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Zamzam Water as Corrosion Inhibitor for Steel Rebar in Rainwater and Simulated Acid Rain

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***Abstract*—**Corrosion inhibitors are widely used in concrete industry to reduce the corrosion rate of steel rebar which is present in contact with aggressive environments. The present work aims to using Zamzam water from well located within the Masjid al-Haram in Mecca, Saudi Arabia 20 m (66 ft) east of the Kaaba, the holiest place in Islam as corrosion inhibitor for steel in rain water and simulated acid rain. The effect of Zamzam water was investigated by electrochemical impedance spectroscopy (EIS) and Potentiodynamic polarization techniques in Department of Civil Engineering - IUT Saint-Nazaire, Nantes University, France. Zamzam water is considered to be one of the most important steel corrosion inhibitor which is frequently used in different industrial applications. Results showed that zamzam water gave a very good inhibition for steel corrosion in rain water and simulated acid rain.

***Keywords*—**Zamzam water, corrosion inhibitor, rain water and simulated acid rain.

I. Introduction

ZAMZAM water according to Islamic belief, it is a miraculously-generated source of water from God, which began thousands of years ago when Abraham's (Ibrāhīm) infant son Ishmael (Ismāīl) was thirsty and kept crying for water [1]. The name of the well comes from the phrase Zomë Zomë, meaning 'stop flowing', which, according to legend, was a command repeatedly by Hagar mother of Ishmael during her attempt to contain the spring water [2].

Zamzam water is unique in its natural characteristics; successful, useful for plants and treat communicable diseases such as special optical parameters, Changes in Growth in Lentils ,a strong anti-inflammatory, reduce the size of tumor and Ameliorates Oxidative Stress and Reduces Hemoglobin A1c in Type 2 Diabetic Patients that are different from those of bottled drinking and distilled water [3]-[7]. A total of 34 elements have been found with calcium (Ca), magnesium (Mg), sodium (Na) and chloride (Cl) in the highest concentrations. Hydrochemical studies of Zamzam water have indicated that it is a sodium chloride water and of meteoritic origin. The four toxic elements arsenic (As), cadmium (Cd), lead (Pb), and selenium (Se) have been found below the danger levels for human consumption [3]. In the present work Zamzam water has special corrosion inhibition qualities due to its higher content of Calcium and Magnesium Salts and fluorides.

The aim of this work is to explore corrosion inhibition of steel by using zamzam water i.e. its ability to reduce the corrosion rate and its spread.

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II. Experimental

A. Laboratory Analysis

The analyses for Zamzam water were carried out at the King Abdul Aziz City of Science and Technology (KACST). The analysis were for sodium (Na), calcium (Ca), magnesium (Mg), potassium (K), chloride (Cl), fluoride (Fl), nitrate (NO_3), bicarbonate (HCO_3), and sulphate (SO_4). The pH and the total dissolve alkalinity (TDS) were also measured using different instruments as shown in the (Table I).

TABLE I
Chemical Analysis of Tap and Zamzam Water [8], [9]

Elements	Tap Water	Zamzam well water [a]
Na	37.8	133
Ca	75.2	96
Mg	6.8	38.88
K	2.7	43.3
HCO_3	70.2	195.4
Cl	73.3	163.3
Fl	0.28	0.72
NO_3	2.6	124.8
SO_4	107	124
pH	7.2	8
TDS	350	835

[a]Note: all values except pH are in mg/l

B. Corrosion within Two Solutions Rainwater and Acid Rain

Firstly, the natural rainwater (RW) in Loire-Atlantique France (with pH around 7.8) was investigated. Secondly, acid rain (AR) solution, prepared from distilled water and analytical grade reagents. Composition of Acid rain is listed as follows: 35.90 mg dm^{-3} SO_4^{-2} ,1.08 mg dm^{-3} NO_3^{-1} ,0.152 mg dm^{-3} Cl^-,3.37 mg dm^{-3} $NH4^{+1}$,4.80 mg dm^{-3} Ca^{+2},0.063 mg dm^{-3} $K^{+1}$and 0.103 mg dm^{-3} Na^{+1}. The pH value of the solution ranged from 3 to 2.5 with the addition of sulphuric acid [10].

C. Electrochemical Cell

The cell is a straight-sided glass jar that had a wide mouth covered with a plastic cap with three holes to fit the two electrodes and thermometer. Experiments were conducted using carbon steel bars (Deformed bar) with a diameter of 8 mm which is called working electrode. Saturated calomel electrode (reference electrode) used to measure the potential of the working electrode and titanium/platinum used as counter electrode Fig. 1.

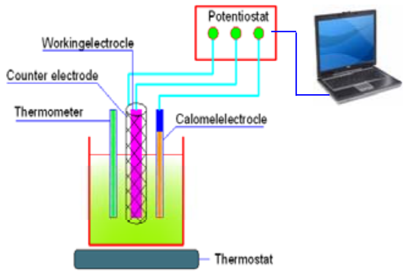

Fig. 1 Cathodic electrochemical treatment (CET)

Before being tested as per ASTM [G1-03] [11] the working electrodes were cleaned by a pickling solution for the removal of unwanted deposits or rust over the surface of the rods. Carbon steel samples were dipping in a pickling solution consist of 184 milliliters hydrochloric acid (37%), 2g hexamethylene tetra mine and the balance deionized water to make 1 liter of solution. After cleaning, the bars were rinsed, dried with hot forced-air, and weighed to the nearest 0.0001 gram. Finally, the cleaned bars were photographed and stored in dessicators to prevent further atmospheric corrosion. During this treatment vinyl examination gloves were worn to prevent contamination. The chemical compositions of the metals under investigation and the parameters used in corrosion rate calculations for the metals under investigation are shown in Table II.

TABLE II
CHEMICAL COMPOSITION OF CARBON STEEL

Metal	C (%) Max	Mn (%) Max	Si (%) Max	N(%) Max	S (%) Max	P(%) Max	CEV (%) Max
Carbon Steel	0.22	0.58	0.18	0.013	0.05	0.05	0.52

D. Electrochemical Measurement

This investigation is carried out by using direct current DC measurements techniques (open circuit potential E_{OC}, linear polarization LP and potentiodynamic scan GC). The Electrochemical Impedance Spectroscopy (EIS) technique was used to investigate the change in the electrochemical properties of the passive film formed on the metal surface when steel is immersed in two solutions. The electrochemical measurements were carried out after 3 days of immersion.

III. RESULTS OF CARBON STEEL IMMERSED IN RAINWATER ADMIXED WITH ZAMZAM WATER AS CORROSION INHIBITOR

A. Potentiodynamic Polarization Results

Potentiostatic cathodic polarization was carried out in rainwater RW with different dosage of natural Zamzam water Fig. 2. The various electrochemical parameters were calculated from Tafel plots and shown in Table III. The corrosion current density (Icorr) was calculated by extrapolating the cathodic Tafel line to the steady state potential (corrosion potential).

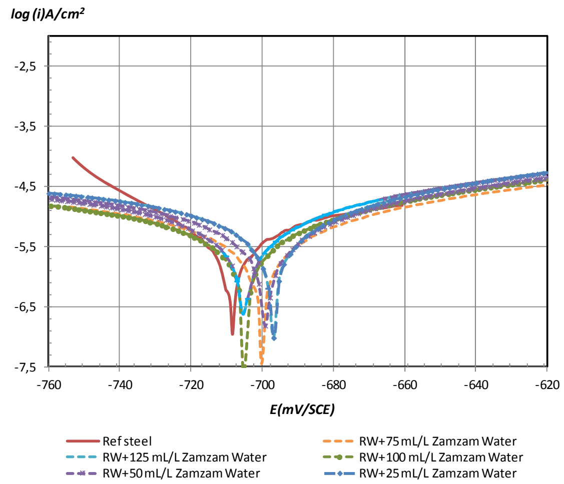

Fig. 2 Potentiostatic polarization of steel in inhibited and uninhibited Rainwater solutions by zamzam water

It is found from Fig. 2 and Table III that the presence of natural Zamzam water slightly shifted the corrosion potential towards the cathodic direction. The inhibition efficiency increased with decrease of natural Zamzam water dosage. It is of interest to note that the values of inhibition efficiency are higher than those obtained by tap water. This result may be due to an adsorption of natural Zamzam water molecules at the electrode surface. This adsorption results in decrease in the rate of anodic dissolution of the electrode.

TABLE III
INHIBITION EFFICIENCY FOR DIFFERENT DOSAGE OF NATURAL ZAMZAM WATER

Dosage (ml/l)	Inhibition Efficiency % inh	-Ecorr (mV)	Icorr (μA/cm2)
0.00	-	713.2	3.21
25	69.158	690.3	0.99
50	65.732	695.7	1.1
75	62.616	700.1	1.2
100	60.124	708.2	1.28
125	50.467	710.2	1.59

Guidance for interpretation of results is given in the ASTM standard C876-99[12]. The systems showing that potentials lesser negative than−276 mV versus SCE are treated as passive systems and systems showing more negative than −276 mV versus SCE are treated as active. The rest potentials increase with time suggesting that the inhibiting action occurred by simple blocking of the available cathodic and anodic sites on the metal surface.

The percentage of inhibition efficiency (%inh) were calculated from polarization measurements using the relation

$$\%inh = ((i_0 - i)/i_0) \times 100$$

where i_0 and i are the corrosion current density in the absence and presence of Zamzam water. In Fig. 3 according to RILEM studies [13], 4 ranges of corrosion activity can be distinguished from negligible (<0.1 μA/cm^2), to weak (0.1μA/cm^2), to moderate (–1μA/cm^2) and up to high (1–10 μA/cm^2). However, it is generally observed that, when Zamzam water dosage decrease the corrosion current density (Icorr) decreases and the % inhibition increase.

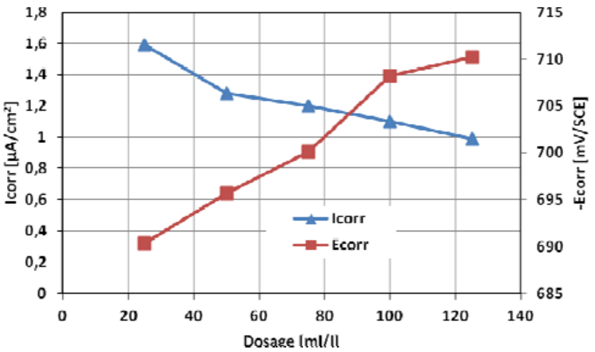

Fig. 3 Variations of the Icorr and Ecorr values against the dosage of Zamzam water in RW solution

B. Electrochemical Impedance Spectroscopy Results

The impedance response in the Nyquist plots consisted of characteristic semicircles Fig. 4. These semicircles are of a capacitive type whose size increases with decreasing **the** dosage of Zamzam water; a further increase of the Zamzam water dosage leads to a decrease in the size of the semicircle.

These plots have characteristic semicircles of a capacitive type whose size depends on the type and chemical constituent of Zamzam water molecules.

The order of increasing the size of the semicircle is:

125 ml/L < 100 ml/L < 75 ml/L < 50 ml/L < 25 ml/L

This behaviour suggests that the semicircles are corresponding to an adsorption film of Zamzam water molecules on steel surface. These deposits may be formed from a wide variety of simple and complex inorganic inhibition salts of calcium carbonate, calcium sulfate, magnesium hydroxide, calcium fluoride and calcium phosphate which accumulate on the metallic surfaces of water usually useful in providing inhibition.

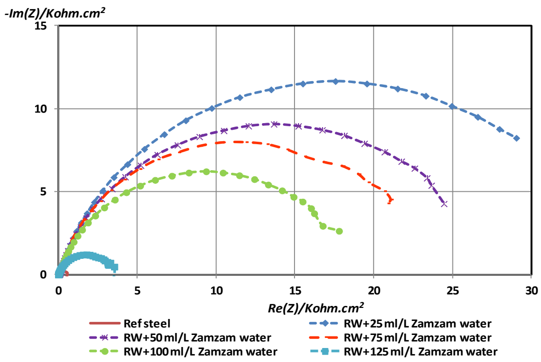

Fig. 4 Nyquist plots for different dosage of Zamzam water in WR solution

The impedance spectra for different Nyquist plots were analyzed by fitting the experimental data to a simple equivalent circuit model $R_{el}+C_f/R_f+C_{dl}/R_{ct}$ for steel treated with inhibitors (Fig. 5) which includes the solution resistance R_{el} and the double layer capacitance (Cdl) which is placed in parallel to charge transfer resistance element, Rct. The Rct value is a measure of electron transfer across the surface and is inversely proportional to corrosion rate.

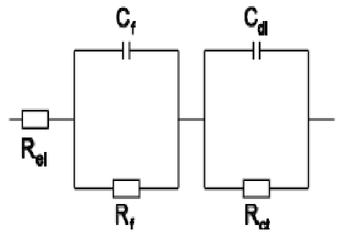

Fig. 5 Representative circuit used to fit EIS

C. The Inhibition Efficiency with Rct and Cdl Values

The values of Rct and Cdl for steel treated by different dosage of Zamzam water are shown in Fig. 6. The data indicate that increasing charge transfer resistance is associated with a decrease in the double layer capacitance.

The numerical values for the critical concentration of different dosage of Zamzam water and the corresponding percentage inhibition are given in Table IV. The % inh were calculated from impedance measurements using the relation

$$\%inh = ((R_{ct} - R_{ct0}) / R_{ct}) \times 100$$

where Rct_0 and Rct are the charge transfer resistances in the absence and presence of Zamzam water.

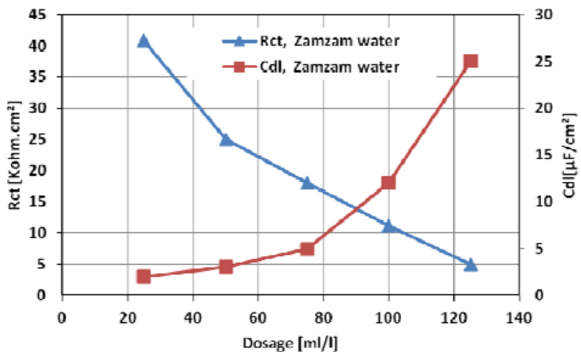

Fig. 6 Variations of the Rct and Cdl values against the concentration of Zamzam water in RW solution

The values of % inh are in quite good agreement with the results obtained previously from polarization measurements (Table III). This demonstrates the fact that the corrosion rate depends on the chemical nature of the electrolyte and the temperature of the medium, rather than the applied technique.

TABLE IV
ZAMZAM WATER DOSAGE (ML/L) AND PERCENTAGE INHIBITION EFFICIENCY (% INH) IN RW

Zamzamwater	25	50	75	100	125
% inh	69.0	65.1	63.6	60.0	50.3

IV. RESULTS OF CARBON STEEL IMMERSED IN ACID RAIN ADMIXED WITH ZAMZAM WATER AS CORROSION INHIBITOR

A. Potentiodynamic Polarization Results

Fig. 7 and Table V reveal that, the corrosion potential shifts to the noble direction as the inhibitor dosage is decreased. It is of interest to note that the natural Zamzam water has high inhibition efficiency toward steel corrosion in high acid water.

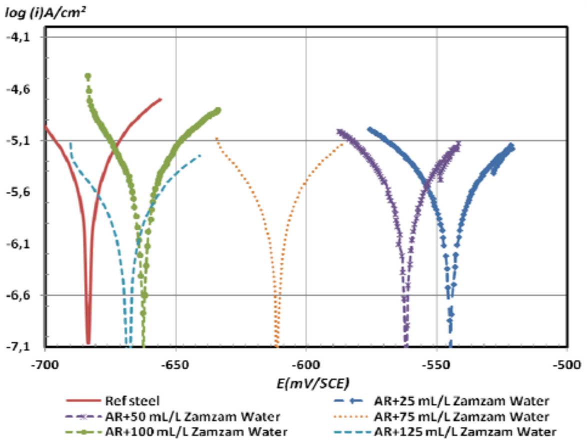

Fig. 7 Potentiostatic polarization of steel in inhibited and uninhibited Acid rain solutions by zamzam water

The value of inhibition efficiency increases with decrease in Zamzam water dosage. Table V show also that, there is almost no change in the values of anodic reaction in absence and presence of Zamzam water. On the other hand, there is a considerable change in the values of the cathodic Tafel constant in presence of Zamzam water. This result suggests that, the presence of Zamzam water may change the mechanism of cathodic reaction and did not affect the anodic dissolution mechanism.

TABLE V
INHIBITION EFFICIENCY FOR DIFFERENT DOSAGE OF NATURAL ZAMZAM WATER

Dosage (ml/l)	Inhibition Efficiency % inh	-Ecorr (mV)	Icorr ($\mu A/cm^2$)
0.00	-	683.2	5.15
25	89.51	538.2	0.54
50	86.40	560.2	0.7
75	82.52	615.1	0.9
100	75.14	660.7	1.28
125	68.73	665.3	1.61

The values of Icorr and Ecorr for steel treated by different dosage of Zamzam water are shown in Fig. 8. However, it is generally observed that, when Zamzam water dosage decrease the corrosion current density (Icorr) decreases, the rest potentials increase and the % inhibition increase.

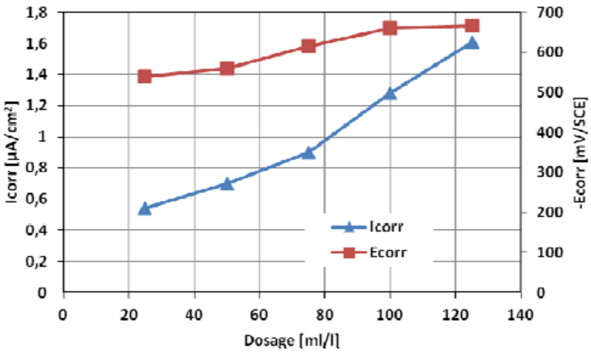

Fig. 8 Variations of the Icorr and Ecorr values against the dosage of Zamzam water in AR solution

B. Electrochemical Impedance Spectroscopy Results

The Nyquist plots of impedance data for steel treated by different Zamzam water dosage in AR are shown in Fig. 9. Semicircles are increases with decreasing the dosage of Zamzam water. The results of the water samples tested by the European laboratories showed that Zamzam water has a special physique that makes it advantageous water.

The main difference between Zamzam water and other water (city water) was in the quantity of calcium and magnesium salts, the content of these was slightly higher in Zamzam water, but more significantly, the water contains fluorides that have an effective inhibition for steel. Moreover, the remarks of the European laboratories showed that the water was germicidal action and fit for drinking [13].

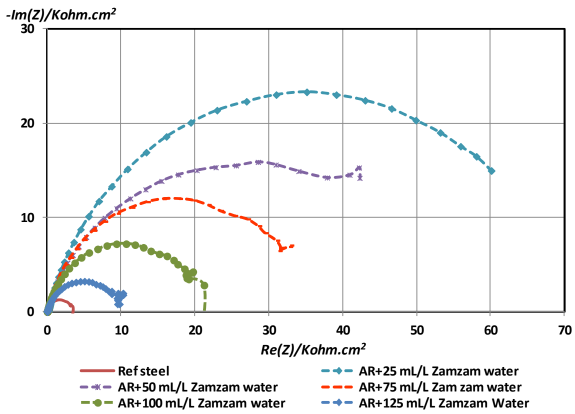

Fig. 9 Nyquist plots for different dosage of Zamzam water in AR solution

C. The Inhibition Efficiency with Rct and Cdl Values

It is found from Fig. 10 the inhibition efficiency with values of Rct and Cdl increases with an increase of natural Zamzam water dosage. The values of % inh are in quite good agreement with the results obtained previously from polarization measurements (Table VI).

TABLE VI
ZAMZAM WATER DOSAGE (ML/L) AND PERCENTAGE INHIBITION EFFICIENCY (% INH) IN AR

Zamzam water	25	50	75	100	125
% inh	89.0	85.9	82.6	75.3	68.3

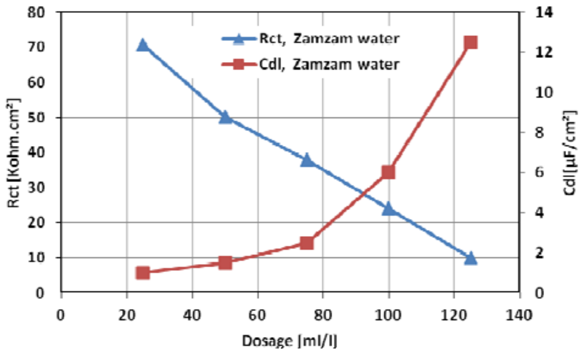

Fig. 10 Variations of the Rct and Cdl values against the dosage of Zamzam water in AR solution

V. Conclusion

The Zamzam water can be used as excellent corrosion inhibitors for steel in simulated acid rain and rain water .The inhibition efficiency for acid rain are higher than those obtained by rain water. Zamzam water can be used to reduce the corrosion rate of metals in contact with acid environments

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