



1. Sami MASADEH, 2. Amin Al-ROBAIDI, 3. Nabil ANAGREH

## ELECTROCHEMICAL CHLORIDE EXTRACTION FROM CONCRETE STRUCTURE EXPOSED TO DEAD SEA WATER

<sup>1-3.</sup> Materials Engineering Department, Faculty of Engineering, Al-Balqa  
Applied University, Al-Sult 19117, JORDAN

**Abstract:** Eighteen concrete samples with different concrete mixes, overlay thicknesses, and w/c ratios were cast and immersed in Dead Sea water bath. Potential readings were recorded over 7-month time period and results were plotted on a time-potential scale. Electrochemical chloride extraction (ECE) treatment was applied for one month, potential values recorded again and final results were plotted and compared. Data collected along 8 months clearly showed that higher w/c ratio (0.7 w/c), lower overlay thickness (2 cm), and the use of a more concentrated Cl<sup>-</sup> water (i.e. Dead Sea water) increased corrosion. ECE treatment has proved to be a successful technique to minimize the destructive effect of corrosion.

**Keywords:** Corrosion, Electrochemical chloride extraction, Deadsea water, Concrete, Steel reinforcement

### 1. INTRODUCTION

The Dead Sea lies between Jordan and Israel. Its water is unique because it contains a number of salts with compositions different than any other sea water in the world. The composition of Dead Sea water is as follows: 14.5% MgCl, 7.5% NaCl, 3.8% CaCl<sub>2</sub>, 0.5% MgBr<sub>2</sub>, 1.2% KCl, and rest is water. Some industrial and tourist structures lay at sea coast; severe corrosion problems encounter sea water due to high chlorides content. In many cases, corrosion can not be controlled unless very special alloy steel is used.

Contrary to common belief, concrete itself is a complex composite material. It has low strength when loaded in tension and hence it is a common practice to reinforce concrete with steel, for improved tensile mechanical properties.

Concrete structures such as bridges, buildings, elevated highways, tunnels, parking garages, offshore oil platforms, piers, and dam walls all contain reinforcing steel (rebar). The principal cause of degradation of steel reinforced structures is corrosion damage to the rebar embedded in the concrete. Iron is unstable in nature, and because reinforcing steel used in pre-cast concrete is made largely of iron, it, too, becomes unstable when exposed to corrosive agents such as salt.

Sound concrete is an ideal environment for steel but the increased use of deicing salts and the increased concentration of carbon dioxide in modern environments principally due to industrial pollution, has resulted in corrosion of the rebar becoming the primary cause of failure of this material. Corrosion of reinforcing steel in bridges and parking garages is a well-known and costly problem. In the presence of chlorides, moisture and oxygen, corrosion takes place at appreciable rates. The resulting corrosion products, which are more than twice the volume of the original uncorroded steel, create tensile stresses in the surrounding concrete. When these internal stresses are excessive, the concrete in the vicinity of the reinforcement cracks and eventually spalls or delaminates.

Until recently, rehabilitating concrete bridge piers involved only removing the damaged concrete and then patching. However, this practice was found to lead to the introduction of new electrochemical cells between the new chloride-free concrete in the patches and the surrounding old concrete that contained varying amounts of chloride [1].

Once chloride-induced corrosion of the reinforcing steel bars has initiated in a concrete bridge, the only truly effective means of stopping corrosion in

the structure is by applying either cathodic protection or the relatively new electrochemical chloride extraction. Electrochemical chloride extraction extends the functional life of the treated structure, but does not require the long-term commitment generally required in other used systems. Electrochemical chloride extraction is operated without requiring the excavation of structurally sound concrete that is contaminated with chlorides. This can provide an advantage that does not exist with other restoration techniques [2].

## 2. ELECTROCHEMICAL CHLORIDE EXTRACTION (ECE)

Since steel corrosion is an electrochemical process, once it occurs in a concrete structure an electrochemical measure, such as electrochemical chloride extraction (ECE) can stop it or slow it down to a significant extent. The ECE process is as follows:

- (1.) A suitable metal is placed or attached to the surface of a concrete structure,
- (2.) An electrical field is applied between this metal and the embedded steel bars by the passage of a direct current through the concrete in such a manner that the bars become negatively charged and the metal becomes positively charged, and
- (3.) The negatively charged chloride ions ( $\text{Cl}^-$ ) in the concrete are drawn away from the steel bars toward the surface of the concrete.

The outward migration of the chloride ions accompanies the movement of other mobile ions in the concrete, each in the direction dictated by its electrical charge, contributing to the conduction of the electric current through the top layer of concrete. Adverse effects are: increased permeability in the concrete, a decreased concrete-to-steel bond, and cracking in the concrete. Concerns for these effects halted research on the application of ECE. These studies, conducted on concrete specimens and small sections of several concrete bridge members, found that by maintaining the applied current to less than  $5\text{A}/\text{m}^2$ , the treatment would have no adverse effect on the concrete [3]. Further, the treatment removed 20 to 50 percent of the admixed chloride from the test concrete slabs and redistributed the remaining chloride well away from the steel bars [4].

Electrochemical treatment of concrete is becoming more popular as a repair and restoration option to stop corrosion and extend the service life of existing reinforced concrete structures. This paper will discuss the theory behind Electrochemical Chloride Extraction (ECE) as well as a number of important services and components required to successfully complete an ECE project [5]

The objectives of this work are:

- To study marine corrosion and its effect on reinforcement steel in concrete due to the severe deterioration of reinforced concrete structure in Dead Sea area.
- To study the effect of w/c ratio; overlay thickness and type of mixing effect on corrosion through the interpretation of potential readings of reinforcement steel bars in concrete.
- The effectiveness of electrochemical chloride extraction in rehabilitation of steel reinforcements by applying ECE to concrete structures having severe corrosion.

## 3. EXPERIMENTAL PROCEDURE

### 3.1. Concrete Casting

Eighteen concrete cylinders were cast with the following mix: (31% percentage by volume for both fine aggregate and cement, 38% coarse aggregate) into molds after inserting steel bars at different distances (2,3 and 4 cm respectively) from mold wall as shown in Figure (1).

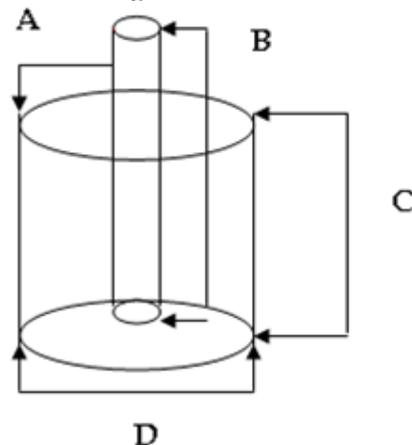


Figure (1): Specimen design showing overlay thickness, height of steel bar as variables and height and diameter of concrete sample as constant.

A: overlay thickness; B: height of steel bar C: height of concrete D: diameter of concrete

After hydration process took place (48 hours) later, concrete cylinders were removed from mold, and left to cure (by wetting them) for 28 days.

Different W/C ratios (0.5, 0.6 and 0.7), mixing water (Tap water and Dead Sea water) were used and different overlay thicknesses. Potential readings were recorded using (Cu-CuSO<sub>4</sub>) reference electrode and according to ASTM C876-80 and plotted versus time.

### 3.2. Electrochemical chloride extraction

After three-month exposure to Dead Sea water solution bath, samples were removed from solution bath and each sample was wrapped with three layers of sponge, galvanized steel wires and sackcloth then enveloped with nylon sheets (Figure 2, Figure 3). Electrochemical chloride extraction was applied by using an external Dc-power supply. Steel reinforcements were connected to the negative and galvanized steel wires (acting as anodes) to the positive terminal of the DC-power supply. Frequent potential readings were taken; results were recorded, plotted, and analyzed.

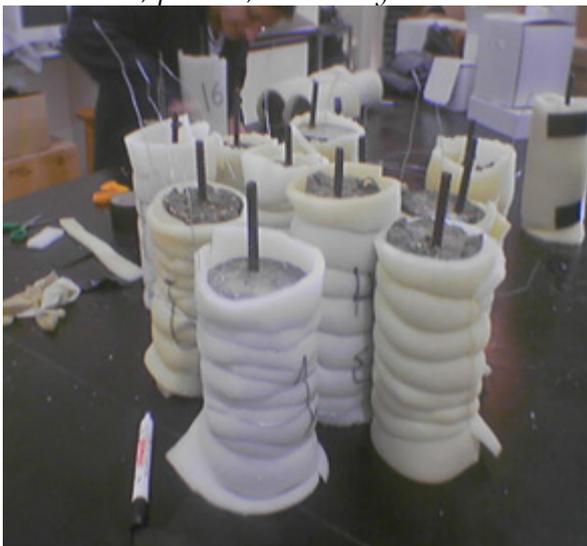


Figure (2): Wrapping with sponge and galvanized steel wires

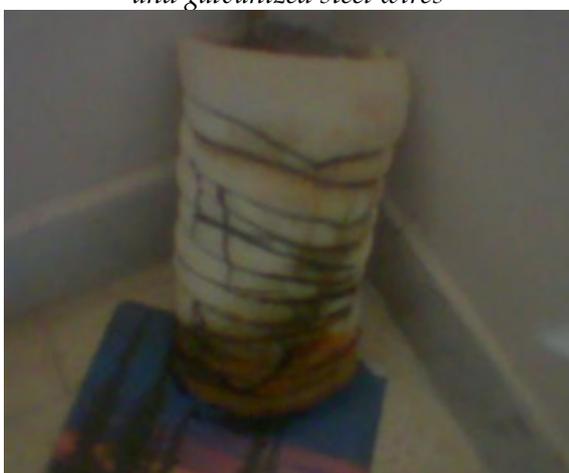


Figure (3): Final appearance after ECE application

## 4. RESULTS AND DISCUSSION

### 4.1. Effect of mixing water

The potentials of concrete blocks prepared by Dead Sea water showed more negative potentials than those prepared by tap water. This behavior was observed for specimens with different W/C ratios and having different concrete overlay thickness.

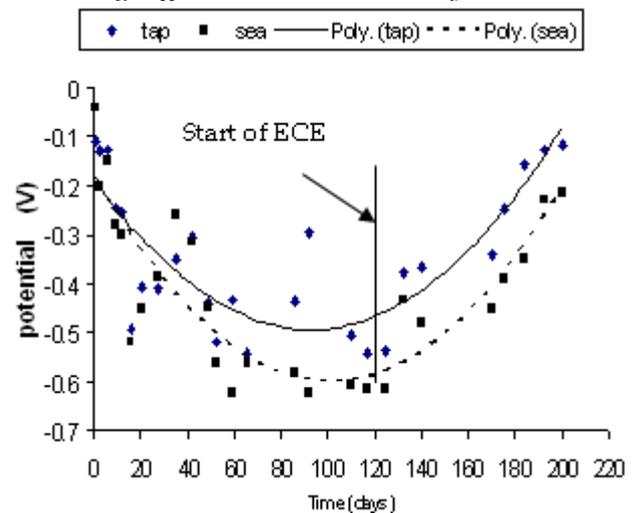


Figure (4): Potential of steel reinforcement Vs time for 0.5w/c ratio and 2 cm thickness and variable mixing water type

### 4.2. Effect of overlay thickness

This figure shows the behavior of steel reinforcement exposed to Dead Sea water and tap water having different overlay thickness for various concrete samples. Potential readings interpreted show that steel reinforcements with higher overlay thickness had more positive potentials.

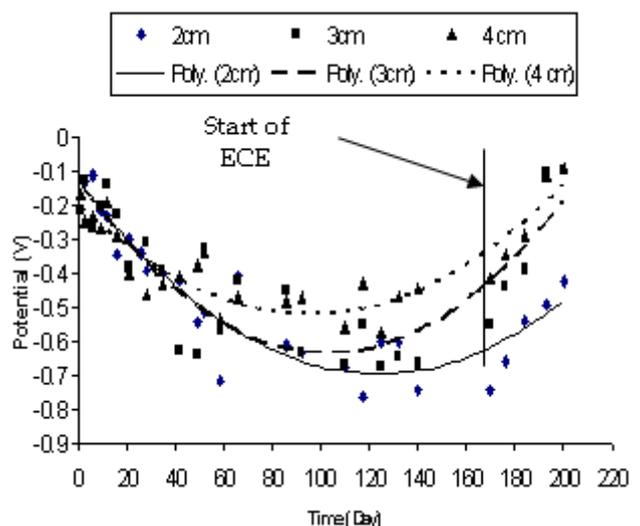


Figure (5): Potential of steel reinforcement Vs time for 0.7 w/c ratio and seawater and different overlay thickness

### 4.3. Effect of $w/c$ ratio

Figure (6) show the behavior of steel reinforcement exposed to Dead Sea water and tap water having different  $w/c$  ratios for various concrete samples.

For the same overlay thickness and concrete mix (i.e. type of water used), 0.7 $w/c$  ratio gave more negative potential readings compared to both 0.6 and 0.5  $w/c$  ratios.

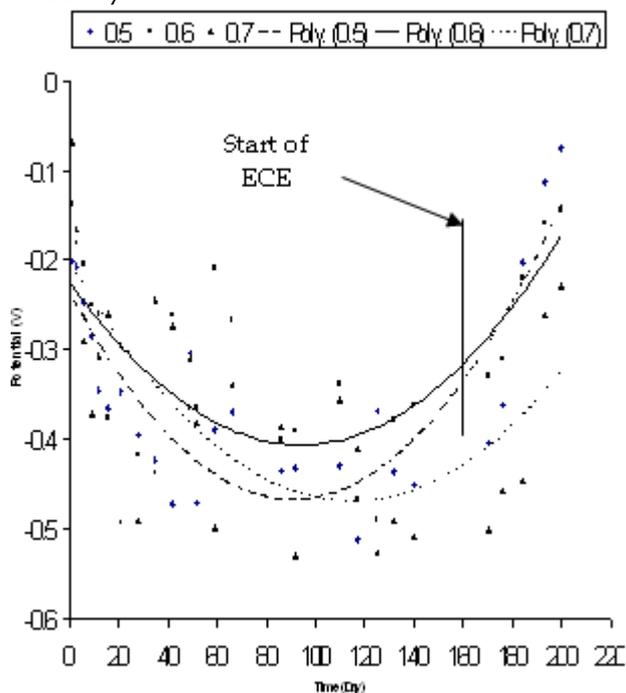


Figure (6): Potential of steel reinforcement Vs time for 3cm over lay thickness and tap water for different  $w/c$  ratio

## 5. DISCUSSION

### 5.1. Effect of mixing water

Concrete cylinders made by mixing with Dead Sea water showed more negative potentials than those mixed with tap water due to:

- Chloride effect:** - Higher  $Cl^-$  ions concentrations destroy the oxide film on the steel bar that formed on the metal surface. Due to high alkalinity, the  $Fe^{2+}$  produced at the steel-concrete interface combines with the  $OH^-$  from the cathodic reaction to ultimately produce a stable passive film. Chloride ions in the solution, having the same charge as  $OH^-$  ions, compete these anions to combine with the  $Fe^{2+}$  cations. The resulting iron chloride complexes are thought to be soluble (unstable); therefore, further metal dissolution is not prevented, and ultimately the buildup of voluminous corrosion products takes place

- Corrosion mechanism in samples using tap water as their mix is mainly due to the slow dominating diffusion process.
- The effect of chlorides is two folds, in that both the pH and the electrical resistivity of the concrete are lowered. Normally, the pH of concrete is 12 or 13, and steel usually becomes passive in environments having pH greater than 11.5. With the addition of chlorides, however, the pH of concrete may drop to 6 or 7, in which steel will corrode readily. The lowered resistivity also enhances corrosion. Concrete cylinders prepared by both mixing water showed severe potential drop but was less negative for samples mixed with tap water.

### 5.2. Effect of overlay thickness

Higher overlay thickness impedes the chloride ions penetration and oxygen enrichment into the depth of the sample and consequently into the steel bar due to shorter path required for the attacking corrosive chloride ions to travel in order to reach the steel bars thereby accelerating corrosion, so, samples with 2 cm thickness experiment showed higher corrosion than those of 3 or 4 cm thicknesses. Inadequate cover is invariably associated with areas of high corrosion risk due to both carbonation and chloride ingress

### 5.3. $W/c$ ratio Effect

- Higher  $w/c$  ratio explicitly indicates larger water volumes used in the concrete mix, which produces more porous concrete making it suitable for corrosion to take place,
- Oxygen enrichment:** The portion of steel bar directly exposed to atmosphere is surrounded by higher oxygen concentration which will lead to a significant difference in potential with the steel bar embedded in concrete thus forming galvanic corrosion cells and initiating corrosion. With the decrease in the  $w/c$  ratio the quantity of permeation oxygen decreases. Therefore decreasing  $w/c$  restrains the cathodic reaction, which leads to a decrease in the corrosion rate.
- Porosities in higher  $w/c$  ratio sample are higher volume thus allowing oxygen and water to penetrate into the depth of the sample, reach the steel bar easier and corrode it. Air and gases may move fairly easily in the pores of dry concrete-if the pores are interconnected-but with

increasing relative humidity, first the fine, then the coarser pores will be filled with water, and this slows down diffusion.

#### 5.4. Electrochemical Chloride Extraction

- a. Electrochemical chloride extraction process began after 170 days of exposure of concrete cylinders to DSW bath in order to rehabilitate and protect steel bars against corrosion by removing chloride ions. Potential readings began to increase (i.e. become less negative, more positive) because of the use of a DC impressed current supply that accelerated the extraction process in 4 weeks to simulate the conditions of concrete under real prolonged service life time and reversed the direction of Cl<sup>-</sup> ions movement from inner steel bar, leaching it to the outer environment of galvanized steel which acts as an anode.
- b. Effects of the three main variables (mixing water, overlay thickness, and w/c ratio) are reversed after the application of electrochemical chloride extraction. Samples mixed with Dead Sea water having lower overlay thickness and higher w/c ratio made the ECE process easier and more effective as expected.
- c. As a result of the applied potential difference between the anode and cathode water was reduced to hydroxyl ions at the reinforcement. After the available oxygen had been consumed, the cathodic reaction produced hydrogen gas. In porous concrete, it may simply diffuse harmlessly to the atmosphere through the pores of the steel-concrete interface. Externally, water or hydroxide was oxidized to oxygen and hydrogen ions. These reactions are referred to as electrolysis, which results in a pH increase around the reinforcement and is an important process for electrochemical process of ECE as shown in the equations (1-5).
- d. The resultant electro deposition helps to passivate the reinforcing steel after current application, and it also suppresses the corrosion of the reinforcing bar in the concrete. Electro deposition had an effect of recovering alkalinity of concrete.

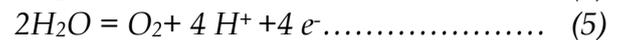
This seemed because of the salt solution in the vicinity of the reinforcing bar that became the high alkali atmosphere by generation of hydroxyl ions

by electrolysis and integration of metal ions to the reinforcing bar.

At the cathode



Anode



#### 6. CONCLUSIONS

1. Increasing the w/c ratio increases corrosion holding overlay thickness and type of water used in concrete mix constant. 0.5 w/c ratio samples were last to corrode compared to both 0.6 and 0.7 w/c ratios.
2. Lower overlay thickness allows higher corrosion of steel bars due to shorter path for Cl<sup>-</sup> ions that has to be traveled for the same w/c ratio and type of water used in the mix. 2, 3, and 4 cm overlay thicknesses corroded respectively.
3. Mixing with Dead Sea water encourages higher corrosion of steel bars at both constant w/c ratio and overlay thickness.
4. Reinforcement in concrete exposed to Dead Sea water would corrode irrespective of the w/c ratio used in concrete preparation.
5. The results of ECE showed that electro deposition made the reinforcing bar surface into the re passivation and that it also suppressed the corrosion of the reinforcing bar in concrete due to high alkalinity of the steel bar as a result of applied potential difference.

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5, Revolutiei,  
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