

The evaluation of Aluminum Alloy Corrosion in Gabraun and Desalination Waters

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Abstract

The aim of this study was to investigate the effect of Gabraun and Desalination waters on corrosion of aluminum alloy. The corrosion tests were carried out at room temperature. The test solutions (electrolyte) used were Gabraun and Desalination water samples. Weight loss method was used. From the results obtained, it was found that the weights of all the specimens after the tests were decreased. Also it was found that that the average corrosion rate of Aluminum immersed in Gabraun water is little bit greater than the average corrosion rate of Aluminum immersed in Desalination water. The results showed that the color of the specimens surfaces immersed in Gabraun water was changed to white-gray color and the color of the specimens surfaces immersed in Desalination water was change to black-gray color. During the corrosion tests period, the Gabraun and Desalination water in the beakers was decreased about 50mL/week. The presence of some alloying elements like iron (Fe), copper (Cu) and Zinc (Zn) are susceptible to the corrosion processes. The Pourbaix diagrams showed Gabraun water and Desalination water are a corrosive mediums. The Langelier Saturation Index (LSI) showed that the Gabraun and Desalination water samples are not corrosive medium.

Keywords: *Aluminum alloy, Gabraun water, Desalination water, weight loss method, corrosion rate, Pourbaix diagram, LSI.*

1. Introduction

The Gaberoun Lake is an inspiring natural art formed deep in the Libyan Desert, which managed to survive the Great Sahara's harsh conditions and sand effects throughout the

age. The lake is about 7.5 meters deep, oddly cooler on the surface than it is in a meter and half below, where it becomes significantly hotter as water depth increases[1]. Aluminium (Al) is an important structural engineering material, its usage ranking only behind ferrous alloys[2]. Moreover, Aluminum is the most heavily consumed non-ferrous metal in the world and the principal elements which are alloyed with the pure aluminum to improve its tensile strength and hardness are copper, silicon, manganese, zinc, magnesium and nickel[3, 4]. In addition the relatively pure Aluminium presents good corrosion resistance due to the formation of a barrier oxide film that is bonded strongly to its surface (passive layer) and, that if damaged, re-forms immediately in most environments; i.e. re-passivation[2]. This protective oxide layer is especially stable in near-neutral solutions of most non-halide salts leading to excellent pitting resistance. Nevertheless, in open air solutions containing halide ions, with Cl^- being the most common, Aluminium is susceptible to pitting corrosion[2]. Although aluminium is a very reactive metal with a high affinity for oxygen, the metal is highly resistant to most environments and to a great variety of chemical agents. This resistance is due to the inert and protective character of the aluminium oxide film which forms on the metal surface [5]. The oxide film is extremely thin, between 50 and 100 Angstroms, it forms a protective barrier between the metal and the surrounding medium as soon as the metal comes into contact with an oxidizing environment, such as water. Aluminum corrosion products in water are white to translucent[6]. At low temperatures an amorphous (non crystalline) alumina (Al_2O_3) film forms at first which then becomes Boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $\text{AlO} \cdot \text{OH}$) and finally Bayerite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$)[6]. The physical-chemical stability of the oxide film determines the corrosion resistance of the aluminium. This stability is dependent upon the pH value of the environment, since the oxide film is stable within the pH range of about 4 to 8. Below and above these values, acid dissolution yields Al^{3+} ions and the alkaline dissolution leads to the formation of $\text{Al}(\text{OH})_4^-$ ions[5]. When aluminum is exposed to alkaline conditions corrosion may occur, and when the oxide film is perforated locally, accelerated attack occurs because aluminum is attacked more rapidly than its oxide under alkaline conditions, the result is pitting. In acidic conditions, the oxide is more rapidly attacked than aluminum, and more general attack should result[7]. Corrosion in aluminium alloys is generally of a local nature, because of the separation of anodic and cathodic reactions and solution resistance limiting the galvanic cell size. The basic anodic reaction is metal dissolution[2, 5]: $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$, while the cathodic reactions are oxygen reduction: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$, or hydrogen reduction in acidified solution such as in a pit environment as a result of Aluminum ion hydrolysis: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ [2, 5]

For the corrosion system of Ti6Al4V in naturally aerated 3.5% NaCl solution, the charging current density increases with the potential[8]. The voltage median evolution of AA5083

Aluminum samples exposed to a 3.5% NaCl solution suggests that the main corrosion process is crystallographic pitting for about the 1st day, but alkaline pitting later[9]. Agung Setyo Darmawan et al[10] Investigated corrosion resistance of 5052 aluminum to increasing salinity in sea water, aggressive NaCl solutions with concentrations of 3.5%, 4%, and 5% were used as artificial sea water corrosion medium and the temperature was 35°C. The results showed that the higher concentration leads to greater corrosion rate. Aisha H. Al-Moubaraki et al[11] investigated The corrosion behavior of Al 7075, Al 2024, and Al 6061 in the red sea water and the results revealed that the corrosion rates of Al alloys decreased with time. Deepa et al[12] concluded that 6063 aluminum alloy undergoes corrosion in phosphoric acid medium and in sodium hydroxide medium and the corrosion rate increases with an increase in the concentration of phosphoric acid medium as well as sodium hydroxide medium also corrosion rate increases with an increase in temperature. Seruga M. & Hasenay D[13] found that the results showed the corrosion of Al in soft drinks is a very slow and corrosion of Al in these drinks occurs principally due to the presence of acids. Nemcova *et al.*[14] studied the corrosion resistance of Aluminum Alloy in the Aqueous solution of Urea, the results showed low corrosion resistance in aqueous solution with chloride ions. Kemal Nişancioğlu[15]. Studied pitting and uniform corrosion of Aluminum alloys and effectiveness of cathodic protection in reducing these corrosion forms. The results revealed that in stagnant waters or presence of low flow rates, pitting may occur.

Sanni *et al*[16] studied the silicone oil as Corrosion Inhibitor for Aluminum Alloy in Aggressive Environment (3.5% NaCl solution) and found that the inhibitor showed a lower corrosion rate values as compared with the corrosion rate samples without inhibitor. Mohammad Asadikiya et al[17] investigate that the inhibition effect of sodium diphosphate on the aluminum in water-ethylene glycol solution can be due to forming a stable passive film on the surface of aluminum. Paulina Arellanes-Lozada et al[18] studied the Inhibition of Aluminum Corrosion in Sulfuric Acid by Poly(1-vinyl-3-alkyl-imidazolium Hexafluorophosphate), the results showed that PILs displayed low efficiencies as corrosion inhibitors against uniform corrosion. The various equilibrium of the Al-H₂O system has been clarified by Pourbaix in a potential versus pH diagram (shown in the Fig. 1). It is revealed that aluminum corrodes in the range of 4 > pH > 8 forming Al³⁺ ions at low pH values and AlO²⁻ ions at high pH values. Aluminum should show passivity (solubility constant < 10) forming Al₂O₃·3H₂O at near-neutral pH values and immunity at very negative potentials[19]. The potential of Aluminum at 25°C is -1.66V[20].

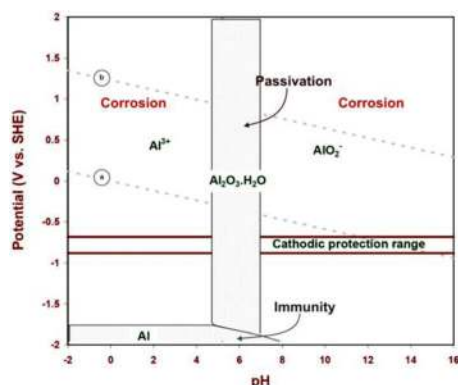


Fig.1 E-pH corrosion diagram (Pourbaix Diagram) for Al/H₂O system at 25 °C[19].

2. Experimental work

2.1. Materials

The material used in this study is Aluminum Alloy with chemical composition obtained by X-ray diffraction as shown in Table 1, which analyzed in the faculty of science, sebha university

Table (1). Chemical composition of Aluminum alloy before immersion

Al (m ass %)	Si (m ass %)	Fe (ma ss %)	Ca (ma ss %)	Th (ma ss %)	Zn (ma ss %)	Cu (ma ss %)	Cl (ma ss %)	S (mas s %)	Mn (mas s %)	Ni (ma ss %)	Ga (mas s %)	Co (mas s %)	Othe rs (mas s %)
94.9	2.19	1.06	0.649	0.543	0.104	0.090	0.089	0.0867	0.0846	0.077	0.0247	0.0107	balance

Ten (10) specimens were used in this study and cut from metal bars with rectangular cross-sectional areas and have dimensions of 36-40mm long, 25mm width and 5mm thickness as shown in Figure (1).

Five (5) specimens were used for Gabraun water and Five (5) specimens were used for Desalination water (treated water). All the surfaces of the specimens were cleaned and washed well and polished with 800 and 1200 grit emery papers to remove oxides and contaminants.

2.2. Corrosion tests

Gabraun, water and Desalination water were used as a test solutions in this study, and a number of 600 ml beakers were used and filled by these types of water. All the specimens were completely immersed in the filled beakers. Each specimen was put in one beaker.

All the specimens were cleaned and weighed before and after the corrosion tests. All the tests were carried out at room temperature. The corrosion test period was 50 days for all the specimens. The chemical analysis of the used Gabraun water and Desalination water are shown in Table (2) and Table (3) were done in faculty of science, sebha university.

Table (2) The analysis of Gabraun's water before tests

Parameter	Gabraun water before immersion
ph	9.66
Conductivity ($\mu\text{S}/\text{cm}$)	162500
Salinity (ppt)	27
TDS (mg/L)	24780
Total Alkalinity(mg/L)	430
Hardness Ca^{++} (mg/L)	83
Hardness Mg^{+2} (mg/L)	28
SO_4 (mg/L)	37
K^+ (mg/L)	34
Na^+ (mg/L)	135
Cl^- (mg/L)	95
Total Hardness (mg/L)	384

Table (3) The analysis of Desalination water before tests

Parameter	Drinking water before immersion
ph	8.77
Conductivity ($\mu\text{S}/\text{cm}$)	103.7
Salinity (ppt)	0.1
TDS (mg/L)	51
Total Alkalinity(mg/L)	25
Hardness Ca^{++} (mg/L)	22
Hardness Mg^{+2} (mg/L)	13
SO_4 (mg/L)	0.5
K^+ (mg/L)	9.5
Na^+ (mg/L)	25
Cl^- (mg/L)	3.9
Total Hardness (mg/L)	38

In order to predict the tendencies of Gabraun and Desalination water to precipitate or dissolve calcium carbonate, the Langelier Saturation Index (LSI) was designed to measure calcite formation and used as a measure of corrosion. Also this index indicates the driving force for scale formation and growth in terms of pH as a master of variable[21].

In order to calculate the LSI, it is necessary to know the alkalinity (mg/L, as CaCO₃, or calcite), the calcium hardness (mg/L Ca⁺² as calcium carbonate), the total dissolved solids (TDS) (mg/L TDS), the actual pH, and the temperature of water (°C)[21].

LSI is defined as the following equation[21]:

$$LSI = pH - pHs \dots\dots\dots(2)$$

Where:

pH is the measured water pH.

pHs is the pH at saturation in calcite or calcium carbonate and is defined as[21]:

$$pHs=(9.3+A+B)-(C+D)\dots\dots\dots(3)$$

$$A=\{\log_{10}[TDS]-1\}/10$$

$$B=-13.12 \times \log_{10}(^0C+273)+(34.55)$$

$$C=\log_{10}[Ca^{2+} \text{ as } CaCO_3]-[0.4]$$

$$D=\log_{10}[\text{alkalinity as } CaCO_3]$$

The LSI indicates three situations[21]:

If LSI is negative: No potential to scale, the water will dissolve CaCO₃.

If LSI is positive: Scale can form and CaCO₃ precipitation may occur.

If LSI is close to zero: Borderline scale potential.

2.3. Corrosion rate calculations

The rate of corrosion of aluminum in water depends on several parameters coupled to water: pH, temperature, electric conductivity, elements in the water and movements of the water. It also depends on the alloy composition, elaboration technique (extrusion, rolling etc), heat treatment and surface state[22]. The composition, size and quantity of alloy constituents such as Al₃Fe, Al₆(Mn, Fe), _(FeSi) or pure silicon affect the corrosion rate. If the constituent's corrosion potential is different from the aluminum matrix galvanic corrosion effects will appear. This will increase the corrosion rate[22].

The corrosion rate was calculated by using the following relation[23]:

$$\text{Corrosion rate} = \frac{W \times 365}{\rho \times A \times T} \dots\dots\dots(4)$$

Where:

W = weight loss (g)

365 = number of days per year (day/year)

A = the area of the specimen exposed to the solution (cm²)

ρ = the metal (Aluminum) density (2.7g/cm³)

T = exposure time of the specimens (50 days)

3. Results and Discussion

It was seen that the color of the surfaces of all the specimens before the immersion in this study was as shown in Figure (2).

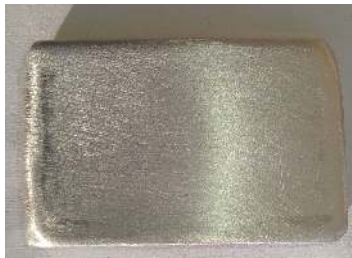


Figure 2 photo for Aluminum alloy before immersion in all the types of water

After two weeks from the immersion the color of the specimens surfaces immersed in Gabraun water start to change to white-gray color as shown in Figure (3) and the color of the specimens surfaces immersed in Desalination water start to change to dark-gray color as shown in Figure (4). These changes of colors attributed to the chemical reaction between the aluminum specimens surfaces and the both types water, Gabraun water and Desalination water, it is suggested that these reactions produced corrosion products with white-gray color and dark-gray color, respectively, while Aluminum corrosion products in water are white to translucent[6]. Moreover when aluminum is exposed to alkaline conditions corrosion may occur[7], this is compatible to the results obtained in this work that show the pH of Gabraun water is 9.66 as shown in Table 2, which indicates that corrosion is occurred and produced from the cumulative of the corrosion products. In the pH range of about 4 to 8.5, aluminum is passive (protected by its oxide film)[24], however the pH of the Desalination water is 8.77 and the corrosion of Aluminum alloy was occurred, this is due to the presence of some alloying elements like iron (Fe), copper (Cu) and Zinc (Zn) which are susceptible to the corrosion processes

As can be seen in figure 3 and figure 4, small spots are appear on the surfaces, these spots are attributed to pitting corrosion which occurred from the presence of chlorine ions (Cl⁻) in the test solutions.



Figure 3 photo for Aluminum alloy after immersion in Gabraun water



Figure 4 photo for Aluminum alloy after immersion in Desalination water

Furthermore the color of the Gabraun water and Desalination water didn't change until the end of the experiments which remained colorless. In addition, after one week from the immersion, it was seen that the level of the water in each beaker was decreased about 50 ml, this lack of the water was attributed to change of the temperature from 25°C to 37°C and this lack of water was substituted continuously until the end of the experiments.

All the Specimens were cleaned after the end of corrosion tests by the Tap water, and distilled water and then weighed and compared by their weights before the tests, it was found that the weights of all the specimens after the tests were decreased as shown in Tables 4 and Table 5. These results were expected to be the result of the chemical reaction between the both types of water and Aluminum alloy specimen surfaces.

Table (4) The results of the corrosion test for Aluminum alloy specimens in Gabraun water.

No. Specime	Weight before immersion (g)	Weight after immersion (g)	Weight loss (W) (g)	Area(Cm ²)	Corrosion rate cm/year
1	12.2840	11.9051	0.3789	24.1	0.04250
2	12.2517	11.8752	0.3765	24.1	0.04228
3	12.3990	12.0160	0.383	24.1	0.04296

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4	12.3182	11.9425	0.3757	24.7	0.04112
5	13.3759	12.9661	0.4098	26.5	0.04181

Table (5) The results of the corrosion test for Aluminum Alloy specimens in Desalination water

No Specime	Weight before immersion (g)	Weight after immersion (g)	Weight loss (W) (g)	Area(Cm ²)	Corrosion rate cm/year
6	12.2046	11.8326	0.372	24.1	0.04173
7	13.2953	12.8881	0.4072	25.9	0.04250
8	12.1513	11.7783	0.373	24.7	0.04082
9	12.0553	11.6885	0.3668	24.1	0.04115
10	12.7646	12.3747	0.3899	25.3	0.04166

Table (6) The average corrosion rate (cm/year) of Aluminum in Gabraun and Desalination water

Type of water	Gabraun water	Desalination water
Average Corrosion rate (cm/year)	0.04213	0.04157

Referring to the Table 6, the results show that the average corrosion rate of Aluminum immersed in Gabraun water is little bit greater than the average corrosion rate of Aluminum immersed in Desalination water, this is because of the presence of higher chlorine ions (Cl⁻) and sulfides (SO₄) in Gabraun water than in Desalination water as shown in Table 2 and Table 3.

According to the pourbaix diagram in figure 1, It is revealed that aluminum corrodes in the range of 4 > pH > 8 forming Al³⁺ ions at low pH values and AlO²⁻ ions at high pH values and the potential of Aluminum at 25°C is -1.66V [19, 20]. Likewise, the pH of the Gabraun water is 9.66, hence, this result show that Gabraun water is a corrosive medium, and the pH of Desalination water is 8.77, this number is more than pH 8, hence the Pourbaix diagram in Figure 1 shows Desalination water is a corrosive medium for Aluminum Alloy as well.

Table 7. Results of The Langelier Saturation Index (LSI)

No.	Water sample	LSI
1	Desalination water	+0.362
2	Gabraun water	+2.482

According to the results obtained from the Langelier saturation index (LSI) shown in table 7, it was found that the LSI for Gabraun water and Desalination water samples are positive this indicates that scale can form and CaCO₃ precipitation may occur. While the results

obtained from the corrosion tests of aluminum alloy, showed that Gabraun and Desalination water are corrosive medium. From this result, the Langelier saturation index (LSI) cannot give the expected results when Aluminum Alloy immersed in both Gabraun and Desalination water.

Table (8). Chemical composition of Aluminum alloy after immersed in Gabraun water

Al (mass %)	Si (mass %)	Fe (mass %)	Ca (mass %)	K (mass %)	Zn (mass %)	Cu (mass %)	Cl (mass %)	S (mass %)	Mn (mass %)	Ni (mass %)	Ga (mass %)	Co (mass %)	Others (mass %)
87.8	4.08	2.24	1.73	1.67	0.34	0.264	0.189	0.293	0.257	0.251	0.079	0.0321	Balance

Table (9). Chemical composition of Aluminum alloy after immersed in Desalination water

Al (mass %)	Si (mass %)	Fe (mass %)	Ca (mass %)	Th (mass %)	Zn (mass %)	Cu (mass %)	Cl (mass %)	S (mass %)	Mn (mass %)	Ni (mass %)	Ga (mass %)	Co (mass %)	Others (mass %)
80.5	5.64	3.60	3.38	2.44	0.570	0.412	0.638	1.52	0.348	0.427	0.128	0.0512	Balance

According to the comparison between the chemical composition of the Aluminum alloy before the immersion in Table 1 and after the immersion in both the Gabraun and the Desalination water in Table 8 and Table 9, respectively, it was found that the amount of aluminum is decreased but the other elements are increased. This result was due to the chemical reaction between the Aluminum Alloy and the test solutions, that produced Aluminum Oxide (Al_2O_3), which is appear on the surface of the specimens as a white-gray color after immersed in Gabraun water and dark-gray color after immersed in Desalination water. Furthermore, the presence of Iron in the chemical composition of the Aluminum Alloy with this amount shown in the Tables above is detrimental to corrosion due to its low solubility and hence ability to form constituent particles which are cathodic to the Al-matrix such as Al_3Fe [2]. And also the presence of Iron may affect on the color of Aluminum oxide.

Table (10). Chemical composition of Aluminum alloy after immersed in Gabraun water

Al_2O_3	SiO_2	Fe_2O_3	CaO	K_2O	ZnO	CuO	Cl	SO_3	MnO	NiO	Ga_2O_3	Co_2O_3	Others
3	2	3						3					

(mas s %)	(ma ss %)	(mas s %)	(ma ss %)	(ma ss %)	(ma ss %)	(ma ss %)	(ma ss %)	(ma ss %)	(ma ss %)	(ma ss %)	(mas s %)	(mas s %)	(mass %)
89.2	4.6 9	1.72	1.3	1.0 8	0.2 27	0.1 78	0.1 02	0.3 93	0.1 79	0.1 72	0.05 71	0.02 43	Balan ce

Table (11). Chemical composition of Aluminum alloy after immersed in Desalination water

Al ₂ O ₃ (mas s %)	SiO ₂ (ma ss %)	Fe ₂ O ₃ (mas s %)	Ca O (m ass %)	Th O ₂ (ma ss %)	Zn O (ma ss %)	Cu O (ma ss %)	Cl (ma ss %)	SO ₃ (ma ss %)	Mn O (ma ss %)	Ni O (ma ss %)	Ga ₂ O ₃ (mas s %)	Co ₂ O ₃ (mas s %)	Othe rs (mas s %)
82.6	6.5 6	2.80	2.5 7	1.5 1	0.3 85	0.2 80	0.3 46	2.0 6	0.2 44	0.2 95	0.09 35	0.03 91	Bala nce

Referring to Table 10 and Table 11, one of the components of aluminum Alloy after immersion is Iron(III)oxide or ferric oxide(Fe₂O₃) which has sometimes black or reddish-brown color, while the other oxides have a white color. So the color of the surfaces of the specimens immersed in Desalination water was suggested to be affected by the color of ferric oxide (Fe₂O₃), this is because ferric oxide on the surfaces of the specimens immersed in Desalination water has an extra amount than that immersed in Gabraun water as shown in Table 10 and Table 11. According to this result, the color of the surface of the specimens immersed in Desalination water appear more darker than that immersed in Gabraun water.

4. Conclusions

The results of the current study reached to the following conclusions;

- 1- The colors of the Gabraun and Desalination water used for Aluminum alloy specimens corrosion tests were not changed.
- 2- the color of the specimens surfaces immersed in Gabraun water changed to white-gray color, while the color of the specimens surfaces immersed in Desalination water changed to black-gray color.
- 3- The color of the specimens surfaces after immersion was suggested to be dependent on the color and amount of Ferric oxide.
- 4- The average corrosion rate of the specimens immersed in Desalination water is less than that immersed in Gabraun water.
- 5- After two weeks from the immersion of the specimens, the amount of water decreased about 50ml from each beaker, this resulted from the raise of the room temperature between 25°C to 37°C, this lack was substituted continuously during the test period.
- 6- The Langelier saturation index (LSI) does not give an expected results when Aluminum Alloys immersed in both Gabraun and Desalination water.

- 7- Small spots are appear on the surfaces, these spots are attributed to pitting corrosion.

Further works

The increase of the alloying elements shown in table 8 and table 9, will be studied in the further works.

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