

Corrosion Inhibition of Galvanic Couple Copper Alloy/Mild Steel in Cooling Water System

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Abstract

The driving idea for the present work was to combine the effect of polyvinyl alcohol (PVA) as corrosion inhibitor with the distance between the anodic and cathodic elements of the galvanic cell, beside their area ratio, in scope of synergistic suppression of galvanic corrosion on Cu/Fe model couple, using weight loss method. The performance affecting galvanic corrosion process has been tested for three major factors affect the process:

1. Four PVA inhibitor concentrations were selected to be (0, 1000, 4000 and 7000 ppm) in simulated cooling water.
2. Two cathode: anode area ratios as 1:1 and 2.4:1.
3. Two distances apart cathode – anode as 3 and 7 cm.

Maximum corrosion inhibition achieved was 86% which indicates that increasing inhibitor concentration leads to decrease dissolution process followed hydrogen evaluation Cu electrode as cathode element in galvanic cell.

Keywords: Galvanic Corrosion, Mild steel, Polarization, Galvanic Current

Introduction

The study of inhibition mechanism, electrochemical, and kinetic behavior of water-soluble polymers such as poly vinyl alcohol as a corrosion inhibitor to protect Cu-CS galvanic couple in aqueous media, contributes to the prevention of corrosion, particularly in industrial equipment which inevitably requires joining pieces of different metals for its construction [1–6]. Cooling water systems are often constructed by dissimilar metals such as copper fins that cool the fluid by convection, internal copper tubes and mild steel shells. The conditions of the cleaning process during the manufacture of heavy duty heat

exchangers promote the dissolution of the anodic metal in a galvanic couple especially with an unfavorable cathode-anode area ratio of 2.4 to 1.0.

The use of polyvinyl alcohol as corrosion inhibitor is related to its outstanding properties. The film forming and adhesive qualities enable nearly all water-soluble polymers to find uses as binders [7, 8, 9].

Galvanic corrosion, resulting from a metal contacting another conducting material in a corrosive medium, is one of the most common types of corrosion. In many cases, galvanic corrosion may result in quick deterioration, but in other cases, the galvanic corrosion of one metal may

result in the corrosion protection of an attacked metal, which is the basis of cathodic protection by sacrificial anode [10].

When two dissimilar conducting materials in electrical contact with each other are exposed to an electrolyte, a current, the galvanic current, flows from one to the other, galvanic corrosion is that part of the corrosion that occurs at the anodic member of such a couple and is directly related to the galvanic current by Faraday's law [11].

Many factors play a role in galvanic corrosion in addition to the potential difference between the two coupled metals. Depending on the circumstance. Compared to normal

corrosion, galvanic corrosion is generally more complex because, in addition to material and environmental factors, it involves geometrical factors [12].

Experimental Work

1. Materials

The materials of electrodes used in this investigation were 2 coupons from mild steel type SA 515 GR 60 having the following dimensions:

- Big coupon (4.9cm length ,3cm width and 0.3 cm thickness).
- Small coupon (2.83cm length , 3cm width and 0.3 cm thickness).

These specimens having the following chemical compositions (% wt) (were supplied by Al-Dura refinery):

Table 1, The chemical composition of mild steel coupon (% wt)

Carbon	manganese	Phosphorus	sulfur	silicon	Fe
0.24	0.9	0.035	0.035	0.15 -0.4	Remainder

The second electrode was copper type ASTM B-111-443 with 3.5 cm length, 4.43 cm width and 0.2 cm thickness having the chemical compositions as follows:

Table 2, The chemical composition of copper coupons (%wt)

Copper	Lead	Iron	Zinc	Arsenic
70 – 73	0.07	0.06	Reminder	0.02-0.06

2. Solution

The chemical composition of water solution used throughout the experiments was actually same as the chemical composition of water used in the cooling system of Al-Dura Refinery Iraq as follows:

Table 3, Chemical composition of tested solution

Component	Concentration, ppm
Na ⁺	441
Cl ⁻	303
SO ₄ ⁻²	352
HCO ₃ ⁻	123
CO ₃ ⁻²	37

The tested solution was prepared by dissolving 500 ppm NaCl, 520 ppm Na₂SO₄, 170 ppm anhydrous NaHCO₃, and 66 ppm Na₂CO₃ in one liter of distilled water. Inhibitor solution was prepared by dissolving appropriate amount of polyvinyl alcohol (PVA).

3. Chemicals

The table below lists the compounds and chemical used in this investigation:

Table 4, Compound used in this investigation

Compounds	Formula	Purity%
Acetone	C ₃ H ₆ O	99.5
Benzene	C ₆ H ₆	-
Hydrochloric acid	HCl	98.9
Poly vinyl alcohol	C ₂ H ₃ OR*	-
Sodium chloride	NaCl	95.5
Sodium carbonate	NaCO ₃	96
Sodium bicarbonate	NaHCO ₃	97.9
Sodium sulfide	Na ₂ SO ₄	90

* where R : H or COCH₃

4. Weight Loss Method

Specimens were abraded in sequence under running tap water using emery papers of grade numbers; 220, 320, 400, and 600 respectively, washed with running tap water followed by distilled water, dried on a clean tissue, immersed in benzene for five seconds and dried with clean tissue, immersed in acetone for five seconds and dried with clean tissue, kept in a desiccator over silica gel for one hour before each run.

Procedure

1. The dimensions of each specimen were measured with vernire to the 2nd decimal of millimeter and accurately weight to the 4th decimal of gram before using.
2. Before each test, the cell was washed with running tap water followed by distilled water and test solution.
3. Specimens were completely immersed in 1000 cm³ solution of corroding contained in the cell. They were exposed for period of 24 hours, desired concentration of inhibitor and the coupons were apart 3 and 7 cm from each other.
4. All the experiments were done with an area ratio of C/A (2.4:1 and 1:1), the working electrode was constructed joining metal coupons

with above mentioned area ratio for mild steel, connected to an insulated copper wire.

5. After each test, the mild steel specimen was washed with running tap water, scrubbed with a brush to remove corrosion products, then washed with tap water followed by distilled water and dried on a clean tissue, immersed in benzene, dried, immersed in acetone, dried and left in a desiccators over silica gel for one hour before weighting then accurately weight to the 4th decimal.

Results and Discussion

A total of 16 runs for weight loss measurements were made expressing rate of two area ratio of mild steel couple to Copper in simulated cooling water system containing different concentration of PVA as corrosion inhibitor. Two levels for both the distance and area ratio of (Ac/Aa) for electrode were adopted, while four levels for inhibitor concentration as independent variables.

Corrosion rate calculations of mild steel (anode) coupled to copper (cathode) from weight loss data were performed using the following equation:

$$CR(gmd) = \frac{Weight\ loss\ (g)}{Area\ (m^2) * Time\ (days)} \dots (1)$$

Table 5, corrosion rate of mild steel coupled to copper in simulated cooling water under different operating conditions

Inhibitors concentrations (ppm)	Corrosion rate (gmd)			
	Distance between Fe-Cu (3 cm)		Distance between Fe-Cu (7 cm)	
	Area ratio Cu/Fe(1:1)	Area ratio Cu/Fe(2.4:1)	Area ratio Cu/Fe(1:1)	Area ratio Cu/Fe(2.4:1)
Blank	11.77	20.95	7.698	15.47
1000	7.756(54)	11.32(46)	5.707(34.1)	9.987(35.5)
4000	3.541(70.7)	6.04(71.1)	2.254(51.5)	5.627(63.6)
7000	1.668(82.9)	4.15(80.2)	1.317(86)	3.306(78.6)

() indicates % inhibition in presence of PVA as corrosion inhibitor.

The quantitative description of the physical condition effect on corrosion rate of mild steel coupled to copper in

simulated cooling water was performed. An empirical modeling technique called response surface

methodology is used to evaluate the relationship between the controllable experimental variables and observed results. [13]. The results were analyzed using the analysis of variance (ANOVA) as appropriate to experimental design used. The regression equations obtained gives the corrosion rate of mild steel coupled to copper as cathodic element in galvanic corrosion, as function of area ratio (X1) and distance between the electrodes (X2), in absence and presence of corrosion inhibitor (0,1000,4000and7000)ppm.

Regression analysis was utilized by using Statistica program version 10.1 to generate four models for given inhibitor concentration with correlation coefficient of $R^2=1.0$.

$$CR_{Blank} = 7.5 + 7.32 X1 - 0.765 X2 - 0.25 X1X2 \quad \dots(2)$$

$$CR_{1000 \text{ ppm}} = 7.13 + 2.16 X1 - 0.64 X2 + 0.13 X1X2 \quad \dots(3)$$

$$CR_{4000 \text{ ppm}} = 3.18 + 1.33 X1 - 0.48 X2 + 0.15 X1X2 \quad \dots(4)$$

$$CR_{7000 \text{ ppm}} = -0.11 + 2.04 X1 + 0.0003 X2 - 0.09 X1X2 \quad \dots(5)$$

Where X1, X2 are the area ratio and distance between electrodes respectively and CR is the corrosion rate in (gmd).

Equations (2 through 5) showed suitable models to describe the

response of the mild steel coupled to copper under investigation. A high values of $R^2 = 1$ justified excellent correlation between the independent variables. This indicates a good agreement between the predicted and experimental values of the corrosion rates of mild steel coupled to copper as shown in table (5).

Thus the effect of distance between the anodic and cathodic elements in galvanic couple and the area ratio of (C/A) on the response can be obtained at fixed levels of inhibitor concentrations (0,1000,4000and7000 ppm). The darker the red color means higher corrosion rate of mild steel coupled to copper, while the darker the green color means the lower the corrosion rate.

Figures (1 through 5) corroborate the fact that minimization of corrosion rate of mild steel coupled to copper as cathodic element is possible in simulated cooling water only at low C/A area ratio and large anode to cathode distance apart.

The corresponding analysis of variance (ANOVA) is represented in tables (6 through 9) in absence of inhibitor and at different inhibitor concentrations. The result obtained from this analysis indicate the significance of variables studied through the p-value (i.e., p-value is less than 0.05).

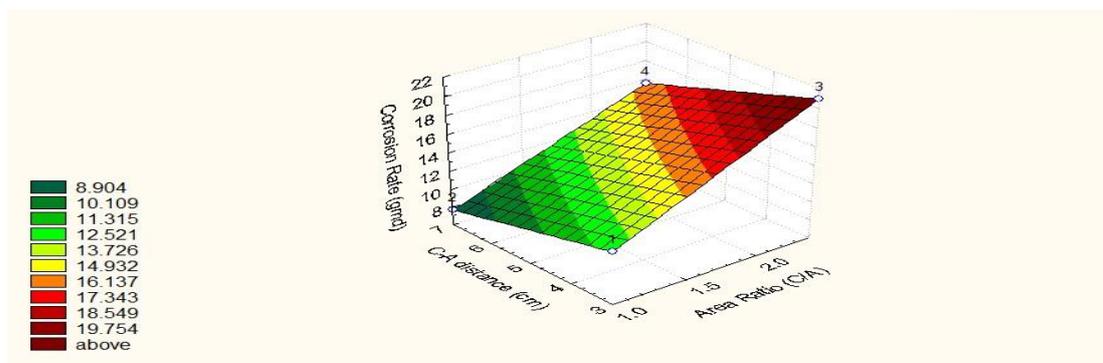


Fig. 1, Three dimensional surface plot showing corrosion rate of Carbon steel coupled to copper in SCW in absence of PVA as corrosion inhibitor at different area ratios and distance between anode and cathode

Table 6, ANOVA for corrosion of mild steel coupled to copper in simulated cooling water in absence of inhibitors, at different area ratios and distances between electrodes

Source of variation	Sum of squares	Degree of freedom	MS effect	F _o	P-value
X ₁	72.0801	1	72.0801	147.102	0.000065
X ₂	22.9441	1	22.9441	46.825	0.00082
X ₁ X ₂	0.5027	1	0.5027	1.0259	0.00825
Error	1.96	4	0.4900		

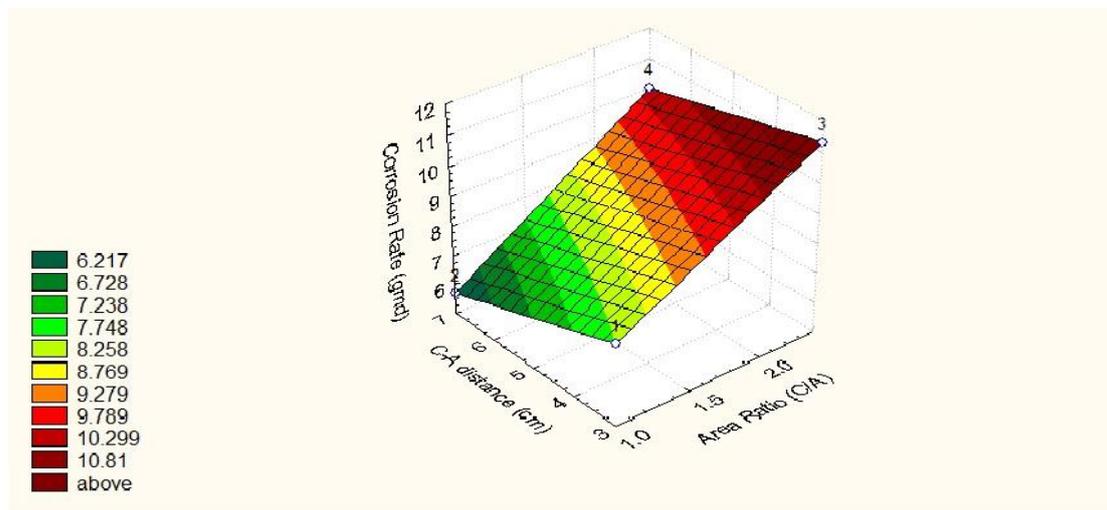


Fig. 2, Three dimensional surface plot showing corrosion rate of Carbon steel coupled to copper in SCW containing 1000 ppm PVA as corrosion inhibitor at different area ratios and distance between anode and cathode

Table 7, ANOVA for corrosion of mild steel coupled to copper in simulated cooling water in 1000 ppm PVA, at different area ratios and distances between electrodes

Source of variation	Sum of squares	Degree of freedom	MS effect	F _o	P-value
X ₁	15.3821	1	15.8321	114.725	0.000074
X ₂	2.8595	1	2.8595	20.721	0.00093
X ₁ X ₂	3.3282	1	3.3282	24.1173	0.00221
Error	0.552	4	0.138		

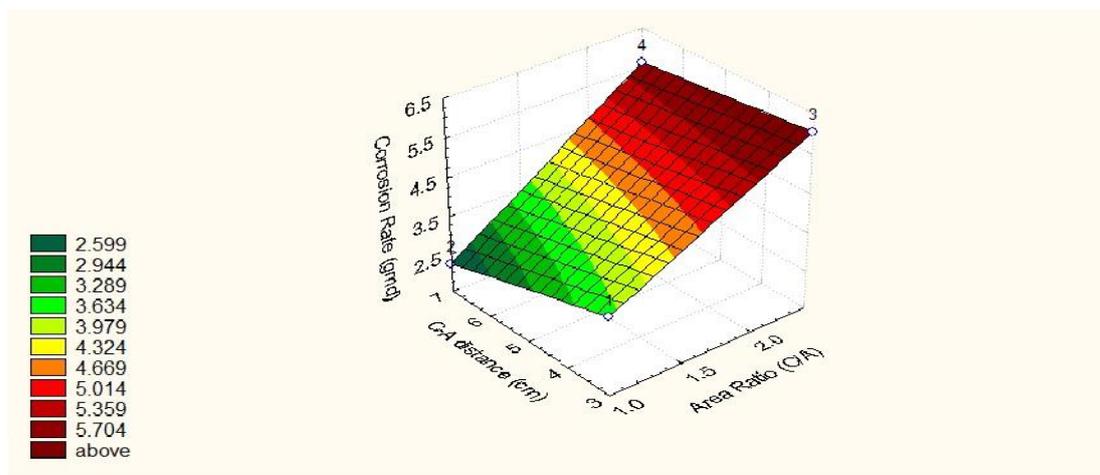


Fig. 3, Three dimensional surface plot showing corrosion rate of Carbon steel coupled to copper in SCW containing 4000 ppm PVA as corrosion inhibitor at different area ratios and distance between anode and cathode

Table 8, ANOVA for corrosion of mild steel coupled to copper in simulated cooling water in 4000 ppm PVA, at different area ratios and distances between electrodes

Source of variation	Sum of squares	Degree of freedom	MS effect	F _o	P-value
X ₁	0.73017	1	0.73017	3.9035	0.000037
X ₂	8.64654	1	8.64654	46.2246	0.00078
X ₁ X ₂	0.18076	1	0.37405	1.9997	0.00482
Error	0.74822	4	0.187055		

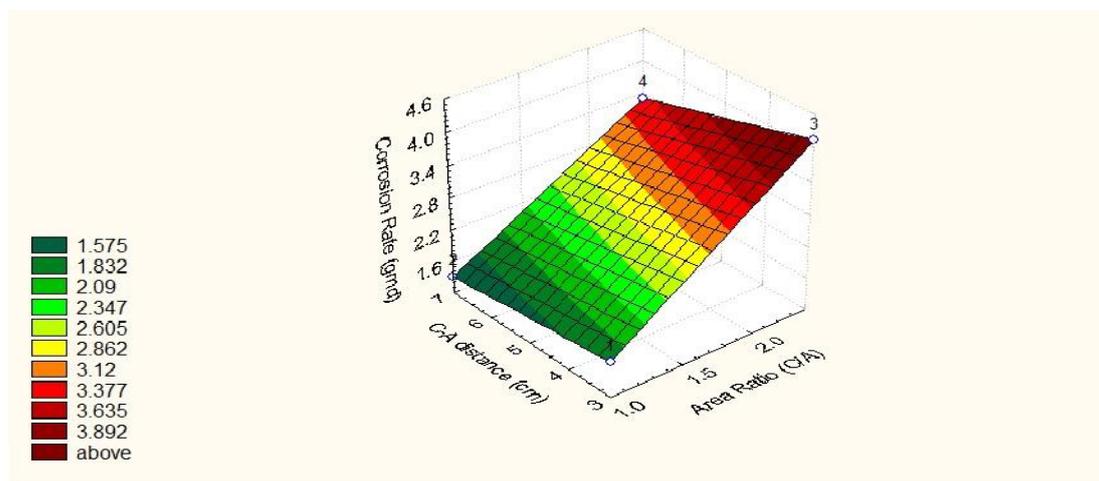


Fig. 4, Three dimensional surface plot showing corrosion rate of Carbon steel coupled to copper in SCW containing 7000 ppm PVA as corrosion inhibitor at different area ratios and distance between anode and cathode

Table 9, ANOVA for corrosion of mild steel coupled to copper in simulated cooling water in 7000 ppm PVA, at different area ratios and distances between electrodes

Source of variation	Sum of squares	Degree of freedom	MS effect	F _o	P-value
X ₁	4.99746	1	4.99746	82.3305	0.000013
X ₂	0.35701	1	0.35701	5.8757	0.00035
X ₁ X ₂	0.6076	1	0.6076	10.0099	0.00591
Error	0.2428	4	0.0607		

Conclusions

On the basis of the results presented, the following conclusions can be drawn:

1. The inhibition action of (PVA) increases with the increase of inhibitor concentration and distance between anode and cathode.
2. The methodology of three level factorial design was shown to be very useful for the process variables evaluation as main and combined effect on the response.
3. The multi-variable regression describes the behavior of the corrosion inhibition process with high accuracy ($R^2=1.0$).

4. The importance of galvanic phenomenon is greater than as the ratio of cathode/anode increases, however the results show compatibility of both materials at both area ratios and (PVA) concentrations except at 7000 ppm the couple not severing from galvanic corrosion.

References

- 1- C. M. Mustafa and S. M. S. I. Dulal, "Molybdate and nitrite as corrosion Inhibitors for copper-coupled steel in simulated cooling water," Corrosion, vol. 52, no. 1, pp. 16–22, 1996.

- 2- E. J. Talbot and D. R. Talbot, Corrosion Science and Technology, CRC Press, New York, NY, USA, 2007.
- 3- J. R. Davis, "Corrosion fundamentals, testing and protection," ASM International and The materials Information Society, Ohio, EE.UU, 2000, <http://www.asm.intl.org/>.
- 4- R. Francis, "Galvanic corrosion of high alloy stainless steels in sea water," British Corrosion Journal, vol. 29, no. 1, pp. 53–57, 1994.
- 5- P. R. Roberge, Corrosion Engineering: Principles and Practice, McGraw–Hill, New York, NY, USA, 2008.
- 6- I. Carrillo, Inhibition of the corrosion in galvanic couples copper and carbon steel of Heat Exchangers for heavy machinery industry, M.S. thesis, Instituto de Ingenieria de la Universidad Autonoma de Baja California for Engineering Master Degree, 2009.
- 7- K. E. Johnson and J. S. Abbott, "Bimetallic Corrosion Effects on Mild Steel in 'Natural Environments: British Steel Corporation Report No. CEL/CC/5/75, February 1975.
- 8- V. Kucera and E. Mattsso~ "Atmospheric Corrosion of Bimetallic Structures," Atmospheric Corrosio~ Hollywood Florid% 5-10 October 1980, John Wdey and Sons, Inc., pp. 561-574, 1982.
- 9- R. J. Schmitt and E. H. Phelps, "Constructional Steels in Marine Applications," Journal of Metals, pp. 47-55, March 1970.
- 10- Uhlig H.H., "Corrosion Handbook", John Wiley and Sons, Inc., 2011.
- 11- Corrosion Inspection and Monitoring by Pierre R.Roberge .Royal. Military college of Canada in (2007).
- 12- Corrosion Science and Technology by David Talbot James Talbot (1998).
- 13- Perry D.H "Experimental Design in Biotechnology", Marcel Dekker,Inc. USA (1989).