

Galvanic Corrosion of Carbon Steel –Copper in Aerated H₂SO₄ Under Agitation Conditions

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ABSTRACT

Galvanic and free corrosion experiments on carbon steel-copper couple in 3% H₂SO₄ in the presence of NaCl salts were carried out under different operating conditions. The effect of temperature, agitation speed, and air bubbling (O₂ concentration) on the free and galvanic corrosion was studied and discussed. The galvanic corrosion was investigated by both weight loss method and by determining the galvanic currents using zero resistance ammeter (ZRA). The results revealed that increasing temperature leads to increase the galvanic corrosion rate and also the free corrosion rate of each metal. Increasing agitation velocity enhanced the galvanic corrosion rate in a manner depending on temperature. The presence of air bubbling increased the corrosion rate and galvanic currents at low air pumping rate, while, at high pumping rate, air bubbling decreased the corrosion rate.

Keywords: galvanic corrosion, copper, carbon steel, sulfuric acid, agitation speed.

التآكل الكلفاني للكاربون الفولاذي-نحاس في محلول الكبريتيك وفي ظروف الخلط بوجود الهواء

الخلاصة

تم اجراء تجارب على عملية التآكل لكل من الحديد والنحاس بصورة منفردة وعند ربطهما معا في محلول ملحي من حامض الكبريتيك 3% وفي ظروف تشغيلية مختلفة وتم دراسة ومناقشة تأثير درجة الحرارة، سرعة الخلط، تركيز الاوكسجين المذاب على معدل التآكل الكلفاني. تم قياس معدل التآكل الكلفاني بطريقتين فقدان الوزن وقياس تيارات التآكل باستخدام الاميتر الصفري. اثبتت النتائج ان زيادة درجة الحرارة يؤدي الى زيادة معدل التآكل الكلفاني وايضا معدل التآكل لكل معدن على حدى. وكذلك فان زيادة سرعة الخلط يسبب زيادة في معدل التآكل الكلفاني اعتمادا على درجة الحرارة. ان زيادة نسبة الاوكسجين المذاب يسبب زيادة في معدل التآكل وكذلك تيارات التآكل الكلفاني عند معدل ضخ الهواء الواطىء بينما زيادة معدل ضخ الهواء اكثر يسبب تقليل في معدل التآكل عند سرع الخلط العالية.

INTRODUCTION

Galvanic corrosion occurs when two different metals are connected in the presence of an electrolyte. Because corrosion is an electrochemical process involving the flow of electric current, corrosion can be generated by a galvanic effect, which arises from the contact of dissimilar metals in an electrolyte (an electrolyte is an electrically conductive liquid). Three conditions are required for galvanic corrosion to proceed, the two metals must be separated in the galvanic series, they must be in electrical contact and they are connected electrically by conducting fluid. Removal of any of these three conditions will prevent galvanic corrosion [1, 2].

There are several industrial operations which involve acid flow system in which an acid solution moves past a metal surface such as: steel strips pickling, industrial acid cleaning and oil well acidizing. Furthermore, acids are widely used in manufacturing processes of different industrial operations [3, 4]. Sulfuric acid is widely used for the removal of rust and scale in several industrial operations. The corrosion behavior of carbon steel in acidic solution is a subject of pronounced practical significance considering its widespread applications, namely in the manufacturers of pipelines for petroleum industries. Sulfuric acids are the most difficult of the common acids to handle from the standpoints of corrosion and materials constructions [1, 5, 6].

Carbon steel, the most widely used engineering material, accounts for approximately 85%, of the annual steel production worldwide. Despite its relatively limited corrosion resistance, carbon steel is used in large tonnages in marine applications, nuclear power and fossil fuel power plants, transportation, chemical processing, petroleum production and refining, pipelines, mining, construction and metal-processing equipment. Steel is one of the major construction materials, which is extensively used in chemical and allied industries for the handling of acid, alkali and salt solutions [7, 8].

Copper and its alloys are very widely used materials for their excellent electrical and thermal conductivities in many applications such as electronics and in the manufacture of integrated circuits. Copper is a relatively noble metal, requiring strong oxidants for its corrosion or dissolution. The chemical dissolution and electrolytic plating are the main processes used in the fabrication of electronic devices [9, 10,24].

There are many factors effecting the galvanic corrosion and these factors are: electrode potentials, reaction kinetics, area ratio, mass transport, bulk solution environment, bulk solution properties, alloy composition, and protective film characteristics [11, 12].

Galvanic corrosion of steels arises practically in different situations such as in case of heat exchangers when the shell made from steel and the pipes made from copper, in case of rivets made steel in contact with plates made from other material such as copper [23].

The purpose of the present work is to investigate the galvanic corrosion of carbon steel-copper under dispersion conditions of air in sulfuric acid H₂SO₄ under different operating conditions of agitation speed and temperature.

Experimental Work

Experiments were carried out to study the galvanic corrosion of carbon steel and copper in acidic salt solution of 0.1 M sodium chloride and 3% sulfuric acid (H₂SO₄) at stationary and flow conditions at temperatures of 33, 45, and 55 °C, and agitation speed range from 0 to 800 rpm . Air was pumped in the solution under each condition.

Dispersion of air bubbles occurred due to mixing conditions. The corrosion rate of each metal was determined by weight loss and the galvanic current was determined by using zero-resistance ammeter (ZRA). Fig. 1 shows the experimental apparatus. It is composed of cylindrical perspex (used and described elsewhere the thickness 4 mm, vessel diameter Dt=300 mm and H=300 mm height, filled with test solution. Five equally spaced vertical baffles made of perspex each of width equal to 25 mm. A perspex 4-blade disc impeller of diameter equal to 100 mm, blade length 25 mm, blade width 20 mm, was used and located 10 mm from the tank bottom [13]. Heater and controller were used to obtain the required temperature of the solution. The PH-meter with accuracy of ± 0.01 was used to measure the PH of solution, conductivity meter was used to measure the conductivity, and the oxygen concentration was measured for each condition and monitored along the run using dissolved oxygen meter. Before each test the vessel was washed with tap water using liquid detergent, rinsed with tap water. The air is pumped through the solution using air pump with different flow rates. The solution is agitated by the agitator with different rotational speeds. Due to shear forces associated the agitation; air bubbles were broken to smaller bubbles and dispersed through the solution.

Before each experimental run, the metal specimens were washed and dried polished successively with emery papers grades (220,400,1200), washed by tap water followed by distilled water, dried with clean tissue, immersed in ethanol for 3 min and dried with clean tissue. The specimens then were stored in a vacuum desiccator over high activity silica gel until use. The same procedure was repeated for the specimens after the experiments. Then, the samples were dried by oven at 100°C for 10 minutes [7, 14].

The galvanic current density (I_G) and galvanic potential (E_G) between the coupled metals were measured with time using ZRA. The luggin capillary of the reference electrode was placed 2 mm from the working electrode to measure the potential of specimen via high impedance voltmeter. Zero resistance ammeters (ZRA) to measure the galvanic current flowing between the specimens under various experimental conditions. Coupons of Cu and CS of dimensions (40×40 mm) were used. They were placed in the solution by fixing them on plate using fine screw and exposed to the solution from one side and connected electrically by connecting wires. So. The weight loss method was used to calculate the corrosion rate (C.R.) by using the following relationship:

$$CR = \frac{\Delta W}{A \times t} \quad \dots \quad \dots \dots (1)$$

Where:

- ΔW : weight loss(g), A: exposed Area (m²), t: exposure time (h)

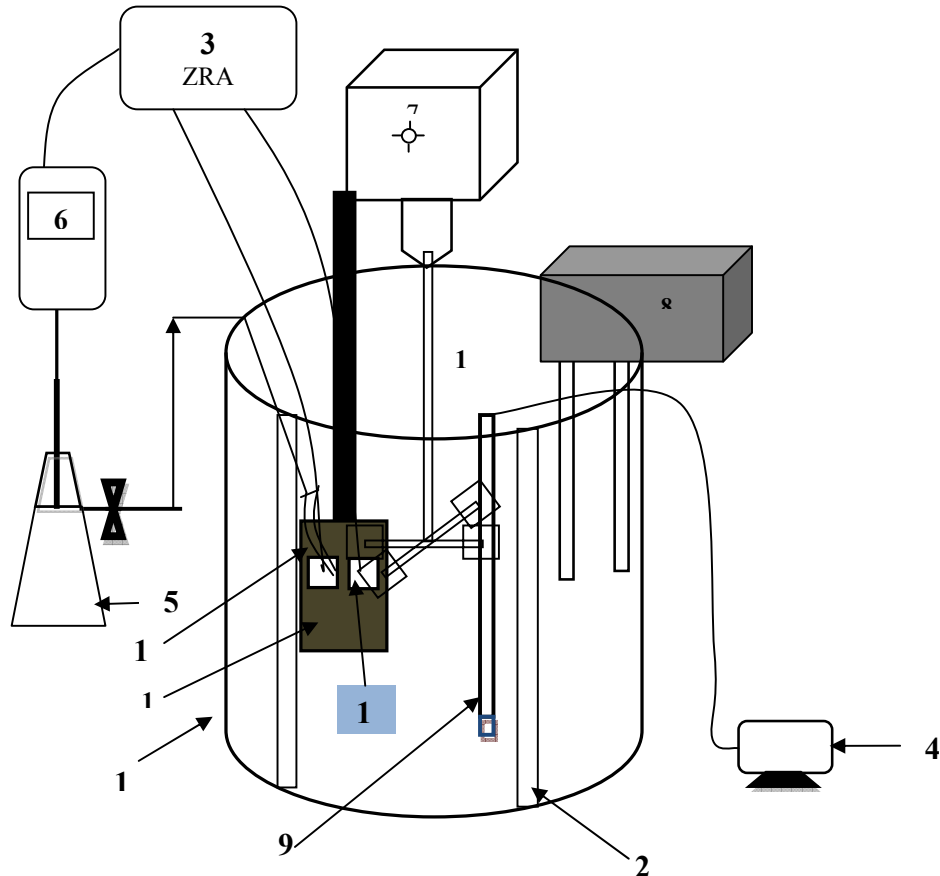


Figure (1). Schematic illustrates of apparatus used in experimental work.

1-Pyrex tank, 2- Baffles, 3-zero resistance ammeter, 4- air pump, 5- calomel electrode (reference electrode), 6- voltmeter, 7- stirrer, 8- Heater and controller, 9- air distributor, 10- working electrode, (specimen), 11- Luggin capillary, 12- plate for specimens, 13- impeller

Result and Discussion

(ZRA) using for V , I , V_g , I_g

Figures 2 and 3 show the time behavior of corrosion potential of copper and carbon steel respectively at three temperatures (33, 45 and 55° C). The corrosion potential decreases with time for all three temperatures. For instance, in Fig. 2, at 33°C the potential equals to -0.514 V at 0 min and decrease to -0.546 V at 60 min and in Fig. 3, at 45°C the potential equals to -0.542 V at time 0 min and decreases to -0.561 V at 60 min. This indicates the corrosion occurs at the start leading to shift the potential to more negative. As the time proceeds, the corrosion continues leading to decrease the surface

activity and formation of passivation layer that restrain the corrosion [15]. This is in agreement with the previous works [1, 10, 16].

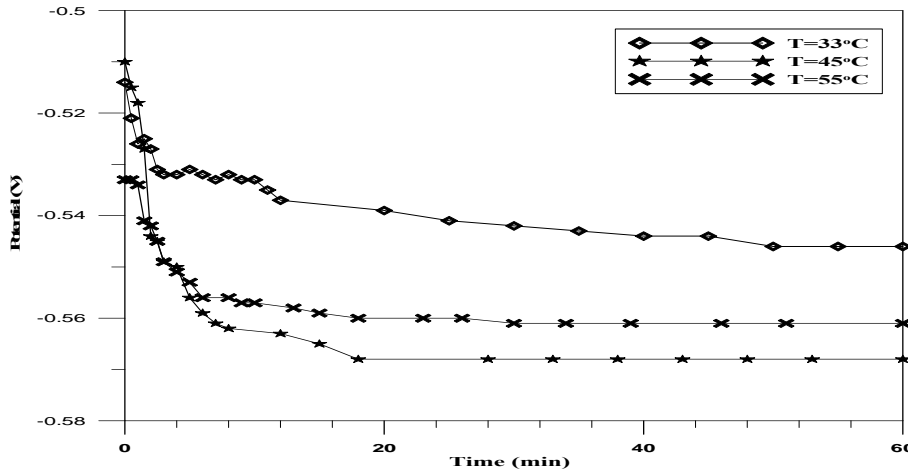
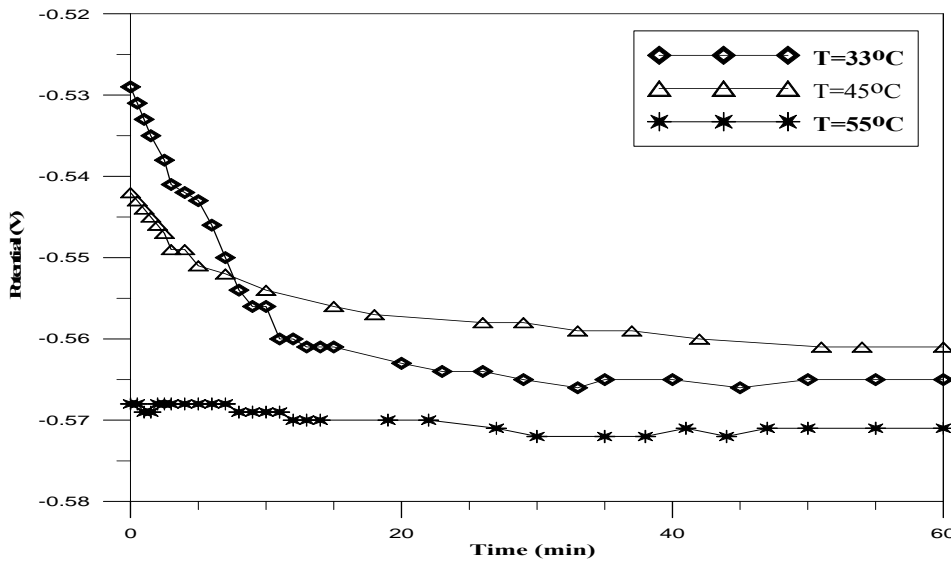


Figure (2): Corrosion potential of copper at different temperatures with air bubbling

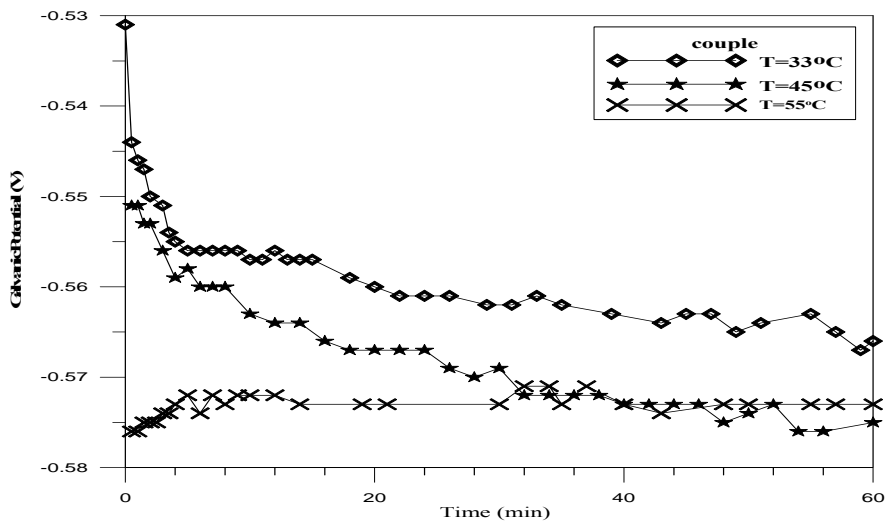


Figure(3): Corrosion potential of carbon steel at different temperatures with air bubbling

Figs. 2 and 3 indicate also that the trend of potential with temperature is unstable. It can be noted that in first few minutes close to time 0 the potential is shifted to more negative with increasing temperature. In general, at 33 °C the potential is more positive than other two temperatures. Beyond that time zero as the time proceeds and the corrosion continues, the trend becomes unstable with temperature. At 45 °C and 50 °C the

potential is low indicating that the corrosion rate is severe at that temperature and the passivation layer is not effective due to the increased temperature.

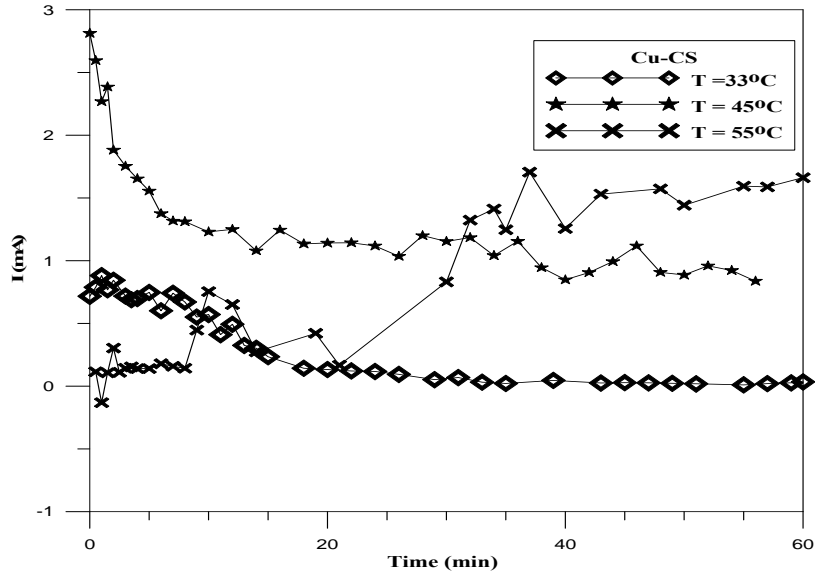
The results presented in Fig. 4 shows the behavior of galvanic potential (E_g) of CS-Cu couple with time at different temperatures (33,45, and 55°C). The metals surfaces at the beginning of corrosion process are clean and active to react with hydrogen and oxygen. During the experiment the corrosion product film will be formed, so the galvanic potential (E_g) is changed with time to more negative values. This time behavior is in accordance with what were noticed by other works [12, 16, 17]. However, Fig. 4 reveals the higher the temperature is the lower the potential will be due to the decrease in O₂ concentration with temperature increase [1,6, 14]



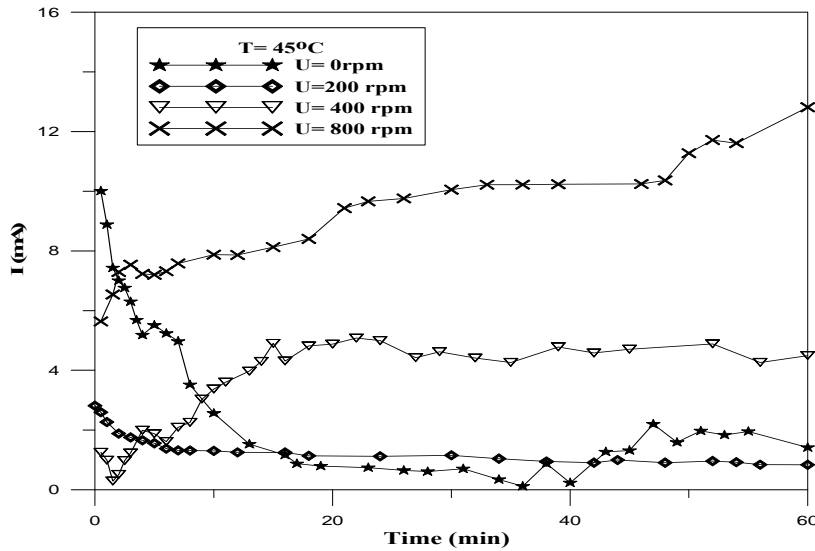
Figure(4) Galvanic potential of Cu-CS at different temperatures and U=0 rpm with air bubbling

Figs. 5 shows the trend of I_g versus time of between CS-Cu couple at different temperatures for stationary conditions. The figure reveals that at start the time has unstable trend with time but at the asymptotic values, the higher the temperature is the higher the galvanic current. Increasing temperature leads to an increase in the oxygen diffusivity and also it promote the reaction kinetic of both anodic and cathodic reactions by decreasing the activation energy [6, 18].

Fig. 6 shows that the galvanic current increases with increasing rotational velocity. This is due to the increase in the amount of oxygen transport to the surface. However, increasing agitation speed leads to a decrease in the thickness of diffusion layer which is the main resistance to mass transport, hence, the arrival of O₂ increases to cathode surface (copper) leading to enhance the corrosion of anodic (carbon steel) and, therefore, increasing the corrosion rate [16, 19].



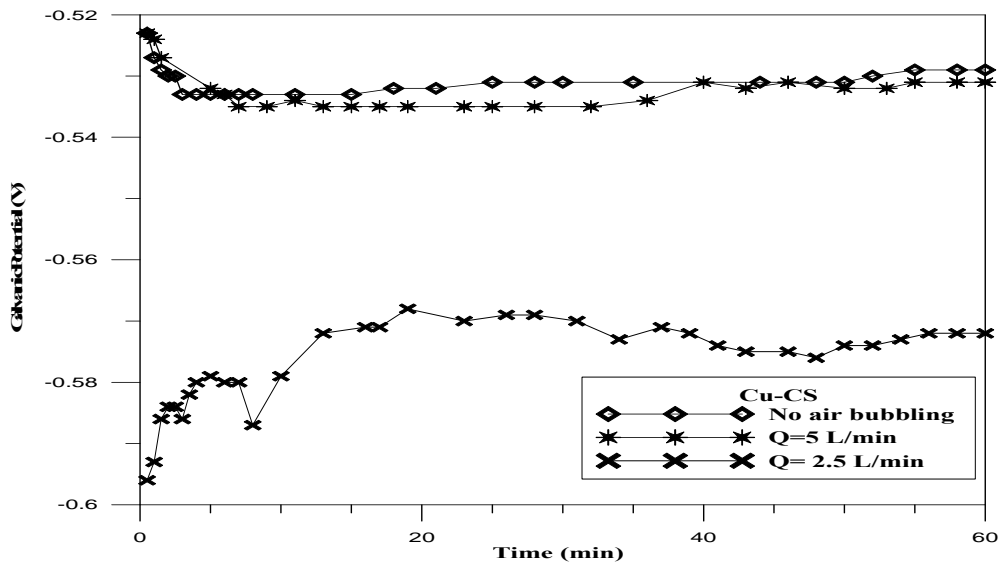
Figure(5): Galvanic current of Cu-CS vs. time at different temperatures with air bubbling



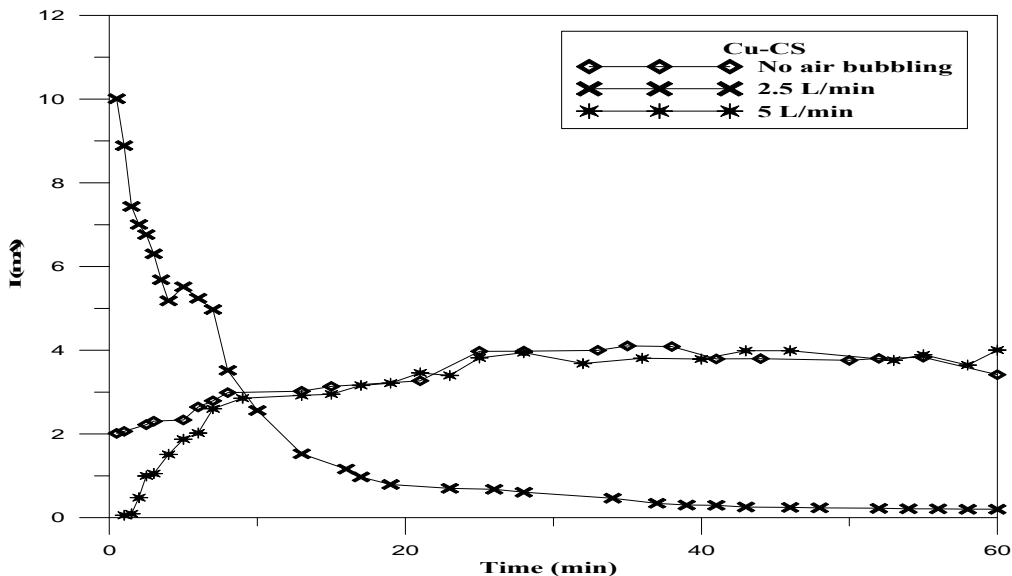
Figure(6): Galvanic Current of Cu-CS at different velocity and T = 45°C with air bubbling (Q=2.5 L/min)

Fig. 7 shows the galvanic corrosion couple versus time with and without air bubbling which indicates that the galvanic potential Decreases when pumping the air at low flow rate (2.5 L/min) with further increase, the potential shifts up. This is interpreted as follows: when air is pumped, its fraction in the acid solution increases leading to increase the electrical resistance of the solution because air is nonconductive to electricity shifting

the potential to negative direction With further increase in flow rate the O₂ concentration increases shifting the potential to more positive. In Fig. 8 it is clear that for low flow rate (2.5 L/min), the galvanic current decreases because of the increase in electrical resistance. With further increase in air flow rate and due to high turbulence associated, the concentration of O₂ increases leading to increase the galvanic current. Thus the maximum rate at which oxygen can be diffused to the surface would be essentially directly proportional to the concentration in solution [20].



Figure(7) Galvanic Potential of Cu-CS at T=45, U=400 rpm, different air flow rate



Figure(8) Galvanic Current of Cu-CS at T=45, U=400 rpm, different air flow rate

Weight Loss Measurements

The experimental data obtained by weight loss measurements were evaluated to determine the corrosion rate of metal after one hour exposure time. These are summarized in Tables 1 and 2. Table 1 indicates that the corrosion rate of copper increases by increasing rotational velocity with air bubbling.. Since the corrosion of Cu and CS in aerated H₂SO₄ solution is under both mass transfer and activation charge transfer control, therefore increasing rotational velocity will increase the amount of oxygen arriving to the surface and hence leads to a higher corrosion rate. This leads to decrease in the thickness of diffusion layer that represents the main resistance to oxygen transport. As the velocity increases the convective mass transport of O₂ will increase.

Increasing turbulence leads to a decrease in the thickness of the viscous sub-layer and the diffusion layer causing the corrosion rate to increase. However, Table 1 indicates that the presence of air bubbling in the solution leads to a decrease in corrosion rate compared with the case of no bubbling. These results of weight loss support the galvanic current results in Fig. 8. This behavior can be attributed to the decrease in the solution conductivity as shown in Table 3. Table 3 shows that the presence of air bubbles leads to a slight decrease in the solution electrical conductivity and slight increase in O₂ solubility. In general, the resultant is a lower corrosion rate. Table 4 shows that for air flow rate of 5 L/min, the increase in O₂ solubility is clear. That is why the corrosion galvanic currents and corrosion rate are high in case of Q-5 L/min. Table 1 indicates also that coupling carbon steel to copper leads to increase the corrosion rate of carbon steel (the anode) and decreases the corrosion rate of copper (the cathode). This behavior agrees with many previous studies [6, 21, 22].

Table (1). Corrosion rate of copper and CS at T = 45°C.

Condition			Copper (gmd)	Carbon Steel (gmd)
Free corrosion of metal	Air Bubbling, Q=2.5 L/min	U = 0 rpm	6.1	68.2
		U = 200rpm	12.2	100.5
		U = 400rpm	15.1	248
		U = 800rpm	37.4	302.5
	Without air bubbling	U = 400rpm	19.5	380.2
Cu-CS corrosion	Air Bubbling, Q=2.5 L/min	U = 0rpm	3.5	104.63
		U = 200rpm	2.5	209.11
		U = 400rpm,	10.5	304.16
		U = 800rpm	12.3	401.5
	Without air bubbling	U = 400rpm	19.5	315.33

Table 2 reveals that the corrosion rate increases with the increase in temperature. This is because of different reasons. The common effect of temperature is on the reaction kinetics and the higher diffusion of reactant toward the metal surface. Besides, high temperature may deliver these by-products to the surface more efficiently [6, 15]

Table (2). Corrosion rate with air bubbling, Q=2.5 L/min and u=0.

Condition		Copper (gmd)	Carbon Steel (gmd)
Free corrosion of metal	T = 33°C	4.35	58.636
	T = 55°C	8.5	104.127
Cu-CS corrosion	T = 33°C	2.5	90.794
	T = 55°C	4.2	122.846

Table (3): pH, conductivity, and dissolved O₂ values at different condition

T, °C	U(rpm)	pH		Conductivity, ms		Dissolved O ₂ (mg/l)	
		Without bubbling	Air Bubbling, Q=2.5 L/min	Without bubbling	Air Bubbling Q=2.5 L/min	Without bubbling	Air Bubbling, Q=2.5 L/min
33	0	1.03	1.03	25.7	25.6	3.95	4.55
45	0	1.06	1.08	24.2	23.9	2.93	3.00
	200	1.09	1.08	23.7	23.3	4.36	4.52
	400	1.09	1.09	23.8	23.1	4.43	4.73
	800	1.09	1.09	23.8	23.1	4.91	5.95
55	0	1.03	1.01	22	21.9	3.07	3.10

Table (4): Values of pH, conductivity, dissolved O₂ for Q=5 L/m, T=45 C, u=400 rpm

Q, L/min	pH	Conductivity, ms	Dissolved O ₂ (mg/l)
5	1.1	23.8	8.2

CONCLUSIONS

- 1- The corrosion rate of carbon steel and copper in 3% H₂SO₄ increases with temperature and agitation velocity.
- 2- Galvanic corrosion between carbon steel and copper increases with increasing temperature and agitation velocity.
- 3- The free corrosion potential and galvanic potential have unstable trend with temperature and flow velocity.
- 4- The presence of air bubbles at low pumping rate leads to a decrease in free corrosion rate and galvanic currents by decreasing the solution conductivity. Further increase in air flow rate, leads to a noticeable increase in the galvanic currents by increasing the O₂ solubility.
- 5- Coupling carbon steel with copper increases the corrosion rate of the former and decreases that of the late.

REFERENCES

- [1].Fontana and Greene, “**Corrosion Engineering**”, Mc Graw Hill, 1984.
- [2].Cifuentes L. “**Anti-corrosion**”, November, 1987.
- [3].El-Nabey, B. A. , E. Khamis, M.Sh. Ramadan, A. El-Gindy, *Corrosion* 52-9 (196) 671.
- [4].F. Bentiss, M. Lagrenée, M. Traisnel, *Corrosion* 56-7 (2000) 733.
- [5].Bellaouchou, A., A. Genbour, A. Benbachir, *corros. NACE* 49 (1993), 656.
- [6].Shreir L.L., R.A. Jarman & G.T. Burstein “*Corrosion Metal / Environment Reactions*” third edition, published by Butterworth-Heinemann Volume I, Great Britain, 2000.
- [7].Hasan B. O., S. A. Sadiq “The Effect of Temperature and Hydrodynamics on Carbon Steel Corrosion and Its inhibition in Oxygenated Acid- Salt Solution”, *Journal of Industrial and Engineering Chemistry (JIEC)*, 2014.
- [8].Uhlig H.H., “**Corrosion Handbook**”, John Wiley and Sons, Inc, 1976.
- [9].Fiala, A., Chibani, A. Darchen, A. Boulkamh, K. Djebbar, Investigations of the inhibition of copper corrosion in nitric acid solutions by ketene dithioacetal derivatives, *Applied Surface Science* 253 (2007) 9347–9356.
- [10].Hack, H.P., “ATM STP 979”, (1988), p339-351.
- [11].Copson H.R., “*Industrial and engineering chemistry journal*”, Vol.8, No.38, P721-723, 1945.
- [12].Stern, M. *Corrosion-NACE*, Vol. 13, pp. 97, 1957.
- [13].S. M. Aziz, B. O. Hasan, ” Corrosion of Carbon Steel in Stirred Two Phase Media of Brine-Gas oil and Brine-CO₂ and Prevention by Cathodic Protection” M. Sc. Thesis, Chemical Engineering Department, Al-Nahrain University, December, 2014.
- [14].Mahato B. K., C. Y. Cha and W. Shemlit, “Unsteady State Mass Transfer Coefficients Controlling Steel Pipe Corrosion under Isothermal Flow Conditions”, *Corrosion Science*, vol.20, pp.421–441, 1980.
- [15].Fathia S. Mohammed, Salaheddin E. A. Abu Yahya², Alyaa G. Elramady, Effect of Temperature and Concentration of Ammonium Nitrate Solution on the Susceptibility of Mild Steel to Stress Corrosion Cracking, *J. Electromagnetic Analysis & Applications*, 2010, 2: 91-97.
- [16].S. Huang and R. A. Oriani, “The Corrosion Potential of Galvanically Coupled Copper and Zinc Under Humid Gases,” Abstract No. 91, Electrochemical Society Extended Abstracts, Fall Meeting, Oct. 10–15, 1993, New Orleans, LA, Electrochemical Society, Pennington, NJ, Vol. 2–93, p. 156, 1993.
- [17].Schweitzer P.A., “*Corrosion and Corrosion protection Hand book*”, Marcel Decker, 2nd ed., (1989).
- [18].Tsujino B. and T. Oki, “Measurement of steel and aluminum corrosion rates using the galvanic couple method”, *NACE, Corrosion*, December, 1988.
- [19].Y.H. Yau and M.A. Streicher, “Galvanic corrosion of duplex FeCu-10%Ni alloys in reducing acids”, *Corrosion (NACE)*, 1987.
- [20].Slaiman Q. J. M. and B. O. Hasan “Study on Corrosion Rate of Carbon Steel Pipe under Turbulent Flow Conditions” *The Canadian Journal of Chemical Engineering*, Vol. 88, pp. 1114- 1120, 2010.
- [21].Mansfeld F., 1971, *Corrosion Journal*, 10, 27, pp. 436-442.

- [22]. Hasan, Basim O., Galvanic corrosion of carbon steel–brass couple in chloride containing water and the effect of different parameters, Journal of Petroleum Science and Engineering 124(2014)137–14.
- [23].Sami I. Al-rubaiey., Eman A. Anoon, Mahdi M. Hanoon “The Influence of Microstructure on the Corrosion Rate of Carbon Steels”, Eng. &Tech. Journal, Vol. 31,Part (A), No.10, 2013.
- [24].Shatha A.Sameh., Issam K.Salih, Sadiq H.Alwash, and AsawerAL-Waisty “Corrosion of Copper in Deaerated and Oxygenated 0.1M H₂SO₄ Solutions under Controlled Conditions of MassTransfer”, Eng. &Tech. Journal, Vol. 27, No.5, 2009.