S.A. Jafar
College of Petroleum and Minerals Engineering, Petroleum Process Engineering Department, University of Tikrit, Iraq
drensaadaj@yahoo.com

Received on: 19/12/2016
Accepted on: 16/03/2017

The Influence of Area Ratio, Temperature and Rotational Speed on Galvanic corrosion between Law Alloy Steel–Copper couple in 4%NaCl Solution

Abstract-*Galvanic corrosion between law alloy steel and copper couple in 4 % NaCl solution was studied and the effect of some variable were investigated. The effect of area ratio, temperature and rotational speed through the electrolyte have been investigated. An increase in galvanic current was observed when we increased the area ratio of law alloy steel to copper and the galvanic potential moved to extra negative direction. When the temperature of solution increase led to increase the galvanic current and shifting the galvanic potential to extra negative direction. The galvanic current rises clearly with increasing of rotational velocity of agitator with shifting the galvanic potential to extra positive due to mass transfer control the process. In addition, increase the diffusion of oxygen from bulk of electrolyte to the metals surface.*

Keywords-*galvanic corrosion, law alloy steel, copper, area ratio, temperature.*

How to cite this article: S.A. Jafar, “The Influence of Area Ratio, Temperature and Rotational Speed on Galvanic corrosion between Law Alloy Steel–Copper couple in 4 %NaCl Solution,” *Engineering and Technology Journal*, Vol. 35, Part A. No. 6, pp. 617-623, 2017.

1. Introduction

Galvanic corrosion is widely noticed in petroleum refining plants, such as pipelines, heat exchanger, distillation tower, and cooling tower and in any places when two dissimilar metals are placed into contact and are immersed in a corrosive or conductive solution. There is a potential difference exists between them which causes a flow of electrons (current) between these two metals. Galvanic corrosion have been observed in pressure vessels where the welds are anodic to base metal (law alloy steel) [1]. The metal with less resistance behaves as anode and tahe more resistance metal becomes cathode [2]. Such situation are often encountered problems with galvanic corrosion are the most acute in heat exchangers in which law alloy steel tube sheets are used with copper tubes at junctions between piping when the cathode to anode area ratio is large [3]. Law alloy steel, the most widely used engineering material for petroleum pipelines because it has good resistance, strength, hardenability, weldability, toughness, formability and its mechanical properties is influenced by heat treatment [4]. In petroleum refining plants, law alloy steel always bring to attach with different metals causing galvanic corrosion. Copper has outstanding electrical and thermal conductivities therefore; it is used in many industrial applications like pipes, tubes, valves in heat exchanger and condenser [5]. Therefore, the design of many industrial plants are directly fixed by galvanic corrosion [6]. In galvanic corrosion, the galvanic current density (i_g) with respect to the anode should be equal to the difference between current density of anode (i_A) and the limiting diffusion current density for oxygen (i_{LO2}).

$$ig = iA - iLO_2 \qquad (1)$$

Since the corrosion current density of the anode $I^A_{corr.}$ Equal to i^L_{O2}
Equation (1) can be written as:

$$ig = iA - IAcorr \qquad (2). [3]$$

The galvanic current density can be expressed as:

$$ig = \frac{Ig}{A} \qquad (3)$$

Where: I_g is the galvanic current flowing between two metals.
A is the surface area of exposure. Galvanic corrosion is one of the most common types of corrosion. Metals immersed in an electrolyte for example (NaCl solution) lead to release some amount of its cations into the solution and gain a specific value of an electrical potential against the electrolyte. This open circuit potential (OCP) is specific for combination of metal and electrolyte and is known as corrosion potential (E). The

https://doi.org/10.30684/etj.35.6A.9
2412-0758/University of Technology-Iraq, Baghdad, Iraq

metals with higher corrosion potential act as a cathode, and the metal with lower corrosion potential act as anode [7]. Galvanic corrosion is influence by different parameters such as area ratio between anode/cathode, temperature of electrolyte, and rotational speed of agitator through the electrolyte. Area ratio effect in galvanic corrosion involve the ratio of the surface area of the more noble metal (cathode) to the surface area of more active metal (anode). When the surface area of the more noble metal (cathode) is larger in comparison to the more active metal (anode), an un favorable area ratio occurs in which a couple is under cathodic controller. The larger cathdic area related with the anode, the extra O_2 reduction on it and great the galvanic current. On the cathode (copper), the following reaction occurs and the excess electrons, which form at the surface, are consumed.

$$O2 + 2H2O + 4e \rightarrow 4OH \quad (4)$$

In addition, on the anode (law alloy steel) the iron on it is oxidized according to the following reaction.

$$Fe \rightarrow Fe+^2 + 2e \quad (5)$$

Previous studies for various couples [5,8] showed different couples with different area ratio. The influence of temperature on galvanic corrosion is particularly important. When temperature rise lead to provide enough additional energy to accelerate the reaction at the metal surface, resulting in rapid corrosion. This behavior can be explained as follows: increasing temperature lead to change two variables, first acceleration the reaction rate and diffusion rate of oxygen by increasing the molecular diffusions coefficient, second the solubility of oxygen decreases as the temperature increases, but in a closed system the oxygen cannot escape leading to increase rate of corrosion, since in open system, allowing dissolved oxygen to escape, the corrosion rate increased to about 80 º C and then drops to very law rate [9]. In addition, the increasing the temperature causes an increase in the galvanic corrosion current (I_g) and the corrosion potential decreases slightly with increasing the temperature [10]. Previous work of researchers on galvanic corrosion rate with time showed different directions. [11] Observed unsteady direction of the rate of galvanic corrosion with increasing the temperature of solution when coupled stainless steel-Ti in acid salt-water. [12] Fixed that a rise in the galvanic corrosion current when join brass-stainless steel in brine and the galvanic corrosion potential is moved to extra negative side, when the temperature of electrolyte was increased. The effect of rotational speed of agitator through the electrolyte on galvanic corrosion of law alloy steel coupled to copper are very rare in literature. The aim of this work is to find the influence of some parameters for examples area ratio, temperature, and rotational speed with time on the behavior of galvanic corrosion like galvanic corrosion potential and galvanic current between law alloy steel-copper couple in 4 % NaCl electrolyte and comparison the results with free corrosion potential of uncoupled metals.

2. Experimental work

A schematic diagram of the experimental set up is shown in Figure 1 .The law alloy steel specimen have the chemical composition which were analyzed using XRD are shown in Tables 1. The copper purity is 99.9 %. The area of copper electrode (cathode) was kept constant through the whole experiments and the area of law alloy steel (anode) was differed through the runs of experiments.

Area ratio (AR) researched = surface area of law alloy steel / surface area of copper

AR = 0.25 ($A_{LAS} = 20 \times 30\ mm^2$, $A_{Cu} = 60 \times 40\ mm^2$)

AR = 0.5 ($A_{LAS} = 30 \times 40\ mm^2$, $A_{Cu} = 60 \times 40\ mm^2$)

AR = 1 ($A_{LAS} = 60 \times 40\ mm^2$, $A_{Cu} = 60 \times 40\ mm^2$)

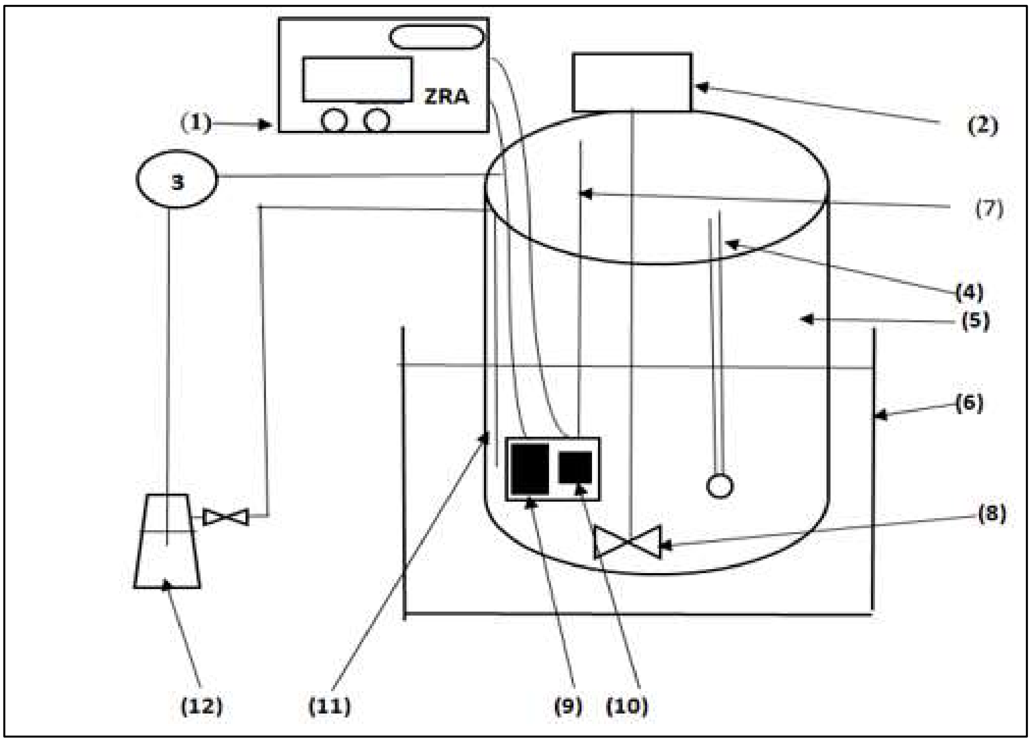
AR = 2 ($A_{LAS} = 80 \times 60\ mm^2$, $A_{Cu} = 60 \times 40\ mm^2$)

AR = 3 ($A_{LAS} = 120 \times 60\ mm^2$, $A_{Cu} = 60 \times 40\ mm^2$).

The specimens were immersed in 4 % NaCl solution, the parameters of experiment are area ratio ($AR = A_{LAS} / A_{Cu}$) range of 0.25 - 3, temperature range of 30 ºC – 50 ºC and rotational velocity range of 0 – 400 rpm. With different time up to 50 min., Water bath was used to control the temperature and mechanical agitator for giving various rotational speed. The specimens of law alloy steel and copper are fixed Teflon plate with 15 mm distance between them and immersed in the solution (electrolyte) so that one side of the surface of samples are exposure to the solution and then connected by electric wire. Zero resistance ammeter, ZRA (ACM Company, United Kingdom) was used to determine the galvanic current between two electrodes in different settings of experiment [13]. Open circuit potential (OCP) of electrodes and galvanic corrosion potential was determined by employing saturated calomel electrode (SCE) as reference electrode, which placed outside the cell, and the potential of specimens is measured through the luggin capillary connected to the negative terminal of voltmeter . The testing method is accomplished by placing the luggin-capillary at distance optimum of 2 mm from the specimen surface. The specimens were abraded in sequence using emery paper of grade number 220, 320, 400, 600, and 1000 respectively, then washed with running tap water followed by deionized water, then dried with clean tissue, degreased by benzene, dried, degreased by acetone and dried with clean tissue and then dried with an air blower, and kept in a desiccators over a silica gel bed until use [14]. After preparing the solution 4% NaCl at needed temperature and needed rotational speed, the working electrode were introduced in right places and the galvanic current and galvanic potential were measured with time until they attained equilibrium rate, each experiment was repeated three times.

3. Result and discussion

Figure 2 shows the relation between corrosion Potential (open circuit potential OCP) with time at 30 ºC and stagnant solution (speed, u = 0). It was observed that the free corrosion potential of copper is less negative than the free corrosion potential of law alloy steel, therefore the copper behaves as cathode relative to law alloy steel which behaves as anode and the tendency of cu to corrode decreases when it coupled to LAS, but the tendency of LAS for corrosion increased when it coupled to cu.



(1)(ZRA) Zero resistance ammeter. (2) Mixer. (3) Voltmeter. (4) Thermometer. (5) Beaker. (6) Water bath. (7) Holder of Specimen. (8) Impeller. (9) Law alloy steel specimen. (10) Copper specimen. (11) Luggin capillary with salt bridge. (12) Calomel reference electrode.

Figure 1: Schematic of test device

Table 1: The chemical analysis of law alloy steel (LAS)

C %	Mn %	P %	S %	Si %	Cr %	Ni %	Cu %	Mo %	Fe %
0.078	0.45	0.058	0.022	0.04	traces	0.62	0.43	0.13	98.17

I - Effect of area ratio

Figure 3 shows galvanic corrosion potential Eg with time at different area ratio (AR) for LAS- cu couple for AR = 0.25, 1, 3. It was observed that the galvanic corrosion potential for equal surface area of two metals (AR = 1) is between free corrosion potential of two metals.

It was also observed that the galvanic corrosion potential and free corrosion potential decrease with time (shifting to more negative direction) is due to the corrosion product which build on the surface of (LAS) which reduces the activity of anode surface [4].

Figure 4 shows the effect of area ratio (AR) on the galvanic current (Ig) with time at stagnant solution (u=0) and at 30 °C. It was observed that the galvanic corrosion current is rise at the beginning and then decreases clearly with time then reach equilibrium value after about 40-45 min.

This behavior noticed with all area ratio. The reduce of galvanic current (Ig) with time was due to the retard of arrival of oxygen to the surface of metal for the result of formation layer of corrosion product which lead to decrease the anodic reaction $Fe \rightarrow Fe^{+2} + 2e$ and also due to increase of ions concentration in the solution which decrease the potential differences between the electrolyte and the anode at the metal electrolyte interface and leading to decrease in galvanic current (Ig) [4]. Also from Figure 4 noticed that the galvanic current (Ig) change with area ratio and increases with increasing of area ratio (AR) because the total area of anode LAS and cathode cu was increased which led to increase of oxidation and reduction reactions with increasing of exposure surface area of metals.

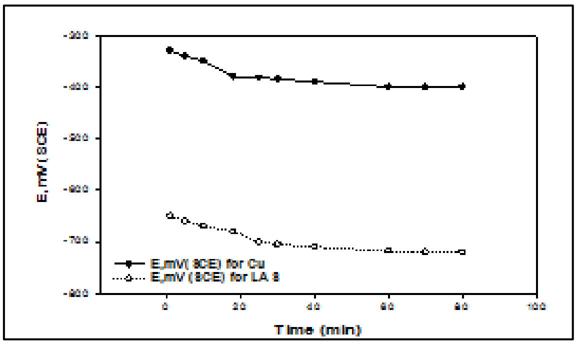


Figure 2: Relation between free corrosion potential (Open circuit potential OCP) with time at 30 °C, stagnant solution (u=0), and 4% NaCl

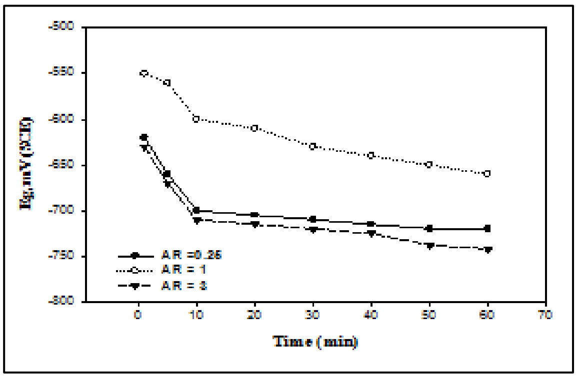


Figure 3: Galvanic corrosion potential Eg, mV vs. time at different area ratio (AR) at 30 °C, stagnant solution (u=0), and 4% NaCl

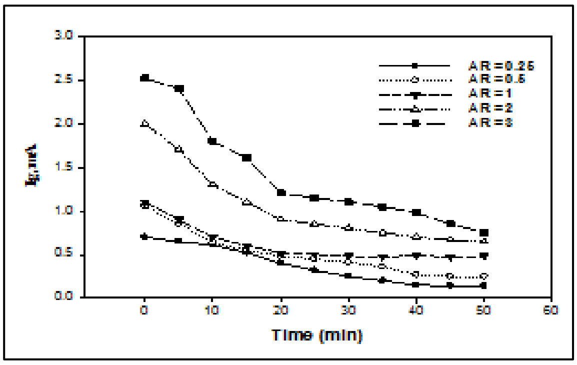


Figure 4: Galvanic current vs. time at different area ratio (AR) at stagnant solution (u=0), in 4% NaCl and 30 °C

Figure 5 shows the influence of area ratio (AR) on the galvanic current density of law alloy steel with time at stagnant solution (u = 0) and at 30 °C. ($i_{LAS} = Ig/ A_{LAS}$). It was observed that when the area of low alloy steel increase led to decrease current density. Also noticed that the smaller surface area of LAS, the larger current density, there for it is unfavorable to use large copper area relative to low alloy steel area because this will cause high rate of corrosion of anode (LAS) duo to the current density on its surface is high [2, 7, 9].

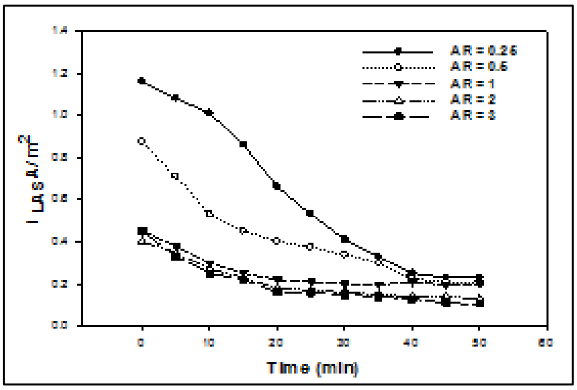


Figure 5: Galvanic current density of low alloy steel (LAS) vs. time at different area ratio (AR) at stagnant solution (u = 0) in 4% NaCl and 30 °C

Figure 6 shows the influence of area ratio (AR) on the galvanic current density of copper with time at stagnant solution (u = 0) and at 30 °C. (i_{cu} = Ig/ A_{cu}). It was observed that the galvanic current density remains constant when area ratio increase because the area of copper (cu) remains constant in all experiments.

I I -Effect of Temperature

Figure 7 shows the influence of temperature on the galvanic current (Ig) with time. At stagnant solution and area ratio equal to one. It was observed that when the temperature of solution increases lead to an increase in the galvanic corrosion current. This behavior can be explained as follows: increasing temperature lead to change two variables that act in conflicting way. Firstly, increasing temperature will accelerate the mass transfer process, which led to increase the reaction rate and diffusion rate of oxygen by increasing the molecular diffusion coefficient of oxygen. Secondly, when the temperature increase the solubility of oxygen decrease. In open vessel, allowing dissolved oxygen to escape, the corrosion rate increasing with temperature to about 80 °C and then falls to very low value from solution because most of oxygen gas escape from solution and reduce reduction reaction (eq.,5) [16]. Sometimes temperature affect indirectly on corrosion attack on metals. In systems where an adherent protective film (from corrosion product) on the metal may be stable in a given solution at room temperature. The protective film may be soluble in solution at high temperature, which lead to increase corrosion rate rapidly and then increase galvanic corrosion current with increasing temperature [7].

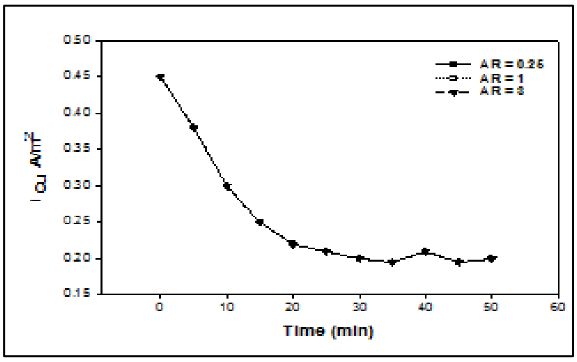


Figure 6: Galvanic current density of copper (Cu) vs. time at different area ratio (AR) at stagnant solution (u = 0) in 4% NaCl and 30 °C

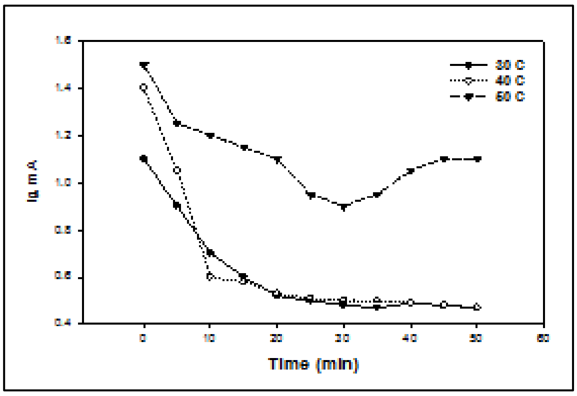


Figure 7: Galvanic current Ig, mA vs. time at different temperature at stagnant solution (u = 0) in 4% NaCl and AR = 1

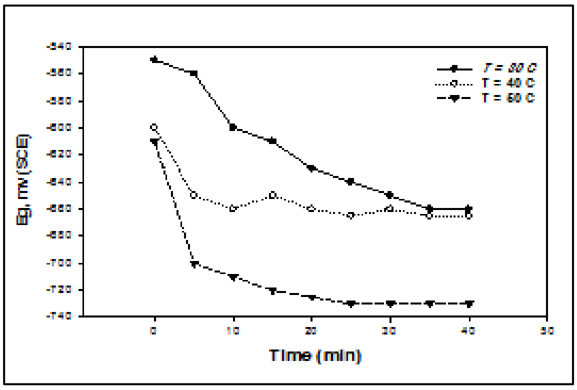


Figure 8: Galvanic corrosion potential (Eg) vs. time at various temperature at stagnant solution (u = 0) in 4% NaCl and AR = 1

Figure 8 shows the influence of temperature on the galvanic corrosion potential (Eg) with time at stagnant solution (u =0) and area ratio (AR =1). It was observed that when increasing the temperature of electrolyte, the galvanic potential decreases to more negative side with time for whole temperatures of experiments. The shifting of galvanic potential to more negative direction with increasing temperature is due to reduce the solubility of oxygen in the solution as described before and because, the corrosion product layer on the LAS may be soluble in the solution at high temperature which shift the potential to more negative.

I I- Effect of rotational velocity.

Figure 9 shows the influence of rotational velocity of agitator on the galvanic current (Ig) with time at area ratio (AR =1) and at 30 ºC. It was observed that at Stagnant solution (u=1) the galvanic current decrease with time, but when the rotational speed of agitator increases, the galvanic current increases due to increase the diffusion of oxygen from the bulk of liquid to the metal surface which lead to increase the reduction of O_2 on the two metals surface of couple because the reduction of O_2 is mass transfer control [17]. And when increase the reduction of O_2 on the cathode (Cu) lead to increase the oxidation reaction (Fe dissolution) on the low alloy steel (anodic reaction) due to galvanic effect, equation (5).

Figure 10 shows the influence of rotational speed of agitator on the corrosion potential, (Eg) with time at the area ratio (AR=1) and at 30 ºC. It was observed that at any velocity from 0-400 rpm the galvanic potential (Eg) decreases with time (shifting to more negative direction), but when the speed increases lead to increase O_2 diffusion from bulk of the liquid to the metal surfaces of two couples and shifting the galvanic potential to more positive [18]. and the galvanic current will be increase.

4. Conclusions

There is a galvanic current appears between law alloy steel and copper when they are coupled and immersed in 4 % NaCl solution because there are two reactions occurs. First oxidation of iron on law alloy steel surface (anode) equation (6) and second the reduction of oxygen on copper surface (cathode) equation (5). Galvanic current is affected by different parameters, it increases when the area of each metal increases and when the area ratio of law alloy steel to copper increase from 0.25 to 3 and shifting the galvanic corrosion potential to extra negative direction. Galvanic current density of LAS decreases when the area ratio increases due to the increasing of the surface area of LAS, but the galvanic current density of copper unchanged when the area ratio increases because the surface area of copper surface remains constant during the whole experiments. Galvanic current (Ig) increases when the temperature of solution (electrolyte) increases from 30-50 ºC with changing the galvanic potential to extra negative. Finally, the galvanic current increases clearly with the increasing of rotational speed of agitator through the solution with shifting the galvanic potential to positive direction due to mass transfer control the process and increasing the diffusion of O_2 to the surfaces of metals.

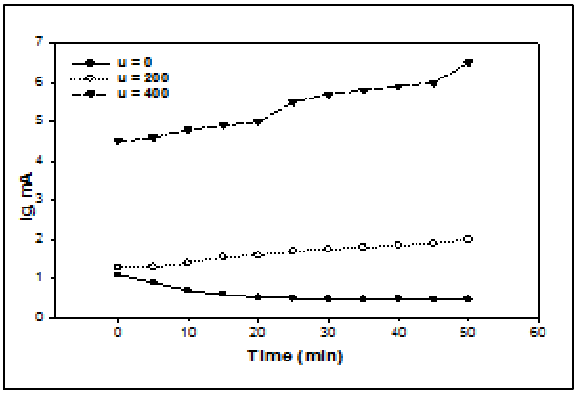


Figure 9: Effect of rotation speed on galvanic current Ig, mA vs. time at different velocities in 4% NaCl at T = 30 °C, AR = 1.

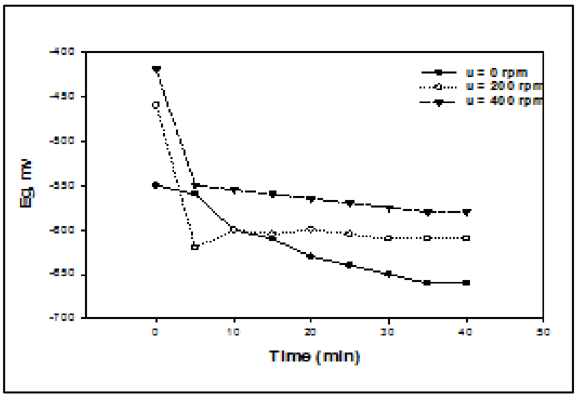


Figure 10 Galvanic corrosion potential Eg, mv vs. time at different velocities in 4% NaCl at T = 30 °C, AR = 1

References

[1] C.G. Arnold, "galvanic corrosion measurement of weldments" paper 71, presented at corrosion 180. Chicago. IL national Association of Corrosion Engineers. March 1980.

[2] M.G. Fontana and N.D. Greene, "Corrosion Engineering" 3rd edition McGraw -Hill Co. Tokyo 1985.

[3] J.K. Lawrence, L.O. David and R.D. Joseph., "Metals Handbook- Corrosion" volume 13 ASM International USA, 1987.

[4] B.O. Hasan, "Galvanic corrosion of carbon steel-brass couple in chloride containing water and the effect of different parameters" Journal of petroleum and engineering 124, 137-145, 2014.

[5] A.Y. Musa, A.B. Mohammed and A.H. Kadhum, "Galvanic corrosion of aluminum alloy (AL2024) and copper in 1.0 M nitric acid" Int. J. Electrochem. Sci, 6, 5052-5056, 2011.

[6] G.L. Song, B. Johanneson, S. Hapugoda and D.S. John "Galvanic corrosion of magnesium alloy AZ91D

in contact with an aluminum, steel, and zinc" Corrosion Science 46, 4, 955-977, April 2004.

[7] D.A. Jones, "Principles and Prevention of Corrosion' Upper Saddle River: prentice-Hall, Inc, ISBN. Q-13-359993-0, 1996.

[8] L.L. Shreir, R.A. Jarmall and G.T. Burstein, "Corrosion Metal /Environment reaction" 3rd edition vol. 1 Butterworth-Heinemann. Great Britain, 2000.

[9] L.L. Shreir, "Corrosion Handbook" 3rd edition part 1, Newnes-Butter, London, 2000.

316 L stainless steel/Al brass in Arabian Gulf water desalination" 161-169, 2004.

[13] J.X. Jia, G. Song, A. Atrens, D.H. John, J. Baynham and G. Chandler, "Materials and Corrosion", 55, 845, 2004.

[14] ASTM G1, 2004.

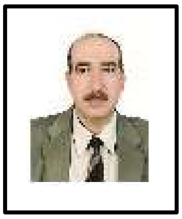
[15] B.O. Hasan, S.A. Sadek, "Corrosion behavior of carbon steel in oxygenated sodium sulphate solution under different operating condition" Adv. Chem. Eng. Res. 2, 3, pp. 61-71, 2013.

[16] R.H. Perry and D.W. Green, "Perrys Chemical Engineers handbook" 7th edition, McGraw-Hill, United states, 1997.

[17] N. Dkhireche, A. Dahami and A. Rochdi, "Corrosion and scale inhibition of low carbon steel in cooling water system by 2-propargyl-s-o-hydroxyphenyl tetrazole", Ind. Eng. Chem, 2013.

[18] M.T. Montanes, R.S. Tovar, G. Anton and V.P. Herranz, "The influence of Reynolds number on the galvanic corrosion of the copper/AISI 304 pair in aqueous LiBr solution", Corrosion Sci., 51, pp. 2733-2742, 2009.

Author(s) biography



Saad Ahmed Jafar, PhD in Chemical Engineering- Corrosion of materials, Moscow Institute of Steels and Alloys, Moscow, Russia.
He published nine scientific articles in the field of corrosion of materials and mass transfer. Associated prof. Jafar now assistant dean of scientific affairs and lecturer in College of Petroleum & Minerals Engineering, Tikrit University, Petroleum Process Engineering department.

[10] A. Ekhlas and S. Al-zubidy, "Simulation of Galvanic Corrosion for aluminum, copper, Iron, and Zink at different PH and temperature" Journal of Al-Nahrain University, Vol. 3, 83-91, 2013.

[11] A.K. Roy, D.L. Fleming and B.Y. Lum, "Galvanic Corrosion-effect of environmental and experimental variables" (99 conference, San Antomo: TX., 25-30, 1999.

[12] M.E. El-dahshan, A.M. Shams El Din and H.H. Haggag, "Galvanic Corrosion in the systems titanium,