CORROSIVE BEHAVIOR OF IRON ALLOY WITH VARIABLE OXYGEN CONCENTRATION IN PRESENCE OF INORGANIC ACIDIC MEDIUM

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ABSTRACT: - Studied iron alloy by Non electrochemical techniques (weight loss method) and electrochemical techniques by polarization techniques, and electrochemical impedance spectroscopy, Polarization studies showed the corrosion currant and corrosion potential, the electrochemical impedance studies the corrosion rate of metal alloys in inorganic acidic medium.

KEYWORD: Metal alloy corrosion, Potentiodynamic polarization, electrochemical impedance.

1. INTRODUCTION:

Corrosion monitoring techniques can be classified into two major categories viz non electrochemical techniques and electrochemical techniques. Traditionally the non electrochemical techniques are widely used through the industry due to their simplicity[-ii], robustness and reliability. However, the drawback of these techniques is that they do not reveal any details about corrosion mechanisms[iii-v]. On the other hand the electrochemical measurements provide a great deal more with regard to the corrosion mechanism. Corrosion is an electrochemical process[-viii], therefore electrochemical methods were designed as a preliminary investigation into the applicability of each technique for more detailed research into metal corrosion[-x]. Laboratory studies using electrochemical techniques such as corrosion current measurements and linear polarization resistance tests have been used in static and flowing conditions with and without inhibitor to identify the corrosion rates of each region of the metal[-xii]. The main advantages of the electrochemical methods are short measuring times, high measurement accuracy and the possibility of continuous corrosion monitoring[xiv-xv].

Corrosion is defined as the destruction or deterioration of a material due to a chemical or an electrochemical reaction with its environment[xvi-xvii], Corrosion behavior of a material is mainly determined by its structure and composition there are several ways of classifying corrosion, One method divides corrosion into low temperature and high temperature corrosion, Electrochemical corrosion reactions are conveniently divided into Dry corrosion which is mainly concerned with the oxidation of a dry metal surface and Wet corrosion in which the reactions occur in an environment under normal conditions[xviii-xx], corrosion behavior of a material is quantitatively expressed in terms of corrosion rates corrosion rates have been

expressed in a variety of ways in the literature[xxi-xxiii], such as percent weight loss, grams per square inch per hour and milligrams per square decimeter per day (mdd).

The parameters, which affect the corrosion rate of a material, can be broadly classified as:

(a) Solution of chemistry (Environmental): concentration, pH, temperature, velocity, conductivity, presence of foreign ions, aging of the medium, exposure period, type of exposure (alternate, partial, total submersion etc.), bacteria, microbes etc[xxiv-xxvi].

(b) Metallurgical: microstructure, grain orientation, texture, alloy composition and purity, presence of defects etc.

(c) Mechanical presence of stress (applied, residual and thermal), rate of application, type of stress (tensile, compression or cyclic), strain rate, notches, application of stress before or after exposure to medium.

2. EXPRIMENTAL:

Corrosion rates can be determined by the Non-electrochemical method and electrochemical method.

2.1 Materials:

Material having compositions of 0·08% Phosphorus, 0·27% Silicon, 0·01% Aluminum, 0·04% Manganese, 0·15% C, 0·04% Sulphur and the remaining Iron were used for the electrochemical polarizations and impedance measurements. The samples of 1×1 cm area were ground with different emery papers of grades 120, 320, 400, 800, 1000 and 2000; they were degreased with AR grade ethanol, acetone and dried at room temperature and then stored in desiccators before use. The acid solutions were made from analytical grade 34% HCl by diluting with double-distilled water.

2.2 Weight loss method:

The weight loss measurements enable us to illustrate the importance of the environment in the process of rusting, weight loss method is Non-electrochemically, the rate of corrosion is determined by the conventional weight loss technique Using this technique, the loss of a metal due to corrosion is measured by exposing the metal specimen of known area to the corrosive environment for a particular period and finding the difference in weight before and after exposure The expression 'mils per year' (mpy) is the most widely used way of expressing the corrosion rate, Corrosion rate is calculated using the formula,

Corrosion Rate (mpy) = $\dfrac{534\ W}{DAT}$

Where,

W = Weight loss in mg.

D = Density of the specimen in g/cm.

A = Area of the specimen in sq.

T = Exposure time in hr.

The weight loss measurements were carried out by weighing the prepared material before and after immersion for 24, 48, 72, 96, 120 hours in 50 ml of inorganic acidic solutions (HCl, H_2SO_4, HNO_3) in the presence and absence of various concentrations of Amoxicillin and variable concentration of oxygenation. From the weight loss data, the percentage inhibition efficiency (IE %) was calculated at different concentrations at 30 ºC using following equation.

$$IE\% = 100 \times \frac{W_0 - W_{corr}}{W_0}$$

Where,

IE% : Inhibition efficiency.

W_{corr} : Corrosion rates of iron with inhibitor.

W_0 : Corrosion rates of iron without inhibitor.

2.3 Electrochemical method:

This technique uses data obtained from cathodic and anodic polarization measurements. Cathodic data are preferred, since these are easier to measure experimentally. The total anodic and cathodic polarization curves corresponding to hydrogen evolution and metal dissolution are superimposed as lines. It can be seen that at relatively high applied current densities the applied current density and that corresponding to hydrogen evolution have become virtually identical. To determine the corrosion rate from such polarization measurements.

At the corrosion potential, the rate of hydrogen evolution is equal to the rate of metal dissolution in inorganic acidic medium (HCI, H_2SO_4, HNO_3), and this point corresponds to the corrosion rate of the system expressed in terms of current density. Polarization curve must be calculated from both the anodic and cathodic portions of the polarization curve. The units of the polarization curve are V/decade. A decade of current is one order of magnitude. A polarization curve calculation is illustrated in Figure. These measurements may be complicated by interfering phenomena of concentration polarization. Concentration polarization occurs when the reaction rate is so high that the electro active species cannot reach the electrode surface at a sufficient rapid rate and the reaction rate becomes diffusion controlled.

2.4 Electrochemical impedance spectroscopy:

The electrochemical measurements are performed using a Zive SP5 electrochemical workstation. A conventional three-electrode cell is used. It contains the platinum electrode as the auxiliary electrode, the saturated calomel electrode (SCE) as the reference electrode, and the iron sample as the working electrode. The iron samples are cut into $1\times1\times1cm$ dimensions, only $1cm^2$ is exposed to air, and other sides are coated with an insulating material. The samples are ground with a series of SiC waterproof abrasive papers from 200# to 2000#, washed with acetone and ethanol, and then dried in the air. In electrochemical experiment, all the conditions are the same as accelerated corrosion experiments.

Electrochemical impedance spectroscopy measurements were conducted using an electrochemistry system in a conventional three-electrode electrolyte cell with a saturated calomel reference electrode (SCE) and a platinum rod counter electrode. The sample was the working electrode immersed in the cell containing inorganic acidic solution, presence and absence of inhibitor (Amoxicillin). The working electrode surface area exposed to the inorganic acidic solution was 1-2 cm^2. The amplitude of applied AC potential was 10 mV and the frequency range was from 1µHz to 1 M Hz. Impedance spectra were measured at the open-circuit potential (OCP) immediately after the samples were immersed in the solution. Their EIS spectra were measured immediately after immersion (i.e., at 0 h).

2.5 Field Emission Scanning Electron Spectroscopy:

The surface morphology of the corroded iron sample immersed in inorganic acidic solution was studied by using field emission scanning electron microscopy. The immersion time of the sample for SEM analysis was 24 hours, immediately after the corrosion tests, the samples were subjected to SEM studies to know the surface morphology of corroded iron sample by Hitachi S-4800 SEM was used for the experiments.

3. RESULTS AND DISCUSSION:

3. 1 Weight loss Method:

From the observation it reveals that, corrosion rate of iron and weight loss of iron is decreases in presence of organic inhibitor (Amoxicillin). Corrosion rate of iron and weight loss of iron are maximum in fully saturated oxygenation as comparative to saturated oxygenation and absence of oxygenation in absence of organic inhibitor Amoxicillin. Also corrosion rate and

weight loss of iron are decrease in absence of oxygenation and saturated oxygenation as comparative fully saturated oxygenation in presence of organic inhibitor Amoxicillin. Inhibition efficiency of corrosion rate and weight loss of iron is increases in concentration of amoxicillin increases in acidic solution.

Acid	O_2fully Saturated	O_2Saturated	O_2Absent	O_2fullySaturated (Inhibitor)	O_2Saturated (Inhibitor)	O_2Absent (Inhibitor)
HCI	1.23	1.18	1.01	0.91	0.86	0.91
H_2SO_4	2.24	2.20	2.01	1.35	1.28	1.10
HNO_3	1.11	1.02	0.95	0.80	0.80	0.78

Table 1 Weight loss of iron in gm. (24 Hours in 1N Solution)

Acid	O_2fully Saturated	O_2Saturated	O_2Absent	O_2fullySaturated (Inhibitor)	O_2Saturated (Inhibitor)	O_2Absent (Inhibitor)
HCI	2.08	2.01	1.98	1.55	1.58	1.8
H_2SO_4	3.06	2.76	2.72	2.76	2.60	2.55
HNO_3	1.93	1.79	1.60	1.60	1.50	1.58

Table 2 Weight loss of iron in gm. (48 Hours in 1N Solution)

Acid	O_2fully Saturated	O_2Saturated	O_2Absent	O_2fullySaturated (Inhibitor)	O_2Saturated (Inhibitor)	O_2Absent (Inhibitor)
HCI	2.44	2.33	2.33	2.20	2.14	2.11
H_2SO_4	2.88	2.89	2.87	2.10	1.98	1.80
HNO_3	2.09	1.76	1.70	1.90	1.60	1.50

Table 3 Weight loss of iron in gm. (72 Hours in 1N Solution)

Acid	O_2fully Saturated	O_2Saturated	O_2Absent	O_2fullySaturated (Inhibitor)	O_2Saturated (Inhibitor)	O_2Absent (Inhibitor)
HCI	2.39	2.36	2.35	2.24	2.21	2.19
H_2SO_4	2.77	2.96	2.95	2.34	2.33	2.28
HNO_3	2.12	1.72	1.60	1.98	1.90	1.87

Table 4 Weight loss of iron in gm. (96 Hours in 1N Solution)

| Acid	O_2fully Saturated	O_2Saturated	O_2Absent	O_2fullySaturated (Inhibitor)	O_2Saturated (Inhibitor)	O_2Absent (Inhibitor)
HCl	2.37	2.26	2.36	2.21	2.18	2.22
H_2SO_4	3.15	2.88	2.85	2.98	2.70	2.60
HNO_3	2.21	1.88	1.80	2.02	1.65	1.40

Table 5 Weight loss of iron in gm. (120 Hours in 1N Solution)

**3.2 Potentiodynamic Polarization Study:**
From the following table and plot in Potentiodynamic polarization study corrosion potential increases progressively by increasing the concentration of inhibitor Amoxicillin, and corrosion current decreases progressively by increasing the concentration of inhibitor Amoxicillin. By using the inhibitor Amoxicillin control the corrosion of metal alloys in acidic medium. There is no passivation observed of iron in inorganic acidic solution decreases the rate of corrosion concentration of inhibitor increases.
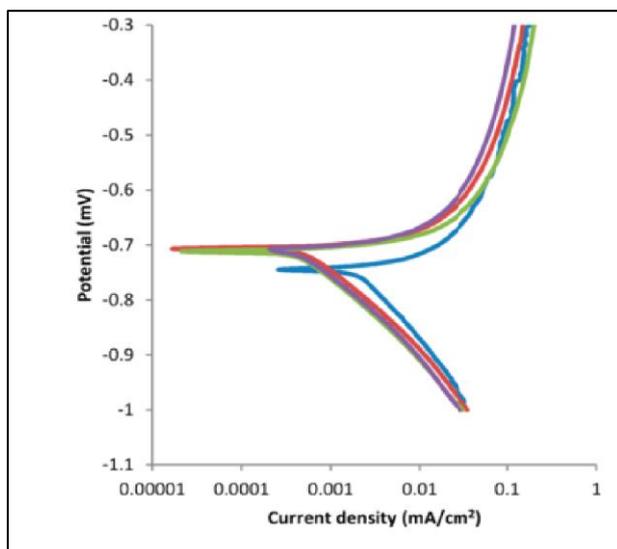
Plot 1 Polarization curves for Iron in HCl
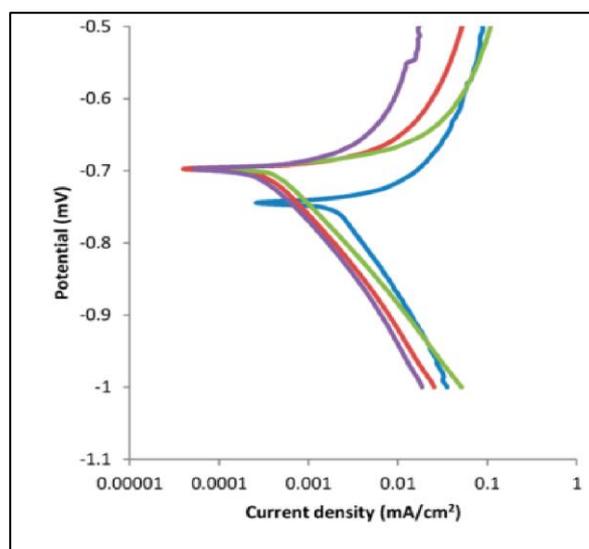
Plot 2 Polarization curves for Iron in H_2SO_4
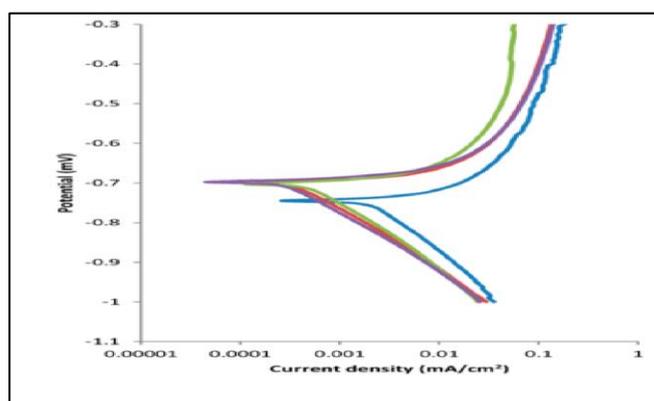
Plot 3 Polarization curves for Iron in HNO_3

HCI Acid	Corrosion Current I_{corr} (μ A cm^{-2})	Corrosion Potential E_{corr} (V_{SCE})	Inhibition Efficiency IE (%)
Blank	650	-0.50	0
0.10 gm	20.1	-0.54	96.9
0.20 gm	18.2	-0.56	97.2
0.30 gm	17.3	-0.58	97.3

Table 6 Potentiodynamic polarization parameter of iron in HCI acid

H$_2$SO$_4$ Acid	Corrosion Current I_{corr} (μ A cm^{-2})	Corrosion Potential E_{corr} (V_{SCE})	Inhibition Efficiency IE (%)
Blank	660	-0.54	0
0.10 gm	22.1	-0.56	96.6
0.20 gm	21.3	-0.58	96.7
0.30 gm	20.4	-0.60	96.9

Table 7 Potentiodynamic polarization parameter of iron in H$_2$SO$_4$ acid

HNO$_3$ Acid	Corrosion Current I_{corr} (μ A cm^{-2})	Corrosion Potential E_{corr} (V_{SCE})	Inhibition Efficiency IE (%)
Blank	640	-0.51	0
0.10 gm	20.2	-0.52	96.8
0.20 gm	19.5	-0.54	96.9
0.30 gm	18.7	-0.55	97.0

Table 8 Potentiodynamic polarization parameter of iron in HNO$_3$ acid

3.3 Electrochemical impedance spectroscopy:

Electrochemical impedance spectroscopy measurements were carried out using A Volta lab Zive SP5 Fitting with analysis program. Impedance spectra were obtained in the frequency range between 100 k Hz and 50 m Hz using 10 steps per frequency decade at corrosion potential after 30 min. of immersion in acidic solution without and with different concentrations of the studied inhibitor. AC signal with 10mV amplitude peak to peak was used to perturb the system. The following EIS plot and table are given in the Nyquist representation.

As seen from Table, the Rct values of inhibited substrates are increased with the concentration of inhibitors Amoxicillin. On the other hand, the values of Cdl are decreased with increase in inhibitor Amoxicillin concentration which is most probably is due to the decrease in local dielectric constant and or increase in thickness of the electrical double layer. The value of inhibition efficiency calculated from following equation.
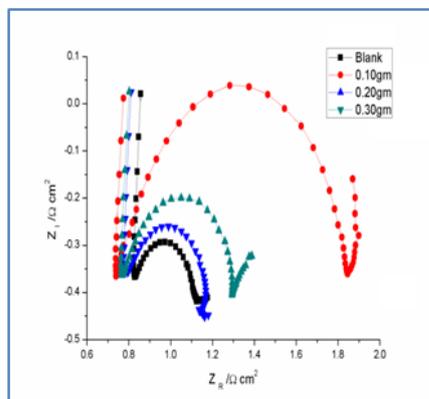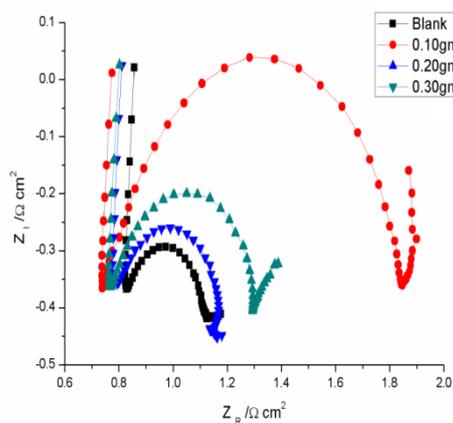
$$\%IE = \frac{(1 - R^0_{ct})}{R_{ct}}$$

Where
$R°$ and R are the charge transfer resistance in the absence and presence of different concentrations of inhibitor in inorganic acidic solution, respectively.
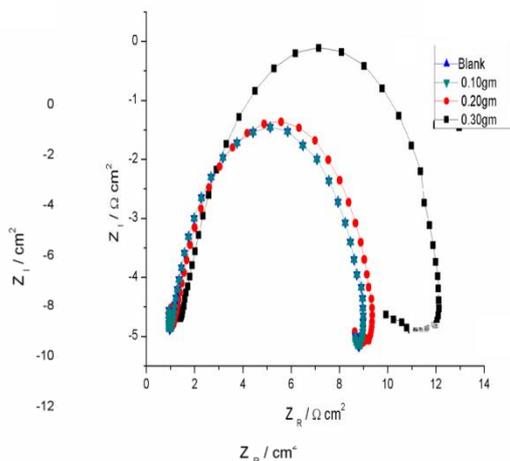
Plot 4 EIS of Iron in HCI   **Plot 5 EIS of Iron in H₂SO₄**

Plot 6 EIS of Iron in HNO₃

HCI Acid	R Ct (Ωcm⁻²)	C dl (μΩ⁻¹ cm⁻²)	Inhibition Efficiency IE (%)
Blank	180.8	2512	0
0.10 gm	318.9	1810	43.3
0.20 gm	423.8	1780	57.3
0.30 gm	587.9	1760	69.2

Table 9 EIS parameter of iron in HCI acid

H_2SO_4 Acid	R_{Ct} (Ωcm^{-2})	C_{dl} ($\mu\Omega^{-1} cm^{-2}$)	Inhibition Efficiency IE (%)
Blank	209.7	2612	0
0.10 gm	318.8	1970	34.2
0.20 gm	421.9	1940	50.2
0.30 gm	512.6	1890	59.0

Table 10 EIS parameter of iron in H_2SO_4 acid

HNO_3 Acid	R_{Ct} (Ωcm^{-2})	C_{dl} ($\mu\Omega^{-1} cm^{-2}$)	Inhibition Efficiency IE (%)
Blank	180.8	2470	0
0.10 gm	213.9	1890	15.4
0.20 gm	312.8	1850	42.1
0.30 gm	414.7	1810	56.4

Table 11 EIS parameter of iron in HNO_3 acid

3.4 Field Emission Scanning Electron Microscopy:
Surface morphology of iron was studied by scanning electron microscopy after immersion in acidic solution (HCl, H_2SO_4, and HNO_3) before and after addition of the inhibitor Amoxicillin. The micrograph obtained in absence of inhibitor Amoxicillin is more corroded.
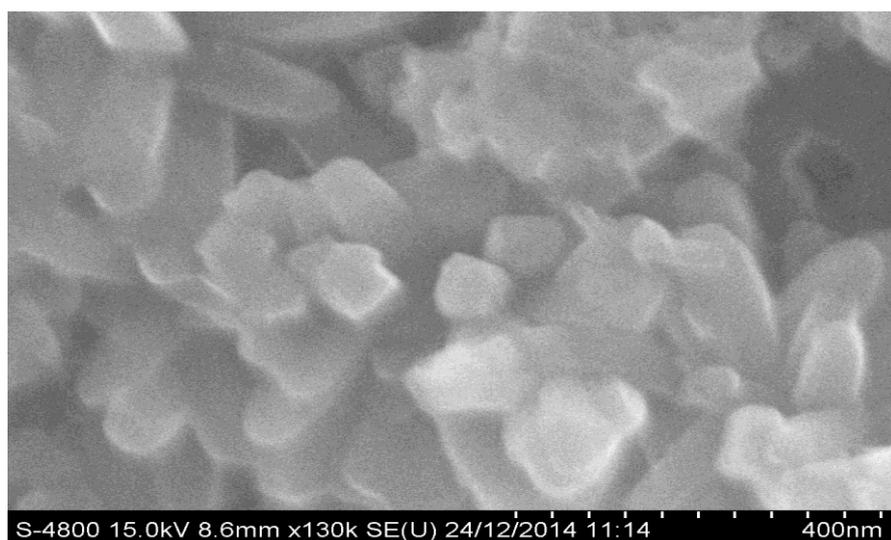
4. CONCLUSION:
From above result and discussion of corrosive behavior of iron alloy with variable oxygen concentration in presence of inorganic acidic medium, the corrosion rate of iron is maximum in absence of corrosive inhibitor and corrosion rate of iron is minimum in presence of corrosive inhibitor, it means that amoxicillin acts as good corrosive inhibitor in inorganic acidic medium, corrosion rate of iron in inorganic acidic medium are maximum in fully saturated oxygenation as comparative to corrosion rate of iron in oxygenation is absent, and corrosion rate of iron in inorganic acidic medium are minimum in oxygenation absent as comparative to corrosion rate of iron in saturated oxygenation. In result and discussion of electrochemical method of potentiodynamic polarization method corrosion current decreases and corrosion potential increases progressively it means that corrosion of iron decreases in inorganic acidic medium in presence of corrosive inhibitor, and electrochemical impedance spectroscopy the charge transfer resistance increases and double layer capacitance decreases

continuously it means that the corrosion rate of iron can be decreased in inorganic acidic medium in presence of corrosive inhibitor.

Corrosive product of iron in inorganic acidic medium can analyzed by using field emission scanning electron microscopy to give the ideas of corroded metal and protected metal.

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