Simulation of Galvanic Corrosion for Aluminum, Copper, Iron and Zinc at different pH and temperatures

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Abstract
Simple model is proposed to describe galvanic corrosion process. Computer program COR was designed and written in visual basic language to simulate the galvanic corrosion reaction that proposed in the model. Input data metals parameters (aluminum, copper,iron, and zinc) and the environment parameters (pHand temperature) was used in the program designed COR and the results (The electrochemical parameters, corrosion rates, activation energies, and thermodynamic parameters)were calculated and discussed.Simulation computational results are compared with theoretical and experimental data, to ensure that the results of this model are corresponding to the results published in the literature. Both of which show the same characteristics of data distribution. The corrosion rates of iron were higher, followed by copper, zinc and finally aluminum.

Keywords: Simulation, galvanic Corrosion.

Introduction
Computer simulation for corrosion process, which is developed based on original experimentalmethods, is an accurate and fast method to evaluate corrosion damage. The results of computersimulation can be used to predict and evaluate corrosion behavior and long term damage degree ofmaterial. The research on computer simulation is composed of two processes, mathematicalmodeling and simulation computation. Mathematical modeling is the basis and core of simulation.

J.Saunier and A. Chauss [1] used a cellular automata model to simulate computation in diffusionprocess of corrosion products and growing process of film. A. Jivkon and N. Stevens[2] built a finiteelement model based on the influence functions of loads in corrosion reaction, stress intensity factorand strain value were calculated. J. R. Ankar and N. R. Iyer [3] abstracted the oval geometric features of pitting mathematical model was settled based on the probabilistic growingfeatures of pitting in aluminum.A. Turnbull [4] set up a model based on the determined equationof distribution statistics according to input parameters.

There is no model that is widely accepted and meets the requirements insimulation results. In this work, theoretical simplified analysis of galvanic corrosion was presented, computer program CORwere designed and applied to calculatethe electrochemical and thermodynamic parameters, and the effects of temperature and pH on the corrosion reactions have been demonstrated.

Mathematical Model
Corrosion reaction of material includes electron transfer, mass transfer and diffusion of ion andmany other complicate physical-chemical processes. Due to the randomness of material structureand chemical reaction process, it is not possible to set up a determined mathematical model todescribe the whole process of corrosion. Therefore, computer simulation research for the corrosionprocess has to start from the simple corrosion process such as the galvanic corrosion.

Mathematical model has been developed based on the ordinarily galvanic corrosion model. When the reactants reach the metal surface, various electrochemical reactions take place between the metal surface and the environment.

Anodic reaction:

$M \rightarrow \quad M^{n+} \quad + \quad ne^-$ ....(1)

atom in metal ion in solutionelectrons in metal

Cathodic reaction:

$2H^+ \quad + \quad 2e^- \rightarrow \quad H_2$ ....(2)

adsorbed on metal in metal gas

The mathematical representation of the galvanic corrosion involves the statement of the electrical charge conservation equation in the electrolyte given by [5]

$$\nabla^2 E = 0 \quad (3)$$

WhereE is the potential inside the electrolyte.The corrosion current density into the electrode assumed given by the Butler-Volmer equation [6]

$$i_{corr} = i_a - i_c = i_\circ \left[\exp\left(\frac{n \propto_a F \eta}{R T}\right) - \exp\left(\frac{n \propto_c F \eta}{R T}\right)\right] \quad (4)$$

Where, i_a,i_c,i_o are the anodic, cathodic, andexchange current density, (α_a, α_c) are the charge transfer coefficients for the anodic and cathodic processes at the electrode respectively, F is Faraday's constant, R is the gas constant and Tis the temperature, and$\eta$is the overvoltage given by

$$\eta = E_{corr} - E_{eq} \quad (5)$$

E_{corr} is corrosion potential and E_{eq} the equilibrium electrode potential given by the Nernst equations for both electrodes [7]:

$$E_{H^+} = E^\circ_{H^+} + \frac{RT}{nF}\ln\frac{[H^+]^2}{[H_2]} \quad (6a)$$

$$E_{M^{n+}} = E^\circ_{M^{n+}} + \frac{RT}{nF}\ln[M^{n+}] \quad (6b)$$

Where

$[H^+]$:Concentration of H^+.

$[H_2]$: Concentration of H_2.

$[M^{n+}]$:Concentration ofM^{n+}.

$E^\circ_{H^+}$: Standard potential for the cathodic reactions.

$E^\circ_{M^{n+}}$: Standard potential for the anodic reactions.

Under steady state conditions it is assumed the sum of the mass transfer rates of the reactant are equal to the sum of the electrochemical reaction rates. Hence we can write [8]:

$$i_a = n\,F\,k_{M^{n+}}\,[M^{n+}] \quad (7a)$$

$$i_c = F\,k_{H^+}\,[H^+] \quad (7b)$$

Where,

$k_{M^{n+}}$: Mass transfer coefficient for M^{n+}.

k_{H^+} : Mass transfer coefficient for H^+.

The corrosion rate C_R is calculated by [9]:

$$C_R = i_{corr}\frac{M}{nF\rho} \quad (9)$$

Where, M is molecular weight and ρ is mass density.

The dependence of activation energy E_a on temperature can be expressed by the following Arrhenius and transition state equations [10]:

$$C_R = A\exp\left(-\frac{E_a}{RT}\right) \quad (10)$$

Where A the pre-exponential factor. The activation enthalpy ΔH of reaction given by:

$$\Delta H = E_a - RT \quad (11)$$

The activation entropy ΔS of the reaction were given by:

$$\Delta S = \frac{\Delta H - G}{T} \quad (12)$$

Where ΔG is the free energy of reaction and given by:

$$\Delta G = -nFE \quad (13)$$

Program Design

To perform the calculations of this analysis the input data must be presented. These data includes metals parameters (aluminum, copper, iron and zinc) [11] [12] and the environment parameters (temperature and pH) studied in this model. All these data was used in the program designed COR and the results (The electrochemical parameters corrosion rates, activation energies, and the thermodynamic parameters) were obtained. The flowchart that can be explain the COR program shown in Fig. (1).

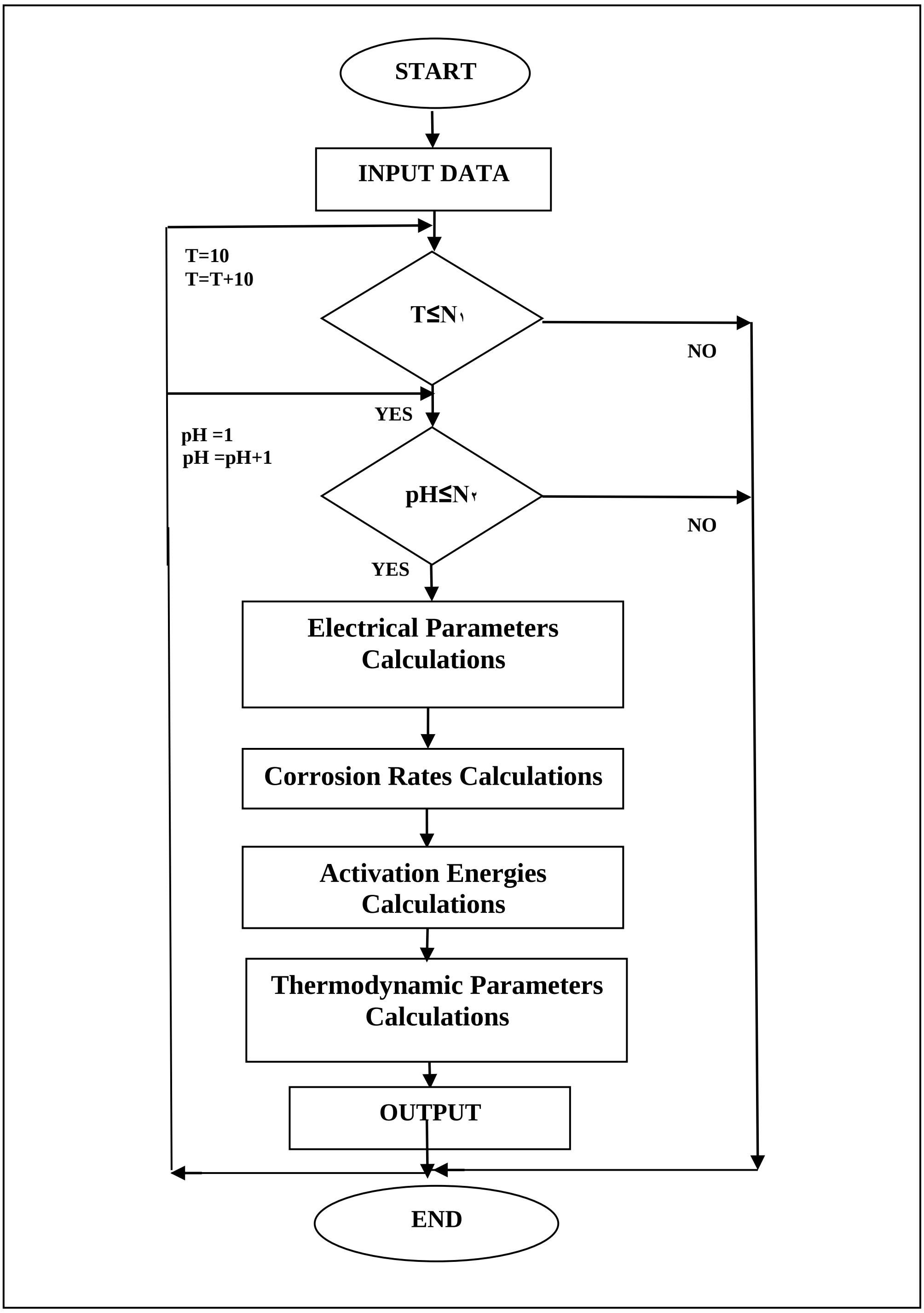

Fig. (1) The flow diagram of COR program.

Result and Discussion

The corrosion behavior of metals when exposed to various environments is an important factor in metals selection that determines the service life of the material. Aluminum, copper, iron, and zinc metals are adopted in this model because a remarkable economic, attractive for engineering applications, and consider as most important metals used widely in different industries.

1.Electrochemical parameters and corrosion rate Calculations

The electrochemical parameters including the cathodic corrosion current densities i_{corr} and corrosion potentials E_{corr} for aluminum, copper, iron, and zinc metals at different pH and temperature are listed in Table (1, 2, 3 and 4) respectively. The corrosion rates of aluminum, copper, iron, and zinc metals as a function of temperature and pH have shown in Fig.(2, 3, 4, and 5) respectively.

Table (1)
Electrochemical parameters of aluminum at different pH and temperatures.

pH	Temperature							
	293 ºK		313 ºK		333 ºK		353 ºK	
	i_{corr} (A/cm^2)	E_{corr} (v)	i_{corr} (A/cm^2)	E_{corr} (v)	i_{corr} (A/cm^2)	E_{corr} (v)	i_{corr} (A/cm^2)	E_{corr} (v)
1	1.9 X10^{-13}	-1.100	3.2X10^{-12}	-1.062	3.8X10^{-11}	-1.024	3.4X10^{-10}	-0.985
2	7.6 X10^{-15}	-1.184	1.1X10^{-13}	-1.154	1.2X10^{-12}	-1.119	1.0X10^{-11}	-1.087
3	3 X10^{-16}	-1.269	4.2 X10^{-15}	-1.243	4.2X10^{-14}	-1.215	3.3X10^{-13}	-1.188
4	1.1 X10^{-17}	-1.353	1.5 X10^{-16}	-1.332	1.4X10^{-15}	-1.311	1.02X10^{-14}	-1.290
5	4.6 X10^{-19}	-1.437	5.4 X10^{-18}	-1.421	4.7X10^{-17}	-1.407	3.22X10^{-16}	-1.391

Table (2)
Electrochemical parameters of copperat different pH and temperatures.

pH	Temperature							
	293 ºK		313 ºK		333 ºK		353 ºK	
	i_{corr} (A/cm^2)	E_{corr} (v)	i_{corr} (A/cm^2)	E_{corr} (v)	i_{corr} (A/cm^2)	E_{corr} (v)	i_{corr} (A/cm^2)	E_{corr} (v)
1	5.8 X10^{-6}	-0.330	1.2X10^{-5}	-0.32	2.3X10^{-5}	-0.328	4.1X10^{-5}	-0.328
2	4.2 X10^{-7}	-0.388	7.7X10^{-7}	-0.39	1.3X10^{-6}	-0.394	2.1X10^{-6}	-0.398
3	3.0 X10^{-8}	-0.446	4.9 X10^{-8}	-0.45	7.5X10^{-8}	-0.461	1.0X10^{-7}	-0.468
4	2.2 X10^{-9}	-0.50	3.1 X10^{-9}	-0.51	4.3X10^{-9}	-0.527	5.6X10^{-9}	-0.538
5	1.6 X10^{-10}	-0.56	2.0 X10^{-10}	-0.57	2.6X10^{-10}	-0.593	2.9X10^{-10}	-0.608

Table (3)
Electrochemicalparameters of ironat different pH and temperatures.

pH	Temperature							
	293 ºK		313 ºK		333 ºK		353 ºK	
	i_{corr} (A/cm^2)	E_{corr} (v)	i_{corr} (A/cm^2)	E_{corr} (v)	i_{corr} (A/cm^2)	E_{corr} (v)	i_{corr} (A/cm^2)	E_{corr} (v)
1	4.2 X10^{-4}	-0.221	1.1X10^{-3}	-0.206	2.7X10^{-3}	-0.192	5.8X10^{-3}	-0.177
2	3.0 X10^{-5}	-0.280	7.3X10^{-5}	-0.269	1.5X10^{-4}	-0.258	3.0X10^{-4}	-0.247
3	2.2 X10^{-6}	-0.338	4.6 X10^{-6}	-0.331	8.8X10^{-6}	-0.324	1.5X10^{-5}	-0.317
4	1.6 X10^{-7}	-0.396	2.9 X10^{-7}	-0.393	5.0X10^{-7}	-0.390	8.1X10^{-7}	-0.388
5	1.1 X10^{-8}	-0.454	1.9 X10^{-8}	-0.455	2.9X10^{-8}	-0.456	4.2X10^{-8}	-0.459

Table (4)
Electrochemicalparameters of zincat different pH and temperatures.

pH	Temperature							
	293 °K		313 °K		333 °K		353 °K	
	i_{corr} (A/cm^2)	E_{corr} (v)	i_{corr} (A/cm^2)	E_{corr} (v)	i_{corr} (A/cm^2)	E_{corr} (v)	i_{corr} (A/cm^2)	E_{corr} (v)
1	3.4 X10^{-8}	-0.450	2.1X10^{-7}	-0.439	1.0X10^{-6}	-0.419	4.1X10^{-6}	-0.399
2	2.5 X10^{-9}	-0.518	1.3X10^{-8}	-0.501	5.8X10^{-8}	-0.485	2.1X10^{-7}	-0.468
3	1.8 X10^{-10}	-0.576	8.5 X10^{-10}	-0.563	3.3X10^{-9}	-0.552	1.1X10^{-8}	-0.538
4	1.3 X10^{-11}	-0.634	5.4 X10^{-11}	-0.625	1.9X10^{-10}	-0.617	5.7X10^{-10}	-0.608
5	9.5 X10^{-13}	-0.692	3.5 X10^{-12}	-0.688	1.1X10^{-11}	-0.683	3.0X10^{-11}	-0.679

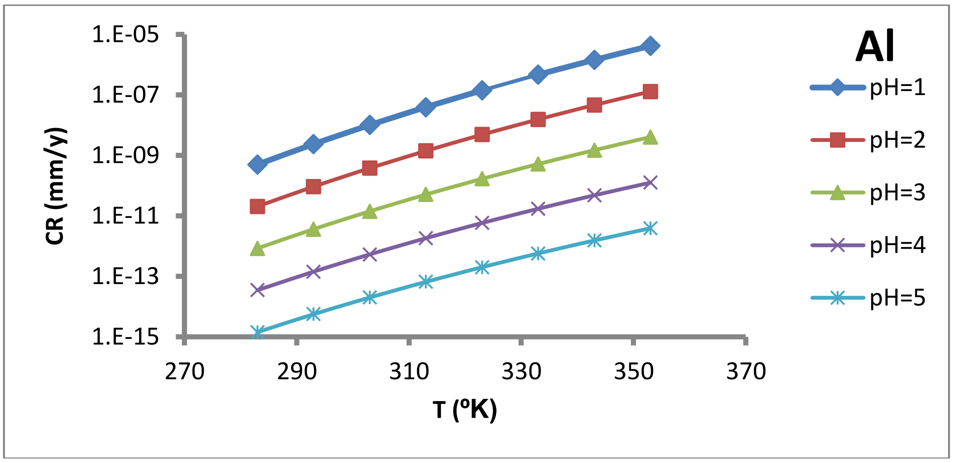

Fig. (2) The corrosion rates of aluminum as a function of pH and temperatures.

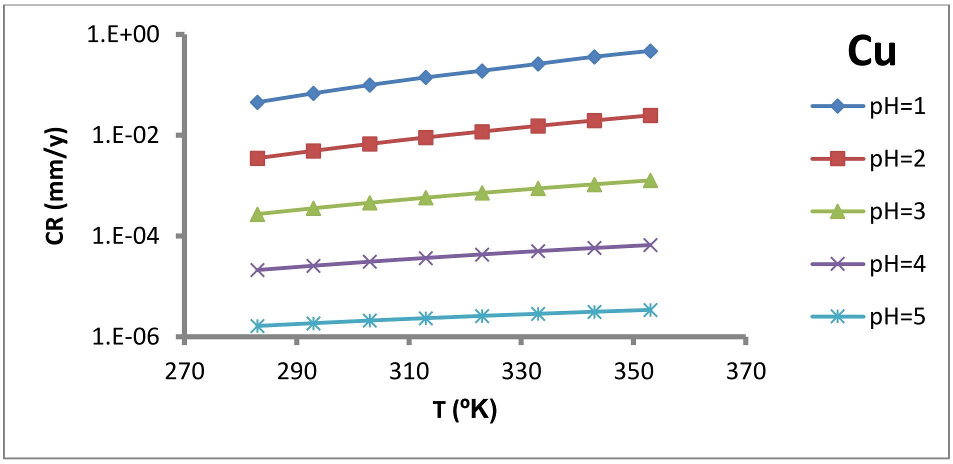

Fig. (3) The corrosion rates of copper as a function of pH and temperatures.

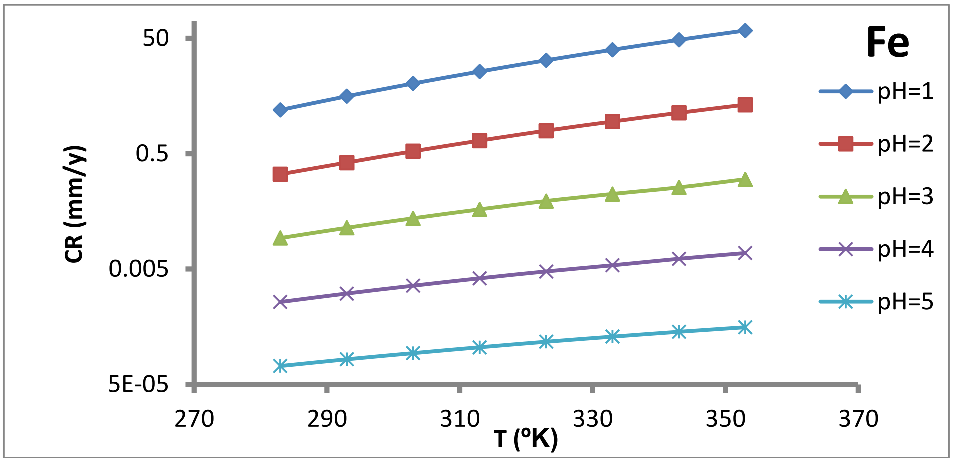

Fig. (4) The corrosion rates of iron as a function of pH and temperatures.

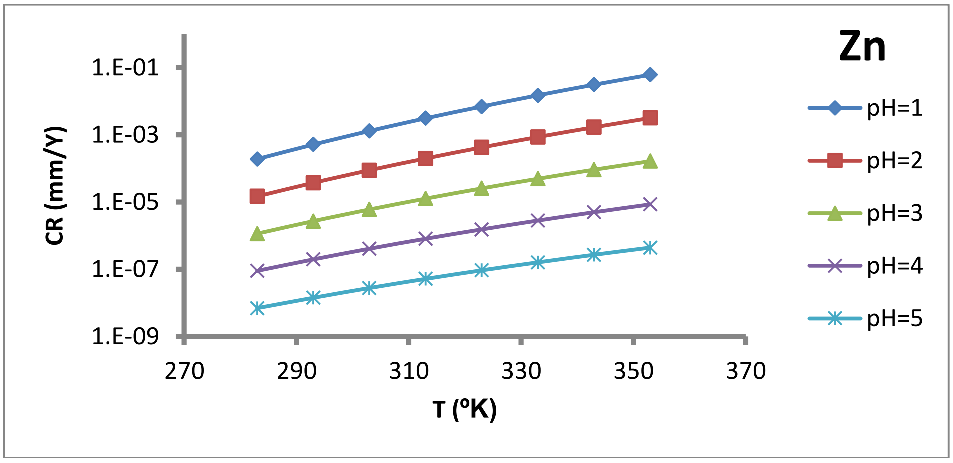

Fig. (5) The corrosion rates of zinc as a function of pH and temperatures.

1. a. Effect of temperature

Temperature has a great effect on the corrosion phenomenon. Generally the corrosion rate increases with the rise of the temperature. These data show that increasing the temperature causes an increase in the galvanic corrosion current, and the corrosion potential decreases slightly with increasing the temperature. The corrosion rates of aluminum, copper, iron, and zinc was high affected by changing temperature from (283ºK -353ºK) especially iron. The corrosion rates of the metals were observed with a change in temperature.

1. b. Effect of pH

The metals corrosion rates were strongly affected by the change in pH. The corrosion rates of iron, copper, and zinc decrease with increasing pH, due to decrease corrosion current but corrosion potential increase.

2. Activation energy and thermodynamic parameters Calculations

The thermodynamic parameters including the activation energy E_a, enthalpy of activation ΔH and entropy of activation ΔS for aluminum, copper, iron, and zinc metals at different pH and temperature are listed in Table (5, 6,7 and 8) respectively.

Table (5)
Activation energy and thermodynamic parameters of aluminum at different pH and temperatures.

pH	Temperature											
	293 °K			313 °K			333 °K			353 °K		
	Ea (KJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)	Ea (KJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)	Ea (KJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)	Ea (KJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)
1	69.9	67.5	-172.5	67.4	64.8	-160.0	64.8	62.1	-149.0	62.3	59.4	-139.2
2	72.2	69.8	-168.3	70.1	67.5	-156.2	67.9	65.2	-145.6	65.7	62.8	-136.1
3	74.5	72.1	-164.2	72.7	70.1	-152.4	70.9	68.2	-142.1	69.2	66.2	-133.0
4	76.8	74.4	-160.0	75.4	72.8	-148.7	74.0	71.2	-138.7	72.6	69.7	-130.0
5	79.0	76.6	-155.8	78.1	75.5	-144.9	77.1	74.3	-135.3	76.0	73.1	-126.7

Table (6)
Activation energy and thermodynamic parameters of copper at different pH and temperatures.

pH	Temperature											
	293 °K			313 °K			333 °K			353 °K		
	Ea (KJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)	Ea (KJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)	Ea (KJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)	Ea (KJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)
1	27.0	24.6	-179.3	26.9	24.4	-161.0	26.9	24.1	-144.9	26.9	23.9	-130.6
2	27.8	25.4	-149.0	28.1	25.5	-133.9	28.5	25.7	-120.6	28.8	25.9	-108..7
3	28.6	26.2	-118.8	29.3	26.7	-106.8	30.0	27.2	-96.2	30.7	27.8.2	-86.9
4	29.3	27.0	-88.5	30.5	27.9	-97.7	31.6	28.8	-71.9	32.7	29.7	-65.0
5	30.1	27.7	-58.3	31.6	29.0	-52.6	33.1	30.3	-47.6	34.6	31.6	-43.1

Table (7)
Activation energy and thermodynamic parameters of iron at different pH and temperatures.

pH	Temperature											
	293 °K			313 °K			333 °K			353 °K		
	Ea (KJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)	Ea (KJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)	Ea (KJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)	Ea (KJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)
1	16.6	14.1	-209.5	15.1	12.5	-184.9	13.7	10.9	-163.2	12.3	9.3	-144.0
2	17.4	15.0	-179.2	16.3	13.7	-157.7	15.3	12.5	-138.9	14.2	11.2	-122.1
3	18.2	15.7	-149.0	17.5	14.9	-130.6	16.8	14.0	-114.5	16.1	13.2	-100.3
4	19.0	16.5	-118.7	18.7	16.0	-103.5	18.4	15.6	-90.2	18.1	15.1	-78.4
5	19.7	17.3	-88.4	20.0	17.2	-76.4	19.9	17.1	-65.9	20.0	17.0	-56.5

Table (8)
Activation energy and thermodynamic parameters of zinc at different pH and temperatures.

pH	Temperature											
	293 °K			313 °K			333 °K			353 °K		
	Ea (KJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)	Ea (KJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)	Ea (KJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)	Ea (KJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)
1	39.5	37.1	-498.6	37.6	34.9	-453.7	35.6	32.8	-414.3	33.6	30.7	-379.3
2	40.3	37.9	-468.3	38.7	36.1	-426.6	37.1	34.4	-390.0	35.5	32.6	-357.5
3	41.1	38.7	-438.0	39.9	37.3	-399.5	38.7	35.9	-365.6	37.5	34.5	-335.6
4	41.9	39.4	-407.8	41.1	38.5	-372.4	40.2	37.5	-341.3	39.4	36.5	-313.7
5	42.7	40.2	-377.5	42.2	39.6	-345.3	41.8	39.0	-317.0	41.3	38.4	-292.0

2. a. Effect of temperature

The activation energy and thermodynamic parameters decreases with temperature was increased. An increase in temperature, increases the number of atoms with energy more than or equal to the activation energy. This causes an increase in the rate of reaction.

2. b. Effect of pH

The activation energy and the enthalpy increased with pH was increased, but the entropy decreases. Results showed that the values of E_a and ΔH of iron are low. This indicates that the corrosion reaction for iron need lower energy to occur compared to another metals, therefore the corrosion rate of iron is high, but for aluminum the values of E_a and ΔH are high therefore the corrosion rate of aluminum is very low.

Program Performance

To test the performance of any simulation design, it is necessary to comparethe computer simulation results with the other theoretical and experimental results to ensure that the results in this search.The comparison is achieved In spite of these simulation model are not identical but the simulation data are correspond to the results published in the literature [13-17].

Conclusions

The analytical model based on simplified approach towards computation of corrosion current, corrosion potential, corrosion rate, activation energy, enthalpy, and entropy at different pH and temperature from galvanic corrosion system developed in this work being in close agreement with the test results predicts and simulates the corrosion. The importance of a model is more reliable than pure intuition; mathematically a model simplifies the analysis. This is the main reason for the experimental data increases slowly comparing with simulating data. The corrosion rates of iron so high as compared with aluminum, copper and zinc due to low activation energy and enthalpy therefore the corrosion reaction taken place easily.

References

[1] Saunier j, Dymitrowska M, Chausse A, Stafiej j, "Diffusion, interactions and universal behavior in a corrosion growth model" J. Electroanalytical chemistry, V.582, pp. 267-273, 2005.

[2] Jivkov A, Stevens N, Marrow T, "A two-dimensional mesoscale model for intergranular stress corrosion crack propagation ". J. Acta Materialia: V. 54, p.3493-3501, 2006.

[3] Rajasankar J, Iyer N, "A probability-based model for growth of corrosion pits in aluminium alloys" J. Engineering Fracture Mechanics: V. 73, pp.553 –570, 2006.

[4] Turnbull A, McCartney L, Zhou S, " A model to predict the evolution of pitting corrosion and the pit-to-crack transition incorporating statistically distributed input parameters" J. Corrosion Science: V. 48, pp.2084 -2105., 2006.

[5] Sunil Kumar T, "Modeling and simulation of galvanic corrosion pit as a moving boundary problem" J. Computational Materials Science V. 65, pp. 269–275, 2012.

[6] Gulikers J, " Theoretical considerations on the supposed linear relationship between concrete resistivity and corrosion rate of steel reinforcement" J. Materials and Corrosion, V. 56, pp. 393–403, 2005.

[7] Winston Revie R, Herbert Uhlig H, "Corrosion and Corrosion Control" Wiley-Interscience Fourth Edition, p.24-25, 2008.

[8] Luis C, Toma´s V, Leandro H, "Determination of electrochemical parameters and corrosion rate for carbon steel sodium chloride solutionsusing a superposition model " J. Corrosion Science V.49, pp. 3168–3184, 2007.

[9] Nestor Perez, "Electochemistry and Corrosion Scinence" © Kluwer Academic Publishers, pp.92-93, 2004.

[10] Shivapura S. Shivakumar, Kikkeri N. Mohana "Corrosion Inhibition Character of Azure B for Mild Steel in Hydrochloric Acid Solution" J. Electrochem. Sci., V. 7, pp. 1620 – 1638, 2012.

[11] Baboian R, "Corrosion Tests and Standareds" Second Edition, pp.27-31 2005.

[12] Mackinnon D.J, Ingraham, T.R., and Kerby, "Copper cementation on nickel disc" J. Canadian Metallurgical Quarterly, V. 10, No. 3, pp.165-169, 1971.

[13] Obi-Egbedia N, Essiena K, Obot I," Computational simulation and corrosion inhibitive potential of alloxazine for mild steel in 1M HCl" J. Comput. Method. Mol. Design, V. 1, pp 26-43, 2011.

[14] Ahmed Y, Abu Bakar M, Abdul Amir H, "Galvanic Corrosion of Aluminum Alloy Al2024 and Copper in 1.0 M Nitric Acid" J. Electrochem. Sci, V. 6, pp. 5052 – 5065, 2011.
[15] Osarolube E, Owate I, Oforka N, " Corrosion behaviour of mild and high carbon steels in various acidic media" J. Scientific Research and Essay V. 3, No 6, pp. 224-228, 2008.
[16] Sangeetha T, Fredimoses M, " Inhibition of Mild Copper Metal Corrosion in HNO3Medium by Acid Extract of AzadirachtaIndica Seed "J. Chemistry, V. 8, pp. 1-6, 2011.
[17] Zaifol S, Muhamad D, Radiah M, " Simulation of Galvanic Corrosion usingBoundry Element Methods " J. Nuclear and Related Technologies, V. 8, 2011.

الخلاصة

حيث تم اقتراح نموذج بسيط لوصف عمليات التأكل الكلفاني وتم تصميم وكتابة برنامج حاسوبي بلغة الفيجول بيسك لمحاكاة تفاعلات التأكل الكلفاني المقترحة في الموديل. وقد تم ايضا إدخال نوعين من البيانات، بيانات عوامل المعادن (الألمنيوم، النحاس، الحديد، الزنك) وبيانات عوامل المحيط (الحرارة، الحامضية) في البرنامج المصمم. وتم الحصول على النتائج (العوامل الكهربائية، معدل التأكل، طاقات التنشيط، عوامل الثرموداينمك) ومناقشتها. نتائج المحاكاة تم مقارنتها مع نتائج نظرية وعملية للتأكد من نتائج الموديل بأنها متوافقة مع النتائج المنشورة. كلا النتائج اظهرت نفس الخصائص. ومن خلال النتائج تبين ان معدل تأكل الحديد عالي متبوعا بالنحاس ثم الزنك واخيرا الألمنيوم.