

Cathodic Protection of Carbon Steel Using Aluminum as Sacrificial Anode in Sea Water

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Abstract

The effect of Aluminum as sacrificial anode in seawater (3.5% NaCl) of PH=6.8 was investigated under flow conditions (0-0.262 m/s) for a range of temperatures (25-45°C) using rotating cylinder electrode. And different area of Aluminum at distance of 6cm were used to protect steel from corrosion, these were $A_1=2*2\text{cm}^2$, $A_2=4*4\text{cm}^2$ and $A_3=8*8\text{cm}^2$ under stationary and flow conditions... It is found that the corrosion rate of carbon steel increases with flow velocity when it free and when coupling with Al it has unstable trend with temperature but also the corrosion rate of Fe decreased after coupling. Using small area of Al increase the corrosion rate while using large area will not highly effective on corrosion rate of Fe. The protection percent of Fe increases appreciably (shifts to more positive) with increasing rotation velocity. It shifts to more negative with increasing temperature.

Keywords: Corrosion, sacrificial anode, aluminum, carbon steel, seawater.

Introduction

All metals and alloys undergo a natural process of corrosion depending on the metal and the surrounding environment, if two dissimilar metals are electrically in contact and immersed in the same electrolyte, the more reactive (or baser) metal will part with its electrons more readily and will corrode in preference to the less reactive (or nobler) metal [1,2].

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, chemical processing, petroleum production and refining, construction and metal processing equipment. [3].

Cathodic protection is a method to reduce corrosion by minimizing the difference in potential between anode and cathode and it can be used to protect most metals from aqueous corrosion, it is

most commonly applied to carbon steel in natural environments (waters, soils and sands).

There are two main types of cathodic protection systems: galvanic and impressed current. Galvanic anode systems employ reactive metals as auxiliary anodes that are directly electrically connected to the steel to be protected. The difference in natural potentials between the anode and the steel, as indicated by their relative positions in the electro-chemical series, causes a positive current to flow in the electrolyte, from the anode to the steel. Thus, the whole surface of the steel becomes more negatively charged and becomes the cathode [4, 5].

Generally, Aluminum, Zinc, and Magnesium are the metals mostly employed for sacrificial cathodic protection of metals. It is affirmed that aluminum are the preferred sacrificial anodes for controlling and preventing corrosion in marine environments. The actual limit in the use of magnesium – based sacrificial anodes is their relatively low efficiency which gives rise to the loss of substantial parts of the required current capacity. Aluminum anodes are also favored over zinc anodes for the cathodic protection of offshore structures especially in deepwater exploration because they are lighter and less expensive. Evaluation of the performance of aluminum anodes is necessary to achieve the most cost-effective sacrificial anodic protection design. The usefulness of pure aluminum as an anode material in seawater is reduced significantly by the formation of a protective oxide film, which limits both its current and potential output. [6].

Increasing temperature increases corrosion rates. This is due to a combination of factors- first, the common effect of temperature on the reaction kinetics themselves and the higher diffusion rate of many corrosive by-products at increased temperatures. This latter action delivers these by-products to the surface more efficiently. Occasionally, the corrosion rates in a system will decrease with increasing temperature. This can occur because of certain solubility considerations. Many gases have lower solubility in open systems

at higher temperatures. As temperatures increase, the resulting decrease in solubility of the gas causes corrosion rates to go down.

Velocity has a significant effect on corrosion rates. Stagnant or low velocity fluids usually give low general corrosion rates. Corrosion rates generally increase with increasing velocity due to the depolarizing effect on the cathode [7]. Velocity primarily affects corrosion rate through its influence on diffusion phenomena. It has little effect on activation controlled processes. The manner in which velocity affects the limiting diffusion current is a marked function of the physical geometry of the fluid remains static or in fast motion with respect to the metal surface. However, molecular diffusion is not the only factor which influences the rate of corrosion. In addition, in turbulent fluids, the rate of transport of eddy diffusion appears to participate in the control of the over-all transfer rate. It is only in situations where both anodic and cathodic processes are activation controlled that they will be unaffected by the relative movement between surface and environment [8, 9]. The rate of this half reaction is generally limited by the speed at which oxygen can reach the surface of the metal. This oxygen is transported from the bulk water to the surface across the boundary layer by diffusion [10].

One of the most important parameters in galvanic corrosion is the "area ratio". A high cathode to anode ratio usually resulting in rapid corrosion or high anode (base) to cathode noble ratio giving lower corrosion [11]. Conversely a large area of noble (base) metal in contact with a small area of less noble (base) will accelerate the galvanic corrosion rate [12]. Distribution of the area is

obviously important as is surface shape and condition.

Several previous studies [13,14,15] showed that the corrosion rate generally decreases with time due to corrosion product formation depending on flow velocity. Slaiman and Husan [15] noticed that at high velocity, the formation of corrosion product leads to increasing the limiting current density (corrosion rate) for carbon steel in water by increasing the turbulence resulted from the increased roughness of the surface.

Tai-Ming Tsai studied the performance of Aluminum alloys used as sacrificial anodes for protection of steel in seawater; the results show that steel can be protected under area ratio up to 4000-5000 [16].

Sami and Ghalib [17] studied cathodic protection system for low carbon steel pipe. They investigated the influence of temperature and distance between cathode and anode on the minimum cathodic protection current that would provide a full cathodic protection for steel tube immersed in sea water for temperature range 30-50°C and distance between pipe (cathode) and graphite electrode (anode) of (10-20cm). The experimental results indicated that cathodic protection current density increase with increasing temperature.

In this work Aluminum has been chosen as sacrificial anode for investigation on its effect corrosion rate of carbon steel in seawater. The research is geared towards determining the effect of some operating parameters (velocity, temperature, and area of anode) on the corrosion rate in the presence and absence of Aluminum as sacrificial anode.

Experimental Work

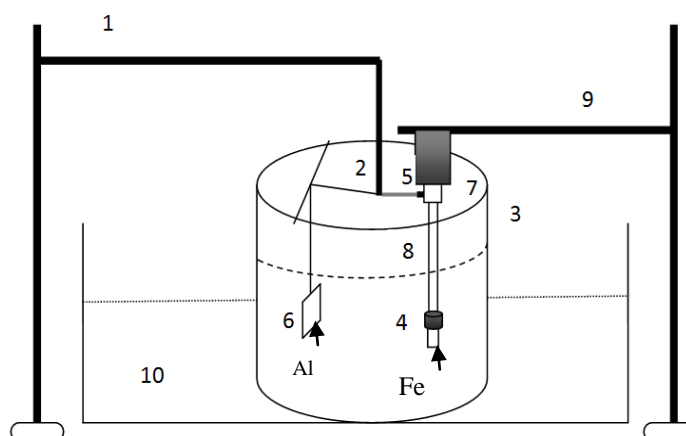


Figure (1): shows the experimental apparatus used for performing the experimental work
 1- Stand 2- connecting wire 3-beaker (3L) 4-cathode (iron) 5- Graphite brush
 6-Anode (Al)
 7-Rotating device 8- Rotating shaft 9- stand 10- water bath with temperature controller

The experimental apparatus was composed of mechanical agitator to obtain different rotational velocities, water bath to obtain different solution temperatures, carbon steel specimen 3 cm length and 2.5 cm outside diameter (cathode) attached to the rod of agitator Digital balance of high accuracy (4 decimal places of gram) to measure the weight loss. The electrical connection between cathode (specimen) and the cell was attained using brush.

The corrosion rate was determined by using weight loss method, before each experiment, the carbon steel specimen (O.D=2.5 cm, L=3cm) was polished with 120, 180, 220, 400 and 2000 grid silicon carbide papers, washed with brushing by plastic brush with running tap water, immersed in ethanol for 30 second dried with clean tissue, and then dried by using electrical oven to temperature of about 110 °C for 10 minute [Mahato et.al, 1980]. The specimen then was stored in vacuum desiccator over high activity silica gel until use. Then the specimen was weighted to nearest 0.1 mg (w1) by using digital balance to measure the weight loss. The carbon steel specimen was immersed in the solution(3% NaCl) at a particular temperature to corrode freely for two hours to measure the corrosion rate at stationary condition at different temperature (25, 35 and 45 °C). At the end of weight loss experiment, the specimen was washed by tap water with brushing to remove the corrosion products that formed on the outside surface and then immersed in 10% hydrochloric acid containing

chemical inhibitor (thioharnstoff) for 30 second, then it washed by tap water, distilled water, dried with clean tissue, rinsed in ethanol and dried by using electrical oven to a temperature about 110 °C for 10 minute. Then the specimen was kept in the desiccators to cool and then weighted (w2).

The corrosion rate was measured at different speeds (200, 400, 800 and 1200 rpm) at constant temperature of 35°C and at each speed the corrosion rate was measured for each specimen before coupling and after coupling Fe with Al by a connecting wire in touch with graphite brush that attached the rotating shaft that hold the carbon steel specimen.

From the weight loss the corrosion rate (CR) was calculated by using:

$$CR \text{ (gmd)} = \frac{\Delta w}{A \cdot t} = \frac{gm}{m^2 \cdot d} \dots (1)$$

Where CR represents corrosion rate in g/m²d. The protection percent (pp) was calculated as:

$$PP \% = \frac{CR_0 - CR}{CR_0} \times 100 \dots (2)$$

where CR₀ and CR are the corrosion rate in absence and in presence of Al as sacrificial cathodic protection of Fe respectively.

The corrosion current density (i_{corr}) was also obtained from weight loss measurement as follows [18]:

$$N_{Fe} = (\Delta w/M)/ (A.t) \quad \dots(3)$$

where Δw represents weight loss, M is the molecular weight of carbon steel (iron), A is the area in m^2 and t is the time in second, N_{Fe} is the moles of Fe lost per unit area per unit time ($gmole/m^2.s$)

$$i_{Fe} = z F N_{Fe} \quad \dots(4)$$

Where i_{Fe} is the corrosion current density in (A/m^2), F is Faradays constant (96487 columb/equivalent), z is the number of electron free by corrosion reaction (for iron $z=2$ & $Al=3$).

$$i_{Fe} = 2*96487* N_{Fe} \quad \dots(5)$$

$$i_{Al} = 3*96487* N_{Al} \quad \dots(6)$$

Results and Discussions.

Tables [1 through 5] show the numerical values of experimental results.

Table (1): values of experimental results Fe corrosion at T=35°C and various velocities

rpm	u (m/s)	ΔW (gm)	CR gmd	I_{Fe} (mA)	i_{Fe} (A/m^2)
0	0	0.0147	75	0.0722	0.0306
200	0.262	0.0197	100.32	0.0967	0.041
400	0.524	0.0302	154.1	0.1483	0.0629
800	1.047	0.0327	166.8	0.1605	0.0681
1200	1.571	0.0416	212.2	0.2042	0.0867

Table (2): values of CR(gmd) of Fe coupled with Al of at T=35°C , $a_{Al}=0.0016 m^2$, and various velocities

rpm	u (m/s)	Fe			AL			O ₂	PP of Fe %
		ΔW (gm)	CR (gmd)	i_{Fe} (A/m^2)	ΔW (gm)	CR (gmd)	i_{Al} (A/m^2)	$i_{O_2} = i_{Fe} + i_{Al}$ (A/m^2)	
0	0	0.008	40.7	0.0302	0.0023	17	0.0015	0.0317	45.58
200	0.262	0.0102	51.9	0.0304	0.0039	29	0.0026	0.033	48.22
400	0.524	0.0137	69.8	0.0285	0.0059	44	0.004	0.0325	54.64
800	1.047	0.0139	70.8	0.0575	0.0153	115	0.0103	0.0678	57.49
1200	1.571	0.0176	89.6	0.0367	0.0157	118	0.0105	0.0472	57.69

Effect of rotational velocity Fe without coupling

Fig. 2 shows the corrosion rate curve of Fe free corrosion at different rotational speed (0, 0.262, 0.0.524, 1.047, and 1.571) m/s at 35°C. In this figure it is clear that the corrosion rate increases as the rotational velocity increases due to increase in O₂ diffusion from solution bulk to the surface and decreasing the thickness of diffusion layer on the metal surface [14,15,19,20]. Evans [21] indicated that greater turbulence due to high velocities results in more uniform O₂ concentration and more likely initiation of corrosion on a previously uncorroded surface.

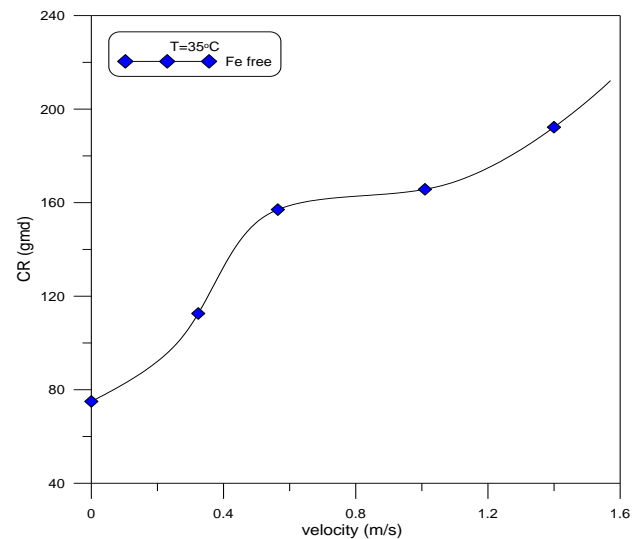


Figure (2): Corrosion Rate of Fe Without Coupling With Al At T=35 °c and Different Velocities

With coupling Fe-Al

Fig. 3 shows the corrosion rate of Fe with coupling and without coupling with Al at various rotational velocities and temperature of 35°C, the corrosion rate increases as the rotational velocity for Al and Fe. Increasing solution velocity will increase the rate of carbon steel dissolution this trend can be attributed to the decrease in the thickness of the hydrodynamic boundary layer and diffusion layer across which dissolved O₂ diffuses to the metal wall [22] with a consequent increase in the rate of O₂ transfer from bulk solution to the surface. Increasing velocity will increase the amount of oxygen arriving to the surface leading to higher corrosion rate. Increasing velocity leads to decrease the thickness of diffusion layer that represents the main resistance to oxygen transport.

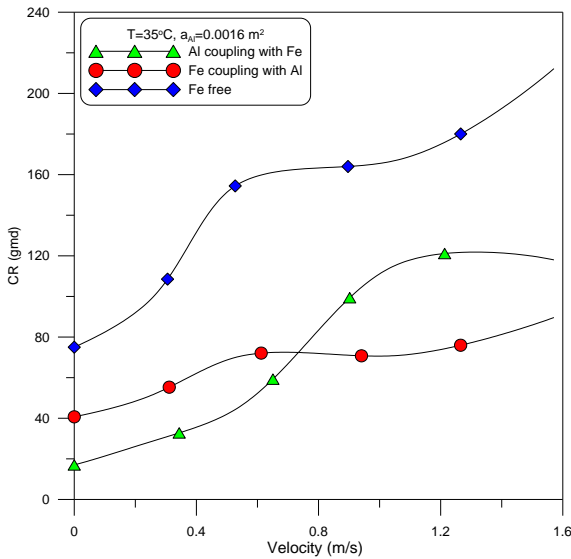


Figure (3): Corrosion rate of Fe with and without coupling with Al at T=35 °C and different velocities

Fig. 4 shows the effect of rotational velocity on the current density of carbon steel specimen coupled with Al. This figure indicates that as the velocity increases both anodic and cathodic currents increase. This increase is due to the increase in oxygen transport to the metals surface enhancing anodic dissolution of O₂ and the cathodic reduction.

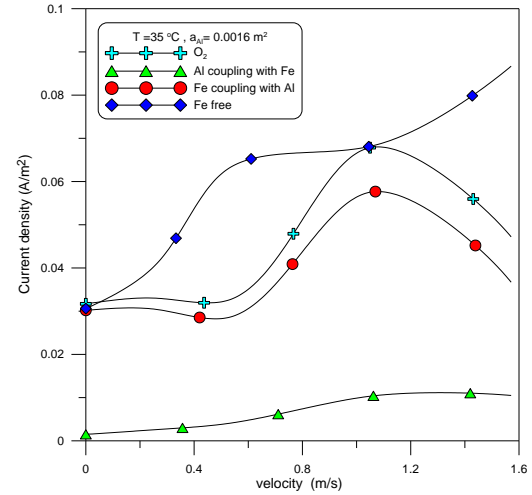


Figure (4): Current density of Fe with and without coupling with Al at T=35 °C and different velocities

Fig. 5 shows the protection percent of Fe at 35°C and different velocities. It is evident that as the velocity increases the percent of cathodic protection increase. In neutral solutions the cathodic corrosion process is usually the reduction of oxygen. The kinetics of this cathodic process are controlled by the rate at which oxygen can diffuse to the surface of metal, which is slower than the rate of consumption of oxygen by the cathodic reaction. Thus, the rate of this reaction remains constant unless the rate of supply of oxygen to the surface of metal is increased by increasing fluid flow rate [23].

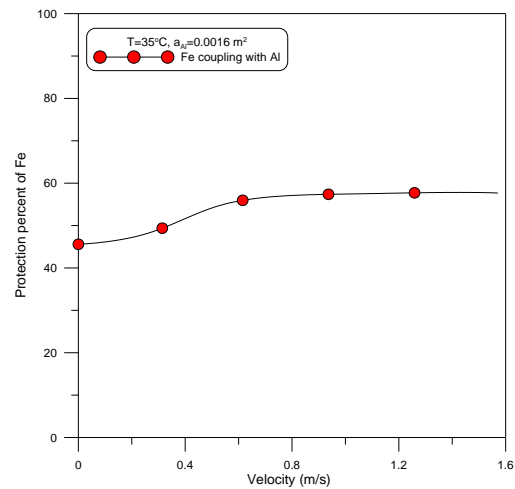


Figure (5): Protection percent of Fe at T=35 °C and different velocities

Effect of temperature without coupling (free corrosion):

Table (3): Values of CR(gmd) of Fe free at stationary conditions and various temperatures

Temp (°C)	ΔW (gm)	CR gmd	i_{Fe} (A/m ²)	$i_{O_2} = i_{Fe}$ (A/m ²)
25	0.0066	34	0.0137	0.0137
35	0.0147	75	0.0306	0.0306
45	0.0063	32	0.0131	0.0131

Fig. 6 shows the corrosion rate of Fe free at stationary conditions and different temperatures (25°C, 35°C and 45°C). From this figure, it can be seen that as the temperature increases the corrosion rate increases for a specific point then increasing temperature lead to decrease the corrosion rate of Fe. This can be ascribed to two reasons: first when the temperatures increases, the O₂ diffusivity increases enhancing the corrosion [2,9] and second it decreases the O₂ solubility the factor that leads to decrease the corrosion rate [2]. The rise in temperature increase the diffusion rate of oxygen species by increasing the molecular diffusion coefficient and decreases the oxygen.

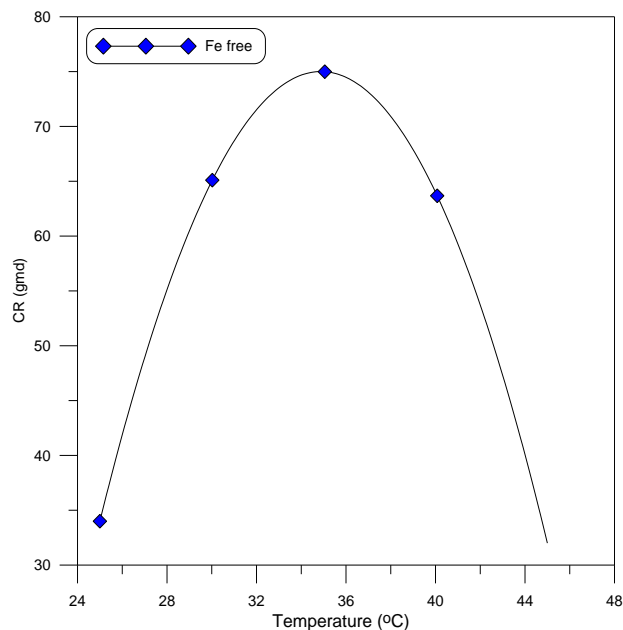


Figure (6): Corrosion rate of Fe without coupling with Al at stationary conditions and different temperatures

With coupling (Fe/Al)

Table (4): values of CR(gmd) of Fe coupled with Al of at stationary conditions and various temperatures, a AL=0.0016 m²

Fe				AL			O ₂	PP of Fe %
Temp (°C)	ΔW (gm)	CR gmd	i_{Fe} (A/m ²)	ΔW (gm)	CR gmd	i_{Al} (A/m ²)	$i_{O_2} = i_{Fe} + i_{Al}$ (A/m ²)	
25	0.0038	19	0.0079	0.0003	2	0.0002	0.0081	42
35	0.0145	41	0.0302	0.0023	17	0.0015	0.0317	46
45	0.005	26	0.0104	0.0036	27	0.0024	0.0128	21

Fig. 7 shows the corrosion rate of Fe free and Fe after coupling with Al at stationary conditions and different temperatures (25°C, 35°C and 45°C). this fig. shows that the corrosion rate of Fe after coupling with Al decreased from (34 gmd to 19 gmd at 25°C, 75 gmd to 41 at 35°C and 32 gmd to 26 gmd at 45°C) and also shows linear effect of temperature on Al that is due to the fact building up of corrosion products which restrain the oxygen transport to the surface, growth of the surface roughness which increases the momentum and mass transport between surface and solution. The formation of corrosion product layer has a noticeable effect on the corrosion rate of the metal depending on the solution nature and on the temperature and hydrodynamics [24].

At temperatures from 25 -35 °C the temperature greatly influences the corrosion behavior of carbon steel in sea water and gives maximum value of decreasing at 35 °C and then the effect of temperature drop down this attributed to the decrease of dissolved oxygen level due to increasing temperature

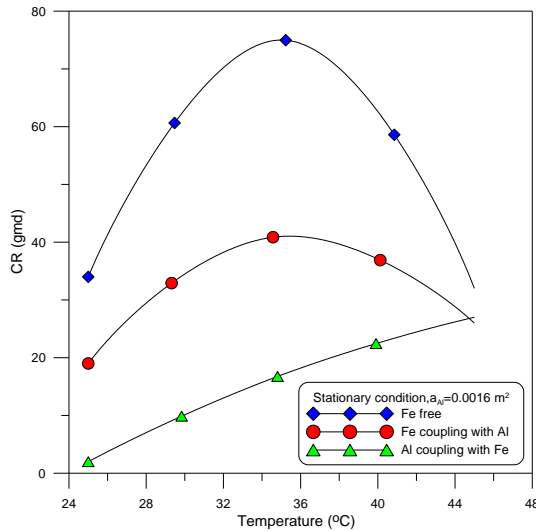


Figure (7): Corrosion rate of Fe with and without coupling with Al at stationary conditions and different temperatures.

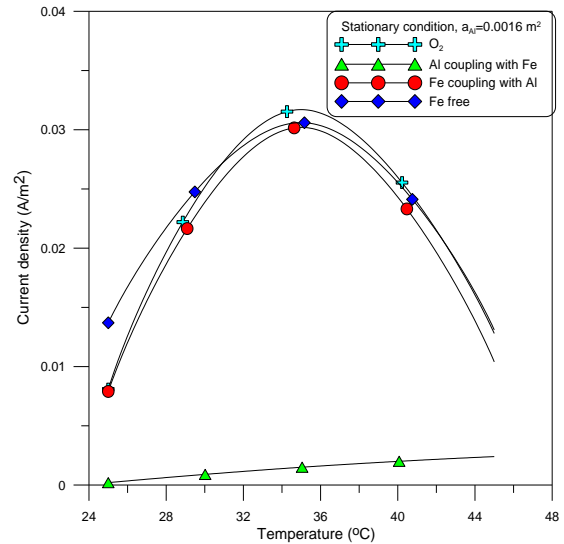


Figure (8): Current density of Fe with and without coupling with Al at stationary conditions and different temperatures

Fig. 8 shows the effect of temperature on current density after and before coupling. the current density of Fe before and after coupling increase with increasing temperature to reach a peak at 35°C then decreasing while Al shows linear effect of temperature.

The current of O₂ which represent the summation of anode (Al) and cathode (Fe) currents also increasing with temperature and reach maximum value at 35°C then decreases due to the continuous growth of the corrosion product layer (fouling layer) which decreases the arrival of O₂ to metal surface and the activity of the surface and hence the corrosion rate. [25]

Carbon steel naturally form passive surface film and this film also reduces the amount of current available for corrosion, so slows the corrosion rate down and also a signature property of aluminum is its tendency to form a strongly bonded passivating oxide film (Aluminium oxide Al₂O₃) on its surface.

The protection percent of Fe at three temperatures (35°C, 45°C and 55°C) coupled with Al is shown in Fig. 9 From this figure it can be seen that the protection decreases as the temperature increases, for example when Fe coupled with Al the protection percent are 42%, 46% and 21% for 25°C, 35°C and 45°C respectively due to the increased reduction of O₂ at the metal surface leading to decrease the corrosion of metal. Fig. 8 also reveals that the protection percent varies with temperature with unstable trend depending on O₂ solubility and diffusivity.

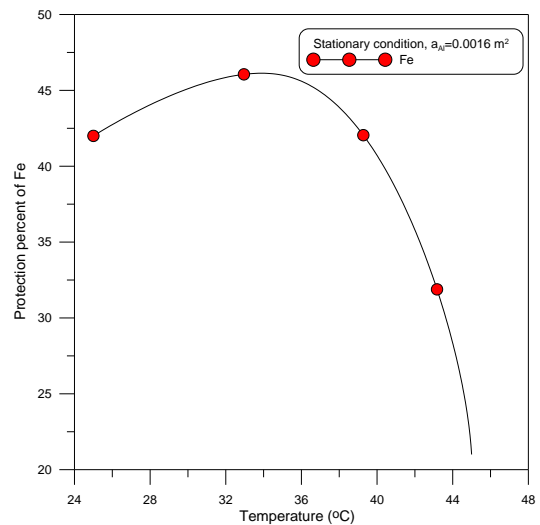


Figure (9): Protection percent of Fe at stationary conditions and different temperatures.

Effect of anode area (Al):

Table (5): values of CR (gmd) of Fe coupled with various area of Al at stationary conditions and 35°C

a_{Al} m ²	$AR = \frac{a_{Fe}}{a_{Al}}$	Fe			AL			O ₂
		ΔW (gm)	CR gmd	i_{Fe} (A/m ²)	ΔW (gm)	CR gmd	i_{Al} (A/m ²)	$i_{O_2} = i_{Fe} + i_{Al}$ (A/m ²)
0.0004	0.49	0.0185	94	0.0385	0.0024	72	0.0016	0.0401
0.0016	0.123	0.008	41	0.0167	0.0023	17	0.001	0.0182
0.0064	0.031	0.0061	31	0.0127	0.0028	5	0.0019	0.0146

Fig .10 shows that Increasing of area ratio (A_c/A_a) leads to increase the corrosion rate of both Fe and Al and that because increasing of area ratio will increase the exposed area to corrosive solution and the relative area of the anode and cathode has a pronounced effect upon the amount of corrosion. The corrosion is concentrated by the area difference. Conversely if the area of the anode is large compared to that of the cathode this dilutes the corrosive effect.

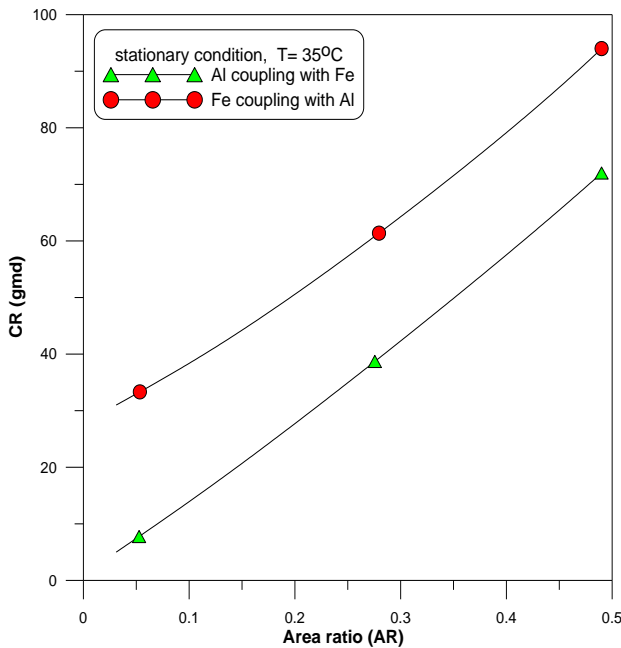


Figure (10): Corrosion rate vs. Area ratio (Fe/Al) at stationary conditions and temperature of 35°C

Fig. 11 Shows that increasing area ratio leads to increase the cathode current (Fe) and leads to decrease the anodic current (Al).

This behavior is interpreted as follows: when a small anode (the less noble metal, such as aluminium) joined to a large cathode (the more noble metal, such as carbon steel) will result in a high current density on the aluminium, and hence a high rate of corrosion.

The approximate proportionality between galvanic current density and cathode surface area suggests cathodic reduction of hydrogen reduction as the rate determining step. Deviations from their proportionality at higher current densities are due to the increasing anodic polarization of the anode electrode. In addition to the cathodic oxygen reduction a further process, namely anode dissolution, also has an influence on reaction velocity [26].

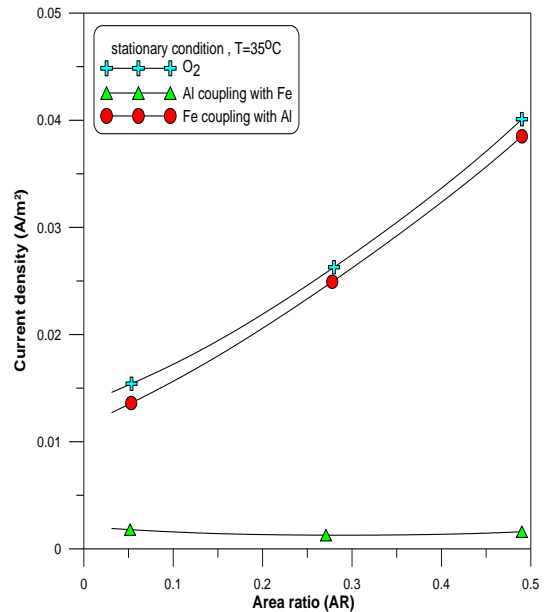


Figure (11): Current density vs. Area ratio AR (Fe/Al) at stationary conditions and temperature of 35°C

Conclusions:

1. The corrosion rate of carbon steel specimen exhibits unstable trend with temperature.
2. Increasing rotational velocity (0-1.571 m/s) leads to increase the corrosion rate of Fe from 75 g/m².d to 212.2 g/m².d and when Fe coupled with Al the corrosion rate of Fe from 40.7 g/m².d to 89.6 g/m².d.
3. Using aluminum as sacrificial anode with carbon steel give protection percent between 21% to 57.69% depending on temperature and velocity.
4. Using small area of sacrificial anode give low protection while doubling the area of sacrificial anode will be not highly effective
5. Aluminum worked as efficient sacrificial anodes in sea water and a variable rotational velocities (0, 200, 400,800 and 1200 RPM) at 35°C.
6. The different sizes of the aluminum anode used confirmed that the effective cathodic protection performance of the anode also depends on its size.

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الحماية الكاثودية للكربون الفولاذي باستخدام الالمنيوم كقطب تضحية في ماء البحر

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الخلاصة

تم اجراء عدة تجارب على عملية تآكل الحديد لوحده وعند ربطه مع انود مضحي من الالمنيوم وتم دراسة تأثير بعض العوامل العملية المؤثرة على معدل التآكل للكربون الفولاذي في المجرى المضطرب بغياب او بوجود الالمنيوم كقطب تضحية وقياس معدل التآكل بطريقة فقدان الوزن. وهذه العوامل هي السرعة الدورانية, درجة الحرارة, ومساحة الالمنيوم. تم مناقشة تأثير هذه العوامل على معدل التآكل للحديد مع ربطه بقطب التضحية وكذلك بدون وجود الالمنيوم. اثبتت النتائج ان معدل التآكل للفولاذ الكربوني بدون وجود الالمنيوم كقطب تضحية يزداد مع السرعة ويكون تغيره مع درجات الحرارة غير ثابت. اما عند ربط الحديد مع الالمنيوم فان تآكل الحديد سيقبل بنسبة كبيرة حتى مع زيادة السرعة ودرجة الحرارة. ان تقليل مساحة الالمنيوم المستخدم كقطب تضحية يزيد من معدل التآكل للحديد بينما مضاعفة المساحة للالمنيوم يقلل من معدل التآكل للحديد ولكن ليس بدرجة كبيرة وان نسبة الحماية للحديد تزداد بزيادة السرعة وتقل بزيادة درجة الحرارة.