	0,082	0,040
	B	1,599	1,276	1,391	0,449	0,219
S 7	A	0,061	0,076	0,076	0,056	0,056
	B	0,372	0,464	0,464	0,342	0,342
S 8	A	0,090	0,216	0,082	0,061	0,042
	B	0,493	1,183	0,449	0,334	0,230

A: Cl % by concrete weight; **B**: Cl% by cement weight.

Tabell 13: Cl % after 90 days of ECE treatment.