

## Carbonation of Reinforced Steel in Concrete with Varied Waters

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### ABSTRACT

The objective of this work is study the carbonation of reinforced steel in different solutions include artificial seawater (3.5% NaCl), river water and domestic water by electrochemical method at room temperature. Corrosion parameters were measured to calculate corrosion rates from polarization curves. Cyclic polarization was tested to know the possibility of occurring for pitting corrosion. Both Tafel plot and cyclic polarization indicate that the corrosion of reinforced steel was the lowest in river water due to the impurities and clay in this water which can be inter to the pores in concrete and it does not allow to occur carbonation of reinforced steel in addition to forming calcium salts with anions in river water more than forming calcium carbonate which close the pores of concrete. The results were supplemented with optical microscopy.

**Keyword:** Reinforced steel, Corrosion in concrete, Tafel plot, Cyclic polarization.

### كربنة فولاذ الكونكريت المسلح في مياه مختلفة

#### الخلاصة:

ان الهدف من هذا البحث هو دراسة كربنة حديد التسليح في اوساط مائية مختلفة شملت ماء البحر الممثل بـ 3.5% وزناً من كلوريد الصوديوم وماء النهر وماء الحنفية الاعتيادي، واجريت الدراسة بالطريقة الكهركيميائية عند درجة حرارة الغرفة. حسبت متغيرات التآكل ومعدل سرعة التآكل من منحنيات الاستقطاب، كما اجري فحص الاستقطاب الحلقي لمعرفة امكانية حصول التآكل النقري. وان كلا من منحنيات الاستقطاب الخطي والحلقي بينت التآكل كان قليلاً في ماء النهر بسبب الشوائب والاطيان الموجودة في ماء النهر والتي تدخل الى المسامات الموجودة في الكونكريت ولا تسمح بدخول ثاني اوكسيد الكربون وحصول كربنة حديد التسليح بالاضافة الى تكوين املاح الكالسيوم مع الايونات السالبة المتواجدة في ماء النهر على حساب تكوين كاربونات الكالسيوم التي تغلق مسامات الكونكريت. وقد دعمت نتائج التآكل بفحص التصوير البصري.

## INTRODUCTION

Concrete is the most widely used constructional material in the world. In spite of the impressive performance of concrete in several structures, the deterioration of concrete has assumed alarming proportion in harsh climatic conditions. Concrete can be defined as the artificial stone produced when cement (usually Portland cement) is mixed with fine aggregate (sand), a coarse aggregate (gravel or crushed stones) and water. The use of suitable mixing water is essential to make good concrete. Any unmineralized water can be used. Water to be excluded includes water containing total dissolved solids higher than 3.5%, sulfates in excess of 0.5%, high acidic water with a low pH (>4.0), industrial water from tanneries, cellulose factories and highly polluted water. Rain water and swamp water may be used for mixing with caution depending on the total dissolved solids [1].

Parker [2] studied the corrosion of concrete sewers exposed to atmospheres containing hydrogen sulphide, there are present large numbers of a sulphuric acid forming species of sculpture bacterium provisionally named *Thiobacillus concretivorus*. The typical corrosion process is a case of bacterial corrosion; it cannot proceed under sterile conditions and can only be carried to the acid stage through the activity of this organism. As the organism cannot exist at a higher pH than 6.5, its activity could not explain the initial stage of the process in which the pH of the fresh concrete surface (11–12) falls to 6.5 or less. It was then suggested that this preliminary drop in pH could be brought about either by purely chemical reactions or by the activity of further species of bacteria.

Newton and Sykes [3] studies corrosion of steel in mortar immersed in simulated sea water and steel exposed to 0.3 M NaOH + 0.6 M NaCl, both as aqueous solution and set with agar gel using galvanostatic pulse technique. Transients were analyzed to provide impedance information. Diffusion impedance was identified for corroding steel embedded in mortar and in gel but not in solution. Three time constants were evident for steel embedded in mortar while only two time constants were identified for corroding steel in alkaline chloride gel and solution. The extra time constant for steel cast in mortar appears to be associated with the dielectric characteristics of the mortar.

Mori et al. [4] studied the little slime layer which found to exist on the walls of sewer pipes in an anaerobic condition when the sewage flow rate was higher than approximately 30 cm/sec. Therefore, H<sub>2</sub>S is not produced from slime layers but from sediments which existed in the main trunk or the pressure main. The H<sub>2</sub>S production rates ranged from 5.5 to 64 µg-H<sub>2</sub>S/g-solid h depending on the contents of organic compounds and the cell numbers of sulfate reducing bacteria (SRB). The limiting nutrients are assumed to be fatty acids by the spike test. The pipe wall in the area just above the sewage level corroded severely, but the crown of the pipe was not heavily corroded. The corrosion rate of the concrete sewer pipe at the Ohmuta treatment plant was 4.3 to 4.7 mm/y in the area just above the sewage level and 1.9 mm/y at the crown. Tardahiro et al. [5] studied the occurrence of heaviest corrosion in the area around the sewage level of the concrete sewer pipe. The corrosion rate of this area was 4.3–4.7 mm/y. The corrosion rates decreased according to the distance from the sewage level. The deterioration at the crown of the sewer pipe was lowest, 1.4 mm/yr. It is concluded

that water and nutrients provided by sewage are important factors for microbial corrosion.

Hussain et al.[6] studied the effect of exposure temperature by curing the chloride-treated specimens at 20 ° and 70 °C. Pore solution was extracted using a high pressure pore solution extrusion device and analyzed for chloride and hydroxyl ion concentrations. Threshold chloride for onset of reinforcement corrosion was computed using threshold  $[Cl^-/OH^-]$  ratio of 0.3. The results showed that Tricalcium silicate  $C_3A$  content and exposure temperature have very strong influence on threshold chloride content. Alkali content of cement has marginal effect whereas presence of sulfates along with chlorides has moderate effect on the threshold chloride content.

Youping and Richard [7] determined the time-to-corrosion cracking from simulated bridge deck slabs. The experimental design considered corrosion rate, concrete cover depth, reinforcing steel bar spacing and size. Three, of the 14 slab series, cracked during the 5 year study. Metal loss was determined for the cracked specimens which had cover depths of 1, 2, and 3 in. (25, 51, and 76 mm). Li et al. [8] used an effective method for early detection of rebar corrosion in concrete, the capability of acoustic emission (AE) technique in detecting a weak stress wave make it a strong candidate. The primary advantage AE offers over other conventional nondestructive evaluation (NDE) techniques is that it can directly detect the process of a flaw growth. When corrosion products are formed on a corroding rebar, they swell and apply pressure to the surrounding concrete. Microcracks will be formed and stress waves will be generated during the expansion process when the pressure is high enough to break the interface layer. The growth of the microcracks is directly related to the amount of corrosion product of a corroding rebar.

John and Mohamed[9] reported the results of an experimental program designed to provide a realistic assessment of the potential of using fiber-reinforced polymer (FRP) materials in the repair and strengthening of reinforced concrete (RC) flexural members. The experimental program included seven RC flexural beams 270 x 400 mm in cross section and 4350 mm in length.

Shamsad[10] in 2003 studied the factors related to the concrete quality, such as water/concrete ratio, cement content, impurities in the concrete ingredients, presence of surface cracks, etc. and others related to the external environment, such as moisture, oxygen, humidity, temperature, bacterial attack, stray currents, etc., which affect reinforcement corrosion. The assessment of the causes and extent of corrosion is carried out using various electrochemical techniques. Prediction of the remaining service life of a corroding RC structure is done with the help of empirical models and experimental methods.

Alessandra et al.[11]in 2006 studied initial rheological description of high performance concrete using the modified slump test. It is known that the rheological behavior of the concrete is close to that of a Bingham fluid and two rheological parameters regarding its description are needed: yield stress and plastic viscosity. According to the results, an increase of yield stress was observed over time, while a slight variation in plastic viscosity was noticed. The incorporation of silica fume showed changes in the rheological properties of fresh concrete. Corral et al. [12]in 2011 investigated chloride ion penetrability and corrosion behavior of steel in concrete with

sustainability characteristics, as well as the partial or total replacement of its components for recycled materials. For the steel bars, the corrosion is the principal problem of durability in reinforced concrete. Coarse Recycled Concrete Aggregates (RCA), Supplementary Cementing Materials (SCM) byproducts of industrial processes such as fly ash and silica fume were used to produce concrete with sustainability characteristics and for the evaluation of its behavior when it is exposed to chlorides. From the resulting test specimens: electrical resistivity, resistance to charge transfer and resistance to chloride ion penetration, were determined; these parameters specify the minimum necessary properties for concretes, according to regulations, to guarantee their durability when they are exposed to chlorides. Abdulkareem and Hani [13] in 2011 studied developing new reinforcement materials by using different coating materials, included zinc, tin and lead. The experimental works included examination of coating detect, coating adhesion study, and the adhesion between concrete and coated bars, and different techniques are employed to assess the performance of reinforcement embedded in concrete at a saline environment of 3.5% NaCl solution.

The aim of this study is to investigate the carbonation of reinforced steel in concrete using different mixing waters include artificial seawater (3.5% NaCl), river water and domestic water at room temperature through pumping CO<sub>2</sub> gas to experimental media. This study carried out using Tafelplot and polarization measurements plot at scan rate 3 mV.sec<sup>-1</sup>.

## **Experimental Part**

### **Preparation of Specimens**

Reinforced steel rod was used in this work with chemical composition shown in Table (1). Preparation of specimens were carried out by cutting the steel rod to cylindrical shape with 10cm diameter and 1cm high, mounting of specimens were achieved to isolated all sides except one side to obtain surface area equal to diameter of rod and the make a hole for electrical connection. The exposed surface was grinded with emery papers for microstructure (600,800,1000) and corrosion test and then embedded with concrete as shown in Fig. (1) with set-up system for corrosion test.

### **Environments**

Three types of solution were selected as corrosion media include artificial seawater (3.5% NaCl), river water and domestic water and the pH of these media are listed in Table (2). All experiments were carried out at room temperature in the absence and presence of CO<sub>2</sub> gas at 120ml/min to study carbonation of reinforced steel in these media after immersion in test media for 7 days to ensure the completely combination between concrete components and environment.

### **Corrosion Test**

Tafel plot and cyclic polarization measurements were carried out with WINKING MLab 200 Potentiostat from Bank-Elektronik with electrochemical standard cell using Pt as counter electrode and SCE as reference electrode. Electrochemical measurements were performed with a potentiostat by SCI electrochemical software at a scan rate 3 mV.sec<sup>-1</sup>.

Polarization experiments were started when the rate at which open circuit potential ( $E_{ocp}$ ) changed was less and more 200mV.

### Optical Microscopy

The microstructure evolution for specimens in the absence and presence of CO<sub>2</sub> gas were investigated by means of optical microscope using (BEL photonics) microscope which connected to computer. figure(5)

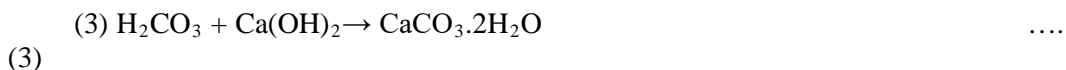
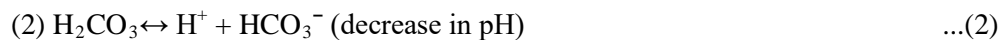
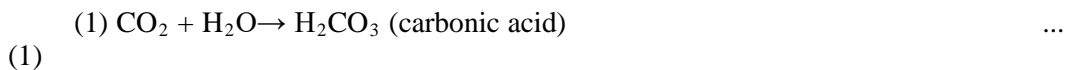
### Results and Discussion

Figures (2) to (4) show the variation of potential with time for reinforced steel in different water include seawater, river and domestic water. This figure shows that the open circuit potential became more negative for carbonated simulated seawater and domestic water. The regular behavior in seawater refer to destroy the passive film which formed on the steel surface, while irregular behavior in case of river and domestic indicates the breakdown and repair of passive film formed on the metallic surface. The potential of the sample was followed as a function of time in order to study the evolution of the film chemistry as it came to equilibrium with solution.

The two most common mechanisms of reinforcing steel corrosion damage in concrete are (1) localized breakdown of the passive film by chloride ions and (2) carbonation, a decrease in pore solution, leading to a general breakdown in passivity.

Table (2) shows the pH values for different waters before corrosion test and after immersion the reinforced steel in it, and then after corrosion test for carbonated waters. From these data can be seen that pH of waters before testing were alkaline 8.31, 8.09 and 8.27 for seawater, river and domestic water respectively. After immersion the embedded steel in concrete, the pH of seawater and domestic water became more alkaline 9.21 and 10.0 respectively due to formation metal hydroxides by hydrolysis of metal oxide in concrete, while little change was occur in the pH of river (8.20) because of presence of other ions and molecules in this water which may be surround the concrete and reducing the hydrolysis of oxides.

The carbon dioxide molecules that penetrate in the concrete react with the solid calcium hydroxide gel, and with alkali and calcium ions in the pore solution of the concrete causing a drastic decrease in the alkalinity due to a fall in pH from 14.0 to about 8.0. At this pH, corrosion is initiated by destruction of the protective oxide layer (Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>3</sub>O<sub>4</sub>). Following is the mechanism of carbonation:



The pH values of waters after pumping CO<sub>2</sub> were 4.92, 5.25 and 5.26 for seawater, river and domestic water respectively.

There are other secondary factors, such as depth of reinforcement cover, moisture conditions, humidity and temperature, which also influence carbonation. Figure (5) shows Tafel plot of reinforced steel in different solutions, this plot shows the cathodic and anodic regions.

At cathodic sites, many reaction can occurring on the surface of the iron that correspond to hydrogen evolution; if the electrode is held at this potential long enough, the inner oxide layer eventually will be electrochemically reduced to yield a bare iron surface exposed to the cement pore solution. Other reactions attributed to the formation of a film of Fe(OH)<sub>2</sub> and/or FeO on the previously reduced iron surface. Also it is believed to correspond to an Fe(II) → Fe(III) transition as ferrous iron of the inner layer is converted to ferric iron in the interfacial region between the inner(compact) layer and the outer (porous) layer. This transition reaction is probably a reversible reaction that is controlled by the diffusion of OH<sup>-</sup> ions within the outer oxide layer [13].

Cyclic voltammetric study indicates reactions attributed to an oxidation reaction within the compact oxide layer, probably involving the formation of Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, or FeOOH [14,15]. There are reactions considered to be the reverse (reduction) reactions corresponding to the anodic reactions [16].

The corrosion parameters were measured using Tafel extrapolation method. These data indicate that corrosion potential shifts to active direction for corrosion in seawater and domestic water, while shifts to less corroded direction in case of river water. Corrosion current density became higher in only seawater, while shifts to lower value in river and domestic water. Cathodic Tafel slopes were increased for carbonated water, while Anodic Tafel slopes were varied. It is referring to that carbonation has more effect on the anodic behavior through the dissolution and passivation.

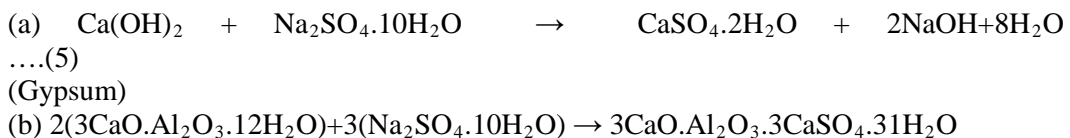
Carbon dioxide present in the atmosphere can reduce the pore solution pH significantly by reacting with calcium hydroxide (and other hydroxides) to produce insoluble carbonate in the concrete as follows:



The passivating ability of the pore solution diminishes with the decrease in pH. Carbonation-induced corrosion tends to proceed in a more uniform manner over the rebar surface than chloride-induced corrosion damage. Carbonation shrinkage decreases the cover to reinforcement and increases the risk of ingress of corrosive species.

Most important however, is the fall in pH as the concrete becomes less alkaline; this can move the steel from the passive region to the corrosion region on the Pourbaix diagram[17].

Concrete in contact with ground water in clays may be subjected to attack by the sulfate salts of calcium, magnesium and sodium. Sulfate salts are also present in seawater and brackish water. Following are the major reactions:





The two products from the reaction, gypsum and calcium sulfoaluminate, have a larger volume than the compounds they replace, hence, the sulfate attack leads to expansion in the volume and disruption of the concrete.

Gypsum and calcium sulfoaluminate, which are formed as shown earlier, are more soluble in sodium chloride, hence, these are leached out by seawater. However, their absorption leads to an increase in the chloride contents which are responsible for the corrosion of reinforcing steel[17].

In river water, we note the lowest corrosion rates compared with seawater and domestic water. This phenomenon may be attributing to presence of clay and other ions which may be fill the pores in concrete and prevent calcium carbonate to presence on pores, in addition to react the CO<sub>2</sub> with other constitutes in river water instead of react it with calcium hydroxide. This result is good agreement with the cyclic polarization test figure(4) that shows that the forward scan the same the reverse scan compared with other waters. This means that river water is more appropriate than sea and domestic water for reducing carbonation of reinforced steel.

Figure (7) to (10) illustrate the optical microscope of corroded steel surface in aerated and carbonated conditions. Appearance of corroded surface supported the corrosion results.

**Table (1): Chemical composition of reinforced steel.**

Metal	C	Si	Mn	P	S	Cr	Mo	Ni	Al	Co	Cu	V	Fe
Wt%	0.324	0.385	1.08	0.032	0.015	0.013	0.015	0.040	0.003	0.010	0.067	0.009	Bal.

**Table (2): pH of different waters used in this work.**

pH	Simulated seawater	River water	Domestic water
Before test	8.31	8.09	8.27
After immersion reinforced steel for 7d	9.21	8.20	10
After carbonation	4.92	5.25	5.26

**Table (3): Corrosion parameters for carbonation of reinforced steel in different mixing waters at room temperature.**

Type of water		-E <sub>corr</sub> mV	i <sub>corr</sub> µA.cm <sup>-1</sup>	Tafel slop mV.dec. <sup>-1</sup>		CRx10 <sup>-2</sup> mm/y
				-b <sub>c</sub>	b <sub>a</sub>	
Artificial seawater	Aerated	589.2	0.8196	76.9	98.9	0.9510
	Carbonated	609.8	5.1600	89.9	100.2	5.9800
River Water	Aerated	913.9	0.2970	85.7	113.9	0.3450
	Carbonated	312.7	0.0172	88.5	89.9	0.0199

<b>Domestic water</b>	Aerated	349.7	1.5900	111.3	125.7	1.8400
	Carbonated	408.8	0.0195	135.5	148.9	0.0227

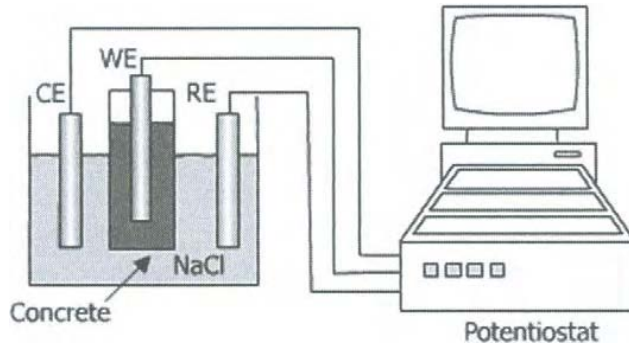


Figure (1): Set-up system for corrosion test.

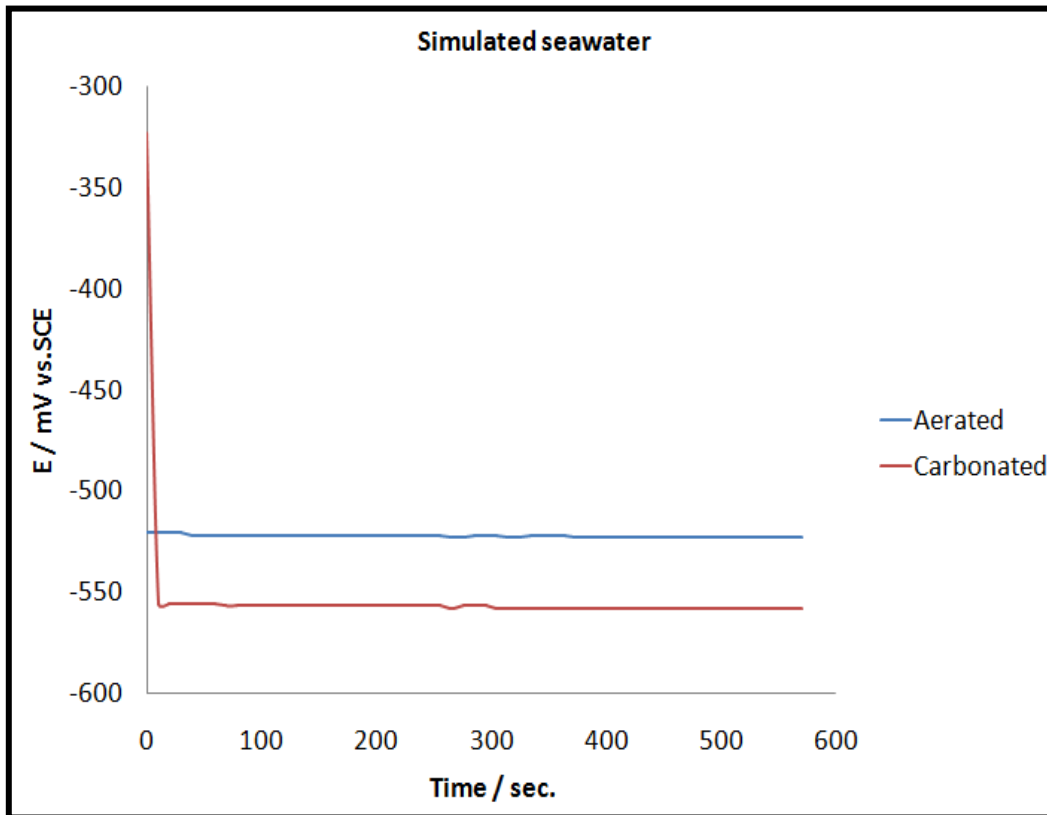




Figure (2): The variation of potential with time for reinforced steel in simulated seawater.

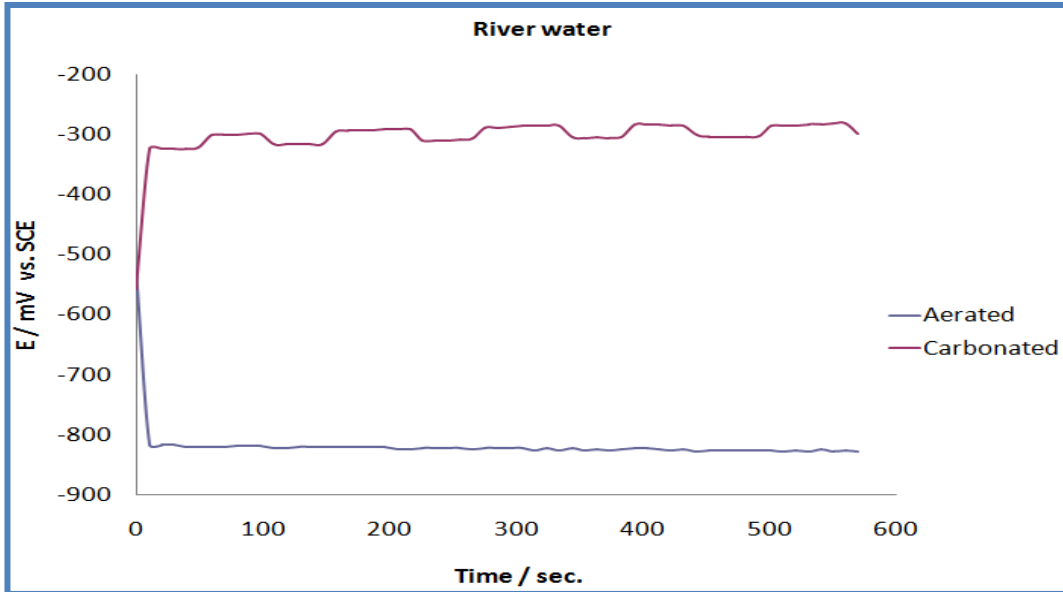


Figure (3): The variation of potential with time for reinforced steel in River water.

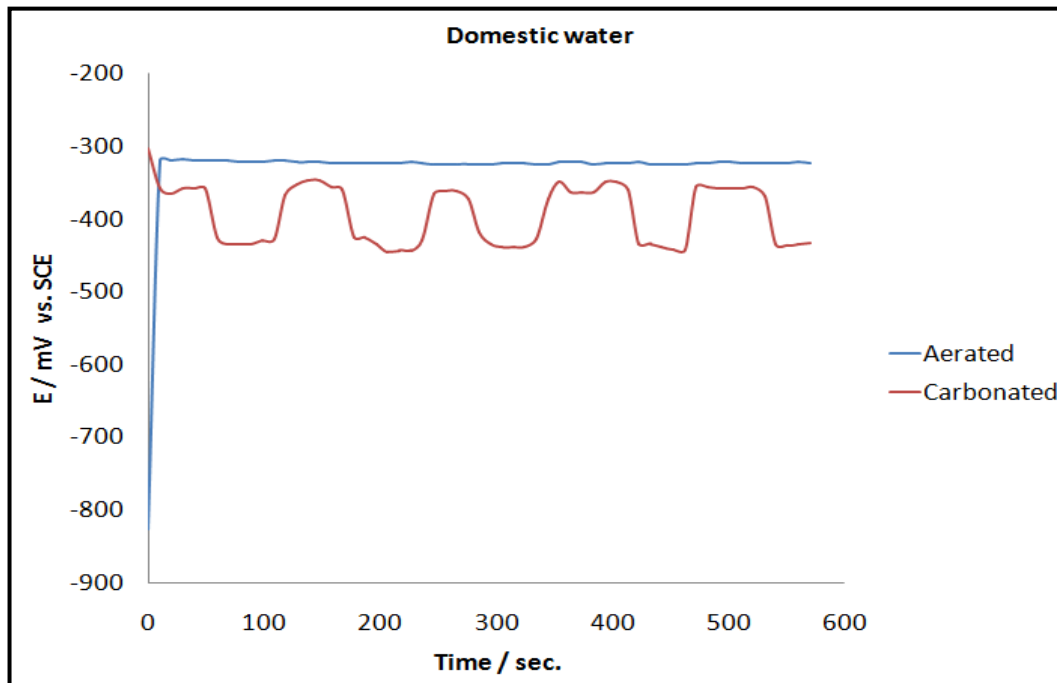


Figure (4): The variation of potential with time for reinforced steel in Domestic water.

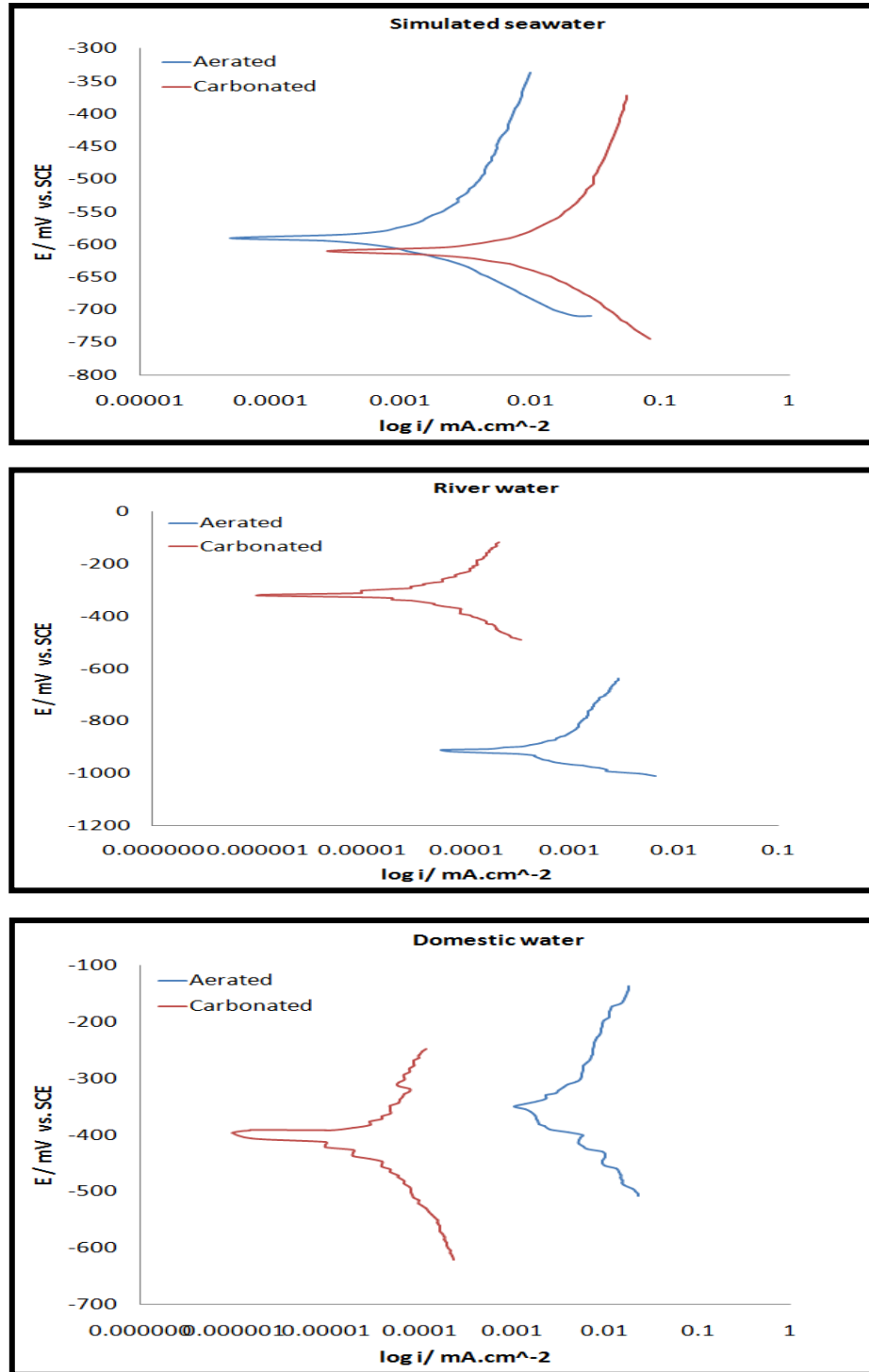


Figure (5): Tafel plot for reinforced steel in different water.

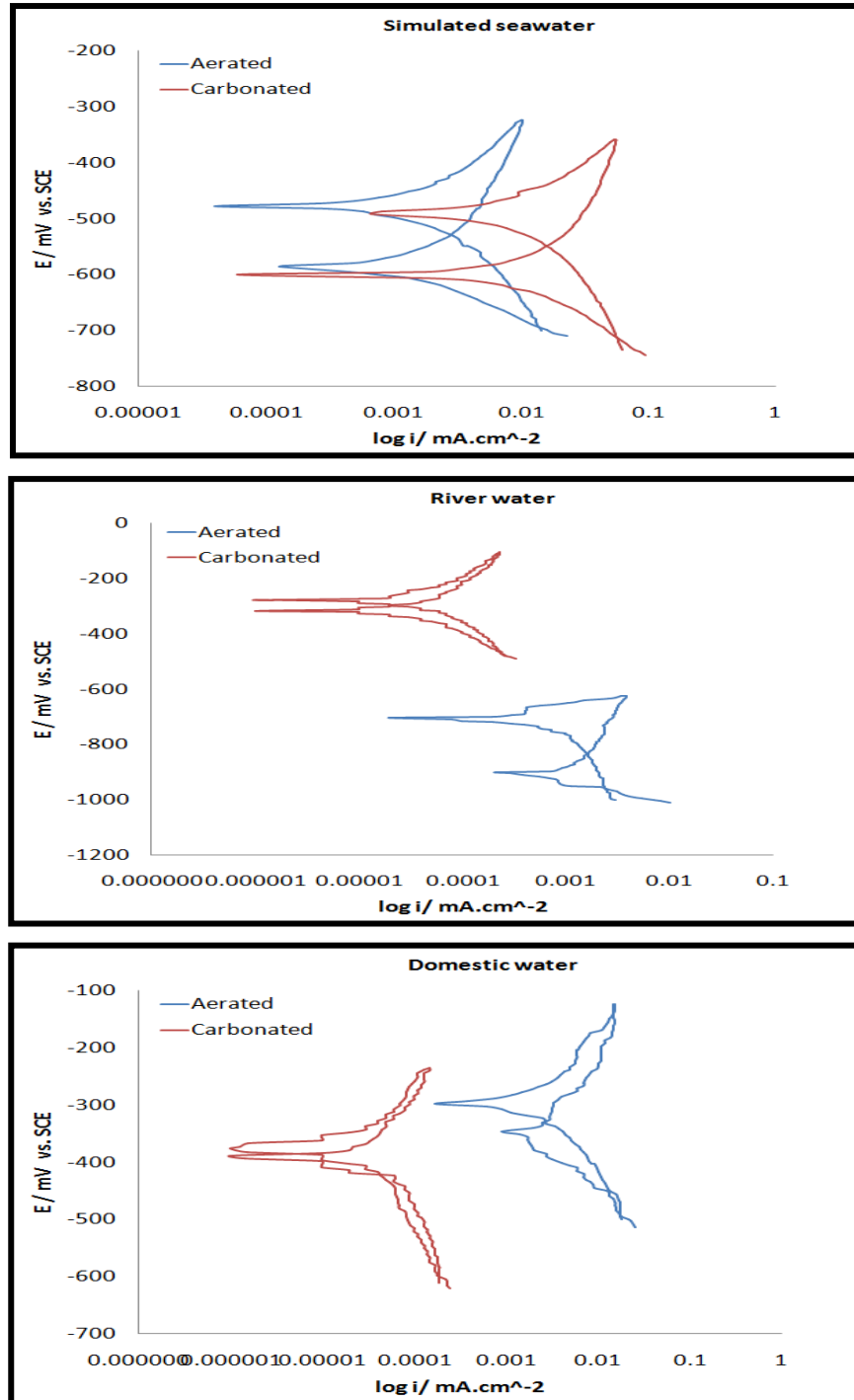


Figure (6): Cyclic polarization for reinforced steel in different water.

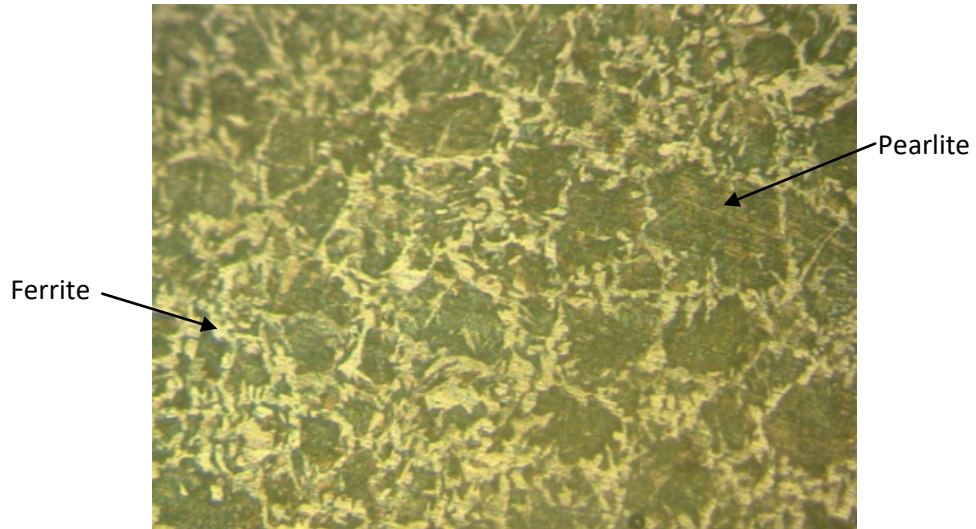
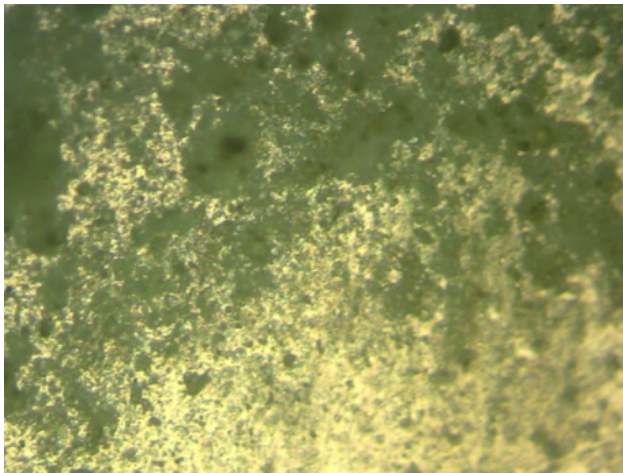
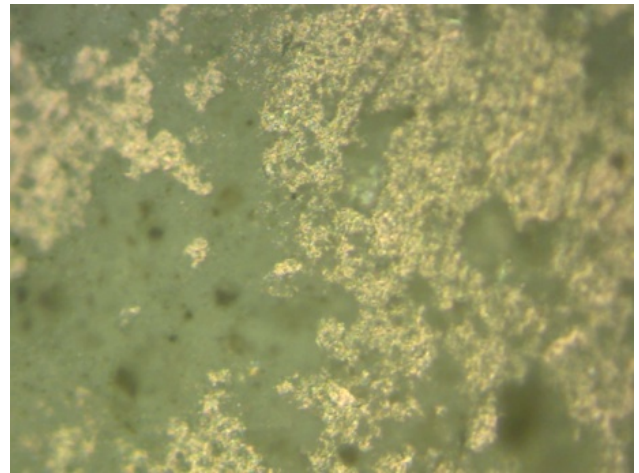


Figure (7): Optical microscope examination (20 X) of corroded surface for Reinforced steel as received

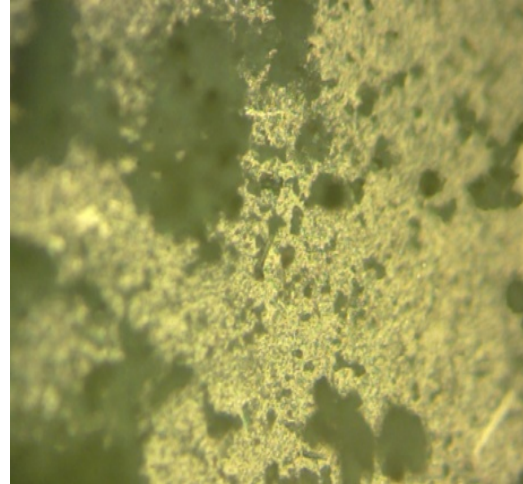
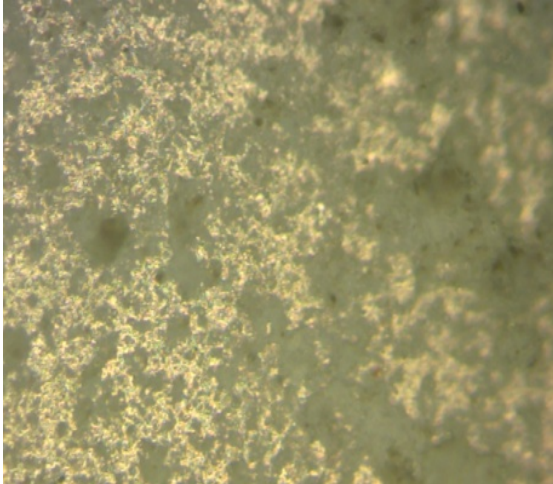


Aerated seawater



Carbonated seawater

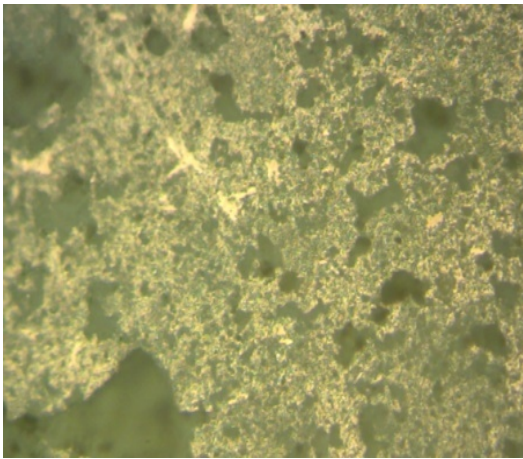
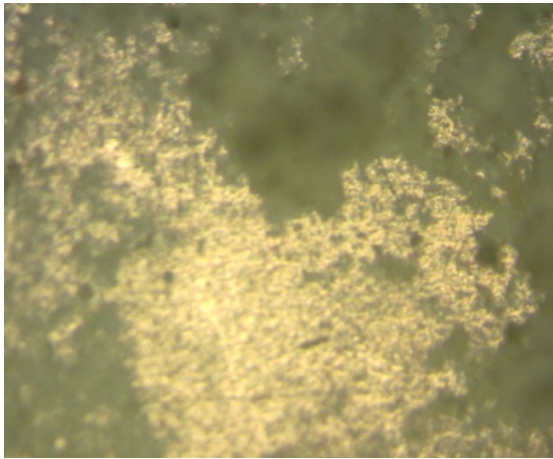
Figure (8): Optical microscope examination (20 X) of corroded surface for Reinforced steel in seawater



**Aerated river water**

**Carbonated river water**

**Figure (9):Optical microscope examination (20 X) of corroded surface for Reinforced steel in river water**



**Aerated domestic water**

**Carbonated domestic water**

**Figure (10):Optical microscope examination (20 X) of corroded surface for Reinforced steel in domestic water.**

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