

A Study Of Corrosion Behavior Of Low Carbon Steel In Acidic And Basic Washing Water Of Crude Oil Solution At Different Temperatures

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Abstract

The corrosion behavior of low carbon steel in washing water of crude oil solution has been studied potentiostatically at five temperatures in the range (303 – 343)K, at pH (4) and at pH (4,6,7,9,11) at (343K)..The corrosion potential shifted to more negative values with increasing temperature and the corrosion current density increased with increasing temperature, the corrosion current density (i_{corr}) decreased with increasing pH in the rang (4 – 7) and it increased with increasing pH in the rang (9 – 11) at (343 K), while the corrosion potential generally variation with increasing pH in the rang (4-11)at(343K. From the general results for this study can be seen that thermodynamic and kinetic function were also calculated (ΔG , ΔS , ΔH and E_a)

Key words: carbon steel , Polarization, washing water of crude oil ,corrosion behavior.

Introduction:

The corrosion of metals have received prime attention of material scientists and chemists since it has many serious adverse effects including economic, health, safety, technological, and cultural consequences. Carbon steel Corrosion is one of the major areas of concern in many industries, where acids are widely used for application such as acid pickling, acid de scaling, and oil well acidizing[1] .

In oil sands slurry, the presence of water and oxygen, combined with various salts, such as Cl^- and HCO_3^- , would result in corrosion of pipe steel, which is accelerated by the flowing slurry and the high content of sand particles .It has been recognized that the synergistic effects of corrosion and erosion can generate material loss much greater than that caused by individually[2].

The effects of temperature become more complex with varying pH and

oxygen concentrations[3]. The effect of temperature changes on the corrosion rate is more complex than the simple chemical principle that an increase in temperature increases the reaction rate. An increase in the temperature of a corroding system has 4 main effects:

- The rate of chemical reaction is increased
- The solubility of gases in the water is decreased.
- The solubility of some of the reaction products may change, resulting in different corrosion reaction products.
- Viscosity is decreased and any thermal differences will result in increased Circulation[3].

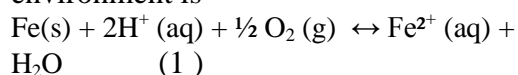
The level of dissolved oxygen plays a role in how iron dissolves, rusts and reacts. the mechanism by which

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corrosion may occur in an acidic environment is



According to the equation(1) , the electrochemical reduction of O₂ will occur with the oxidation of Fe to Fe²⁺ . As the medium becomes saturated with O₂ the dissolution of iron is expected to increase. In this scenario, the metal will be consumed and eventually lead to significant structural damage. As temperature increases, the dissolved oxygen concentration of the of solution will decrease due to the change in solubility of the oxygen allowing the oxygen to leave solution[3]

The aim of this work is to study the effect of temperature and pH on the corrosion of carbon steel in washing water solution of crude oil using potentiostatic polarization measurements.

Materials and Methods:

The corrosion tests were performed on low carbon steel samples with a composition (wt.%): C, 0.187; Mn, 1.03; Si, 0.311; S, 0.012; P, 0.007 and the remainder Fe. The specimens used for electrochemical measurements were cut into square shape with (2×2 cm²) area. and abraded through (120 , 200, 400. 600.800 and 1200) grit abrasive papers in accordance with ASTM G 61, The polishing side was polished mechanically to a mirror finish. The polished face was exposed to the electrolyte and the other exposed face enabled to give electrical connection with the help of a screw tightened against it. The specimen was degreased with acetone and washed distilled water, finally with ethanol and stored inside desiccators. These specimens were used as the working electrode. The basic solution was washing water of crude oil obtained from Washing tanks at Buzurkan oil

field in Missan governorate that used as corrosive media

The Specifications of Washing Water of Crude Oil Solution

Parameter of analysis	Results
PH	4
El Conductivity ms /cm at 25 C ⁰	180.600
Alkalinity mg/l as HCO ₃ ⁻	220
Total hardness mg/l as CaCO ₃	30450
Calcium hardness mg/l as CaCO ₃	24675
Calcium hardness mg/l as Ca ⁺²	9870
Magnesium hardness mg/l as CaCO ₃	5775
Magnesium hardness mg/l as Mg ⁺²	1386
Chloride mg/l as Cl ⁻	98140
Sulphate mg/l as SO ₄ ⁼	2880
Iron mg/l as Fe	0.33
Sulfide % as S ⁻²	4.8

Electrochemical measurements

The electrochemical system consists of potentiostate device (model Mlab 200, Germany), corrosion cell, and electrodes. Corrosion cell made of Pyrex with (1L) capacity consists of two vessels, internal and external. Chiller device was used to make the temperature of water which flows through the external vessel constant at (303 – 343) K , washing water solution of crude oil was added to the corrosion cell with stirring .Three electrodes and thermostat replaced in the internal vessel. The three electrodes consists of reference electrodes, the auxiliary electrode and the working electrode

Before each experiment, the corrosion potential was allowed to stabilize for 0.5 h in test solution. Potentiodynamic polarization curves were obtained by changing the potential automatically from -200 to

+200 mV versus open circuit potential (OCP).

Optical microscopy observation

Surface morphologies of the tested samples immersed in washing water solution of crude oil at different five temperatures (303 -343) K were observed by optical microscopy (Nikon Eclipse ME 600, Japan).

Results and Discussion :

Polarization Curve

Figs.(2) and (3) show Polarization curves for low carbon steel in washing water solution of crude oil at five temperatures in the range (303 - 343)K, at pH (4) and at pH (4,6,7,9,11) at (343K). The corrosion current densities (i_{corr}) and the corrosion potential (E_{corr}) have been obtained by extrapolation of the linear logarithmic sections of cathodic and anodic Tafel lines to the point of intersection [4] .

Tables (1) and (2) appear the electrochemical corrosion kinetic parameters, i.e. corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (b_c , b_a) and corrosion current density (I_{corr}) obtained from the Tafel extrapolation of the polarization curves. Tables (1) and (2) also included cathodic and anodic transfer coefficients α_c and α_a , Weight loss, Penetration loss, polarization resistances R_p , and equilibrium exchange current density i_o . The data of the table (1) show that the corrosion current density (i_{corr}) and corrosion potential (E_{corr}) generally increased with increasing temperature, the results of table (2) show that the corrosion current density (i_{corr}) decreased with increasing pH in the rang (4 – 7) and it increased with increasing pH in the rang (9 – 11) at (343 K), while the corrosion potential generally variation with increasing pH in the rang (4-11) at (343K) . Corrosion processes become

significantly more complex in the presence of solid scales that may form on the metal surface. In general, it is necessary to consider; (1) the precipitation equilibria on the metal surface (2) anodic dissolution processes that occur on the free surface of the metal (3) dissolution kinetics of the solid scale (4) cathodic processes on the free metal surface (5) cathodic processes on the scale surface, which are expected to be considerably slower than those on the free surface (6) local concentrations of active ions close to the metal surface, which are influenced by adsorption and mass transfer and transport of ions through scale, which depends on the permeability of the solid precipitate[5]

Tafel Slope (b) and Transfer Coefficient (α)

Tafel slopes which were obtained from the slopes of the anodic and cathodic Tafel regions of the polarization curves. Values of transfer coefficients have been calculated from the corresponding values of the Tafel slope (b) using the relation[6] .

$$\alpha_c = \frac{2.303RT}{b_c F} \quad (2)$$

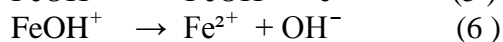
$$\alpha_a = \frac{2.303RT}{b_a F} \quad (3)$$

The tables (1) and (2) show variation in anodic Tafel slopes may be attributed to the variation of the rate – determining step in the metal dissolution reaction.

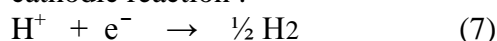
A change in mechanism as well as in the rate – determining step (rds), cannot be ignored throughout the anodic processes, while the variation of the cathodic Tafel slopes could be interpreted in the term of the variation of the rate – determining step from charge transfer process to either

chemical – desorption or to electrochemical desorption[7] .

The mechanism of anodic dissolution of iron has been extensively investigated in acidic solutions .

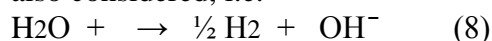


In CO₂ corrosion , cathodic process may be due to the reduction of four separate species, i.e. H⁺ ,H₂O ,H₂CO₃ and HCO₃⁻ . In acidic solutions, the reduction of H is the dominant cathodic reaction :

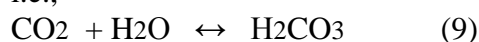


It is generally accepted that the H⁺ reduction reaction may proceed under activation or mass transfer control.

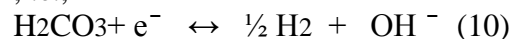
In addition to the reduction of H⁺ ions ,the direct reduction of water is also considered, i.e.



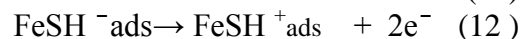
At mildly acidic conditions (pH > 4) reduction of carbonic acid (H₂CO₃) becomes the dominant cathodic process . Carbonic acid results from the hydration of dissolved CO₂, i.e.,



This reaction is followed by the reduction of H₂CO₃ on the surface ,i.e.,



In addition to the cathodic reaction ,the presence of H₂S affects the anodic iron dissolution by adsorbing HS⁻ ions on the surface of the metal and subsequently, accelerate the anodic dissolution of iron :



Reaction (12) are followed by the hydrolysis of the adsorbed (FeSH⁺_{ads}) species. The formation and modeling of the anodic and dissolution of iron through adsorbed intermediates and ionic mass transfer accompanying anodic dissolution of iron in acidic solution. Various species and surface - confined that leads to the formation of the main corrosion products. Surface and cross-sectional images of the passive film on iron and its composition were examined with optical microscopy, that shown in fig. (1).

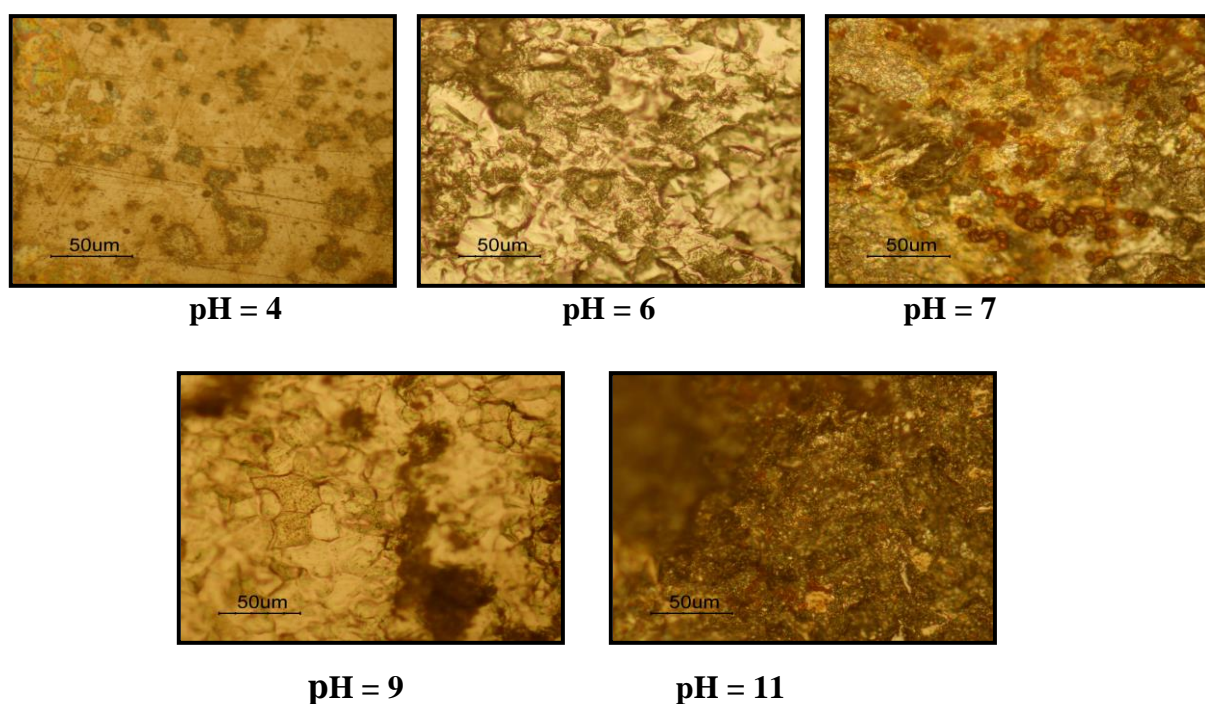


Fig. (1): Optical microstructure of low carbon steel in washing water solution of crude oil at pH (4,6,7,9,11) , 500 X

Polarization Resistance R_p

The polarization resistance, R_p , of according electrode is defined as the slope of a potential (E) – current density (i) plot of the corrosion potential (E_{corr}) as :

$$R_p = \left(\frac{\partial \eta}{\partial i} \right)_{T,C} \text{ at } \eta \rightarrow 0 \quad (13)$$

Where $\eta = E - E_{corr}$, is the extent of polarization of the corrosion potential and (i) is the current density (c.d) corresponding to a particular value of (η). From the polarization resistance, R_p the corrosion current density (c.d) i_{corr} can be calculated as :

$$i_{corr} = \frac{\beta}{R_p} \quad (14)$$

Where β is a combination of the anodic and cathodic Tafel slopes (b_a, b_c) as:

$$\beta = \frac{b_a b_c}{2.303(b_a + b_c)} \quad (15)$$

For the general case, by inserting equation (14) into equation (15) one obtains the so – called the Stern – Geary equation[8] .

$$R_p = \frac{b_a b_c}{2.303(b_a + b_c) i_{corr}} \quad (16)$$

The results of R_p can be summarized as follow :

- 1- R_p decreased with increasing temperature (pH = 4) .
- 2- R_p increased with increasing pH in the rang (4 – 7) and it decreased with increasing pH in the rang (9 – 11) at (343 K) .

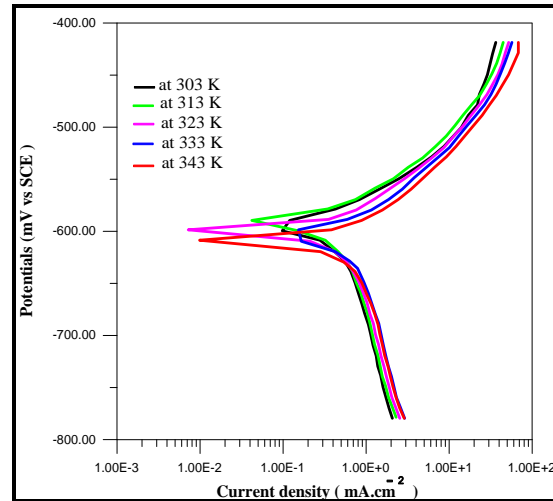


Fig. (2) : The polarization curve. for low carbon steel in washing water solution of crude oil at five temperatures in the range (303 - 343)

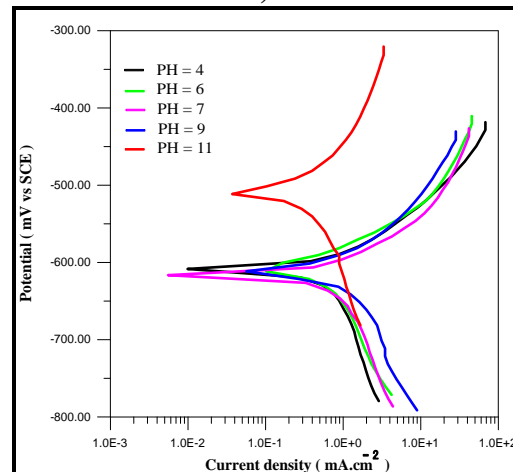


Fig. (3) : The polarization curve. for low carbon steel in washing water solution of crude oil at pH (4,6,7,9,11)

Table (1): Values of corrosion potentials E_{corr} , corrosion current densities i_{corr} , cathodic and anodic Tafel slopes b_c and b_a , cathodic and anodic transfer coefficients α_c and α_a , Weight loss, Penetration loss, polarization resistances R_p , and equilibrium exchange current density i_0 , for low carbon steel in washing water solution of crude oil at five temperatures in the range (303 - 343) K and pH(4).

T (K)	Corrosion		b (V.decade ⁻¹)		α		Corrosion rate		$R_p/10^3$ ($\Omega.cm^2$)	$i_0/10^{-6}$ (A.cm ⁻²)
	$-E_{corr}$ (V)	$i_{corr}/10^{-6}$ (A.cm ⁻²)	$-b_c$	$+b_a$	α_c	α_a	Weight loss / (g.m ⁻² .d ⁻¹)	Penetration loss/ (mm.a ⁻¹)		
303	0.601	313.76	0.124	0.057	0.48	1.05	78.4	3.64	1.91	0.136
313	0.590	386.05	0.199	0.056	0.31	1.12	96.5	4.48	1.53	0.176
323	0.601	471.04	0.202	0.065	0.32	0.98	118.0	5.47	1.28	0.218
333	0.603	569.01	0.211	0.066	0.31	1.01	142.0	6.60	1.06	0.271
343	0.610	579.94	0.203	0.066	0.34	1.03	414.5	6.73	1.05	0.281

Table (2): Values of corrosion potentials E_{corr} , corrosion current densities i_{corr} , cathodic and anodic Tafel slopes b_c and b_a , cathodic and anodic transfer coefficients α_c and α_a , Weight loss, Penetration loss, polarization resistances R_p , and equilibrium exchange current density i_0 , for low carbon steel in washing water solution of crude oil at pH (4,6,7.9,11) in the temperature 343 K

The medium (pH)	Corrosion		b (V.decade ⁻¹)		α		Corrosion rate		$R_p/10^3$ ($\Omega.cm^2$)	$i_0/10^{-6}$ (A.cm ⁻²)
	$-E_{corr}$ (V)	$i_{corr}/10^{-6}$ (A.cm ⁻²)	$-b_c$	$+b_a$	α_c	α_a	Weight loss / (g.m ⁻² . d ⁻¹)	Penetration loss/ (mm.a ⁻¹)		
4	0.610	579.94	0.203	0.066	1.05	0.281	414.5	6.73	1.05	0.281
6	0.610	428.82	0.122	0.061	1.42	0.208	107.0	4.98	1.42	0.208
7	0.617	250.96	0.056	0.038	2.46	0.120	62.7	2.91	2.46	0.120
9	0.609	487.89	0.083	0.058	1.25	0.237	122.0	5.66	1.25	0.237
11	0.510	510.55	0.358	0.198	1.00	0.296	128.0	5.93	1.00	0.296

Weight loss

Effect of pH

The pH of a solution is not only alters the rate of corrosion, but the mechanism by which iron dissolves. In acidic solutions, it has been suggested that (OH^-) absorbs onto Fe to produce $FeOH_{ads}$ and it is the $FeOH_{ads}$ which will undergo further oxidation to eventually form Fe^{2+} and H_2O products. Alternatively, in alkaline solutions, the $FeOH_{ads}$ reacts with H_2O and (OH^-) in a series of steps to eventually form $Fe(OH)_2^+ + OH^-$ [9].

As pH becomes more acidic, E_{corr} will become more negative due to the increase in rate of hydrogen evolution. Subsequently the increase in iron dissolution will result in a larger i_{corr} , decreasing with decreasing acidity attaining minimum values in neutral or nearly neutral media, increasing thereafter as the medium became basic and as the causticity increased[9]. The results of the weight loss in table (2) obtained from potentiodynamic polarization that can be showed the weight loss decreased with increasing pH in the rang (4 – 7) and it increased

with increasing pH in the rang (9 – 11) at (343 K).

Effect of Temperature

The effect of temperature on the performance of low carbon steel in washing water solution of crude oil is investigated by weight loss measurements in the temperature range (303 - 343) K, at pH (4). Table (1) shows values of corrosion rate. Data in Table (1) get the corrosion rates increase with increasing in temperature.

The free – energy change that obtained from the following equation[10] .

$$\Delta G = -nFE \quad (17)$$

where ΔG is the free – energy change, n is the number of electrons involved in the reaction, F is the Faraday constant, and E equals the cell potential ($E = E_{\text{corr}}$).

From the value of ΔG at several temperatures, the change in the entropy (ΔS) of corrosion process could be derived according to the well – known thermodynamic relation :

$$\Delta S = -\frac{d(\Delta G)}{dT} \quad (18)$$

Values of ΔG are usually plotted against temperature (T); thus at any temperature the value of $(-d(\Delta G) / dT = \Delta S)$ which corresponds to the slope of the $(-\Delta G)$ versus (T) plot at that temperature, as shown in fig. (4). The change in Free energy is the thermodynamic property that has been assigned to express the resultant enthalpy of a substance and its inherent probability. At constant temperature, free energy can be expressed as[10]:

$$\Delta G = \Delta H - T\Delta S \quad (19)$$

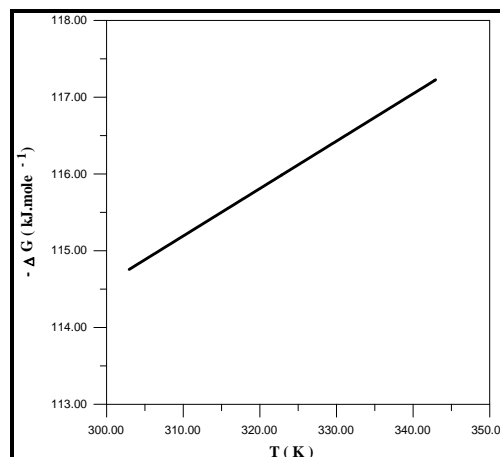


Fig. (4) :The variation of the (-ΔG) with temperature (T) for corrosion of low carbon steel in washing water solution of crude oil at five temperatures in the range (303 - 343)K, at pH (4)

Table (3) values of the thermodynamic quantities for the corrosion of low carbon steel in washing water solution of crude oil at five temperatures in the range (303 - 343)K, at pH (4)

Values of ΔG were negative the ,negative values of ΔG that mean, these reaction are occurring spontaneously. The values of ΔG are increased with increasing temperature

Values of (ΔS) were positive or negative depending on the positive or negative dependencies of (ΔG) values on temperatures. Values of (ΔS) reflect the change in the order and orientation of the solvent molecules around the hydrated metal ions in the corrosion medium when metal atoms were corroded and subsequently hydrated in the solution. Values of ΔS were generally positive due to negativity of ΔG , this suggests a lower order in the solvated states of the metal ions as compared with the state of metal atoms in the crystal lattice of the corroding electrodes.

Values of the enthalpy of corrosion (ΔH) reflect the enthalpy changes associated with the corrosion reaction and ranged from negative to positive

values indicating exothermic or endothermic nature of corrosion reaction. Generally, negative values of (ΔH) indicating a stronger bonding of the metal ions, resulting from electrode corrosion, with the species that are present in the corrosion medium as compared with the bonding of the metal atoms in the crystal lattice of the solid electrode.

Table (3): Values of The thermodynamic quantities for corrosion of low carbon steel in washing water solution of crude oil at five temperatures in the range (303 - 343)K, at pH (4)

T (K)	- ΔG (kJ.mole ⁻¹)	ΔS (J.mol ⁻¹ .K ⁻¹)	ΔH (kJ.mole ⁻¹)
303	115.95	61.76	-97.24
313	113.86		-94.54
323	115.97		-96.02
333	116.37		-95.80
343	117.78		-97.38

Apparent activation energy and pre-exponential factor

Apparent activation energy for the corrosion process is calculated using Arrhenius Eq.[11]

$$r = A \exp(-E_a/RT) \quad (20)$$

Where (r) equals the reaction rate, A is a pre-exponential factor, E_a is the activation energy, R is the gas constant and T is the temperature.

The equation (20) shows that, an increase in temperature will result in an increase in the rate of corrosion when the process is solely governed by metal oxidation. The apparent activation energies (E_a) and pre-exponential factor (A) are determined by linear regression between log I_{corr} and $1/T$ fig.(5) and the results are listed in Table (4). The value of (E_a) was

positive and the (log A) value was negative.

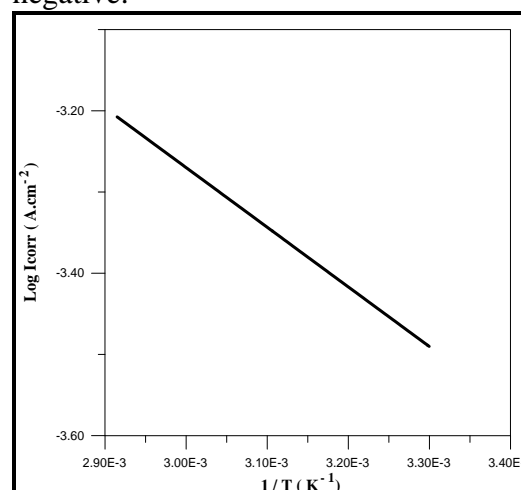


Fig. (5): Arrhenius plots, relating (log i_{corr}) values to (1/T) for the corrosion of low carbon steel in washing water solution of crude oil at five temperatures.

Table (4): Values of activation energy (E_a) and pre- exponential factors (A) of low carbon steel in washing water solution of crude oil

E_a (kJ.mol ⁻¹)	Log A	A (molecules.cm ⁻² .s ⁻¹)
14.26	-1.04	5.758 x10 ¹⁷

Conclusions:

The corrosion rate of low carbon steel in Washing Water of Crude Oil Solution is dependent on some factors like temperature and pH of this solution ,the corrosion rate was increased with increasing temperature in base solution and decreased with increasing pH in the rang (4 – 7).

References:

1- Obuka, Nnaemeka Sylvester P., Okoli Ndubuisi Celestine, Ikwu,Gracefield Reuben O., Chukwumuanya, Emmanuel Okechukwu, (2012) .Review of Corrosion Kinetics and Thermodynamics of CO2 and H2S Corrosion Effects and Associated

- Prediction/Evaluation on Oil and Gas Pipeline System. RJPBCS. 3: 912-922.
- 2- G.A. Zhang a,b, Y.F. Cheng, 2009 . Electrochemical corrosion of X65 pipe steel in oil/water emulsion. Corrosion Science. 51:901–907.
- 3- Katie Sue Webster . 2012 .Effects of NaCl Concentration and Temperature on Corrosion Understanding Material Interactions in Aqueous Environments , MSc Thesis, Boston University.
- 4- L.M.Al-Shamma, J.M.Saleh and N.A.Hikmat. 1987. Adsorption of Carbon Disulphide and Hydrogen Sulphide on Evaporated metal Films, J. of corros. Sci. 27:22
- 5 -Obuka, and others . 2012. Review of Corrosion Kinetics and Thermodynamics of CO₂ and H₂S Corrosion Effects and Associated Prediction / Evaluation on Oil and Gas Pipeline System, IJSTR. 1 156 – 162 .
- 6- L. L. Sherir. 1976. Corrosion, Metal/Environment Reactions, second ed, 1: 4-12
- 7 - J.O.M.Bockris and A.K.N.Reddy. 1970. Modern Electrochemistry, Plenum Press, New York ,.2:883
- 8- Callow, L. M.; Richardson, J. A.; Dawson, J. L. 1976. Corrosion Monitoring using Polarisation Resistance Measurements: I. Techniques and correlations, British Corrosion J. 11(3) :123-131.
- 9 -B. E. Conway, J. O'M. Bockris and R. E. White . 1989. Modern Aspects of Electro chemistry, No. 19, Plenum Press. New York, pp. 78-93
- 10-ASM international Metals Handbook. 1992.Corrosion , vol. 13
- 11- L. M. Al- Shamma, J. M. Saleh, and N. A. Hikmat. 1987. Potentiostatic studies of the corrosion of grey cast iron in sulphuric acid and sodium hydroxide solutions, Corrosion Sci., 27 (3): 221–228.

دراسة سلوك التآكل لسبيكة الفولاذ واطئ الكاربون في الوسط الحامضي و القاعدي لماء الغسيل للنفط الخام عند درجات حرارية مختلفة

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الخلاصة:

تم في هذا البحث دراسة سلوك التآكل لسبيكة الفولاذ واطئ الكاربون بمحلول ماء الغسيل للنفط الخام وتمت الدراسة باستخدام قياس الجهد الساكن و عند خمس درجات حرارية و ضمن المدى (30 – 70) م عند الاس الهيدروجيني (4) ، كذلك دراسة سلوك التآكل ضمن مدى الاس الهيدروجيني (4، 6، 7، 9، 11) و عند درجة حرارة (70) م.

تبين من خلال هذه الدراسة ان جهد التآكل قد انحرف الى قيم اكثر سالبية مع زيادة درجة الحرارة كذلك ان كثافة تيار التآكل تزداد مع زيادة درجات الحرارة ، وتقل كثافة تيار التآكل مع زيادة الاس الهيدروجيني ضمن المدى (4 – 7) و تزداد مع زيادة الاس الهيدروجيني ضمن المدى (9 – 11) ، في حين يتغير جهد التآكل مع زيادة الاس الهيدروجيني ضمن المدى (4 – 11). اما قيم الدوال الترموداينميكية و الحركية ΔH (ΔG , ΔS , and E_a) فقد تم حسابها من النتائج التي تم الحصول عليها في هذه الدراسة.