Protect of Underground Oil Pipelines by Using (Al-Sn-Zn) as Sacrificial Anode in Al-Qasim Region

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Abstract: Sacrificial anode cathodic protection is one of the most widely used methods in protecting buried oil pipe lines against the corrosion damages. In the present work, a series of Aluminum alloys have been prepared as sacrificial anodes candidates to be used in the protection of the oil pipelines that pass through the Al-Qasim region. These prepared alloys were microstructurally and electrochemically characterized to evaluate their performance as Al-sacrificial anodes for cathodic protection of oil pipes. The relationships between the protection potential with time, sacrificial anode life, discharge currents, and capacity of sacrificial anodes were found, taking into consideration the distance between sacrificial anode and protected steel sample. According to the results obtained, the best selection of sacrificial anodes was (Al-4% Zn-0.4% Sn) alloy at 30cm in Al-Qasim region.
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Key Words: Corrosion, sacrificial anode, aluminum alloy, tin and microstructures.

1. Introduction

Corrosion is a natural process, just like water flows to seek the lowest level, all natural processes tend towards the lowest possible energy states. Thus, for example, iron and steel have a natural tendency to combine with other chemical elements to return to their lower energy states [1, 2]. Corrosion is a costly and potentially life threatening problem in any industry [3]. Corrosion can be defined as the deterioration of a material's properties due to its interaction with its environment [4].

The corrosion of underground structures is a very widespread problem, Structures such as natural gas, crude oil pipelines, and water mains are only some of the many structures reported to have been affected by soil corrosion all around the world [5, 6]. The major cause of the deterioration of underground pipeline is the soil. Soil corrosion is caused by moisture, pH, redox potential, microbes in soils and soil type [6]. Corrosion causes gradual decay and deterioration of pipes, both internally and externally [7]. Severe corrosion of buried metal structures has led to explosions, loss of life, and massive environmental clean ups. In addition, leaking water pipes may cause or contribute to landslides and other earth movements [8]. Corrosion is the primary factor affecting the longevity and reliability of pipelines throughout the world [9]. An earlier study estimated the average annual corrosion-related cost in the U.S. for natural gas, crude oil , and hazardous liquids transmission pipelines at $7.0 billion, which the study divided into the cost of capital (38 percent), operation and maintenance (52 percent) , and failures (10 percent) [10,11]. The principal methods for mitigating corrosion on underground pipelines are coatings and cathodic protection (CP). Coatings normally are intended to form a continuous film of an electrically insulating material over the metallic surface to be protected. CP is a technique to reduce the corrosion rate of a metal surface by making it the cathode of an electrochemical cell. This is accomplished by shifting the potential of the metal in the negative direction by the use of an external power source (referred to as impressed current CP) or by utilizing a sacrificial anode[12]. In the galvanic system, the metallic structure is made the cathode (negative) by connecting it to galvanic anodes, which are more negative than the metallic structure to be protected. In this system, the current is generated by the corrosion of active metals, such as magnesium, zinc and also aluminum. These anodes are utilized as sources of electrons which are released when the anodes are buried in the soil corrode. The electrons released pass through the metallic connection between anode and steel, and thus enter the structure to be protected. Aluminum and aluminum alloys are extensively used as sacrificial anodes as they have undeniable economic advantages in view of their merits such as low density, high current capacity and reasonable cost.

Aluminum is the most commonly used sacrificial material for cathodic protection of steel in sea water [13]. 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. In order to improve the efficiency of aluminum anodes, they are typically alloyed with other elements to encourage depassivation (breakdown of the oxide film) and/or shift the operating potential of the metal to a more electronegative direction. The alloying elements used to accomplish this are referred to as depassivators and modifiers. Modifiers that have been used include zinc

(Zn), magnesium (Mg), barium (Ba), and cadmium (Cd). The depassivators commonly used are indium (In), mercury (Hg), and tin (Sn), and also rarely used are gallium (Ga), titanium (Ti) and thallium (Tl) [13].

In this work tin has been chosen for investigation on its effect on Al-Zn alloy as sacrificial anode because of reasons of availability and economy.

2. Experimental work

Preparation of Aluminum Alloys

Casting Process

Aluminum alloys were prepared by melting aluminum at 750 °C. It is then left for5 minutes after each element addition. The melt was stirred using a graphite stirring rod. After that the homogeneous melt was poured into a steel mold of (165, 50, 30) mm as shown in Fig (1a). The Chemical analysis of prepared alloys was carried out using (dissolution spectrometer) in Specialized Institute for Engineering Industries (ISEI) as shown in Table (1).

-a- -b-

Fig-1 a: Steel die, b: Rod ingots

Table-1 the Chemical Composition of Preparing Al-Alloys

alloy (wt %)	Zn	Sn	Fe	Mn	Si	Al
Al-4%Zn	4.2	0.0	0.201	0.002	0.097	Balance
Al-4%Zn-0.4%Sn	3.95	0.392	0.168	0.002	0.119	Balance
Al-4%Zn-0.5%Sn	4.1	0.489	0.168	0.002	0.111	Balance

Samples Preparation:

Samples Used in Linear polarization Test

Steel Samples

A pieces of steel pipe with dimensions (114mm outside diameter ,102 mm inside diameter) and having a chemical composition as shown in the Table (2) was received from (oil pipelines company in Al-Hilla). The samples were then washed with distilled water, rinsed with ethanol, dried and kept in dissector containing silica gel.

Aluminum Alloys Samples

Al-alloys ingots were machined into a circular shape with the dimensions of (13mm diameter, 3mm thickness) , washed with distilled water, rinsed with ethanol dried and kept in dissector contains silica gel.

Samples Used in Sacrificial Anode System Tests

Steel Samples

Samples of steel formed to the required dimensions (20X20, 6mm) length, width and thickness respectively, with a hole of (2mm diameter) drilled for purpose of suspension of the samples in the solutions used.

Aluminum Alloys Samples

Al-alloys ingots were machined into a circular shape with the dimensions of (13mm diameter, 6mm thickness), They were drilled as done with the steel samples.

Surface Preparations of Samples

Preparing the surfaces of the samples includes: grinding using progressively finer abrasive papers (180, 400, 600, 800, 1000, 1200, 2000 grit size). Using Grinder-Polisher machine, type (Buehler, Metaserv-200, 200-240VAC, 50HZ, Made in UK). After the end of each stage the samples were washed with distilled water rinsed with ethanol and dried .Then the samples polished using polishing cloth and diamond paste type (nature diamond, with size 0.1 micron),and then washed with distilled water , rinsed with ethanol , dried, and kept in dissector containing silica gel to protect them from weather conditions.

Preparation of Solutions

The solutions were prepared experimentally, by adding different weights of (NaCl, N_2SO_3,$CaSO_4$) to 1 liter of tap water, according to the chemical analysis of Al-Qasim soil as shown in Table (3). This test is carried out in Babylon University, Civil Engineering College,and Soil& Sanitary Laboratories. The composition of simulated solution as prepared is shown in Table (4). PH value of solution was 8.18. Resistivity of these solution was (793.65) Ω.cm, which was measured through the measuring of conductivity of solution by a device measuring the conductivity type (WTW,CONDE 720),this test is carried out in Babylon University ,College of Science, Department of the Biological Sciences.

Table -2 the Chemical Composition of the Steel Pipe

C%	Mn%	S%	P%	Fe%
0.26	1.22	0.025	0.027	balance

Table -3 Chemical Test of Babylon Soil

Samples%	Cl	SO_3	Gyp
Al-Qasim	0.0136	0.559	1.2

Table -4 Chemical Composition of a Prepared Solutions

Samples %	NaCl	Na_2SO_3	Gyp
Al-Qasim	0.022	0.88	1.2

Electrochemical Evaluation of the Anodes

Cathodic Protection by Sacrificial Anode Method

Description of the System

This system consist of the following items

- **Cathode electrodes:** a sample steel pipe.
- **Sacrificial anode electrodes:** represented by Al-alloys.
- **Electrolyte:** represented by simulated solutions prepared previously.
- **Reference electrode:** saturated calomel electrodes as shown in fig. (2a).
- **Metallic conductor:** copper cable.
- **Glass bath:** Glass bath (920x415x300) mm.
- **Thermometer:** The thermometer was placed in the electrolyte to measure temperature up to 100°C.
- **Avoemeter:** A digital multimeter type (DT9205A) wasused.

Testing Procedure

The following procedures were adopted in this research:

1. Filling the tank with 25 liters of electrolyte.
2. The sacrificial anodic electrode was weighed before immersion by using digital balance type (Sartorius Bp 3015 Max. 303g, d=0.1 mg, Germany).
3. Each specimen of anode and cathode electrically connected by one end of copper wire.
4. Sacrificial anode electrode with required protected steel sample was immersed in the glass tank; the distance between them was between 10 and 30cm.
5. Connect the sacrificial anode electrode with required protected steel sample from the other ends of copper wire to multimeter to follow the free chemical reaction electrons.
6. Put the reference electrode calomel near media length of steel sample after being connected with Aovometer in the cathodic node; then the steel sample was connected to the anodic electrode as shown in fig. (2b).
7. Record the voltages and current each 3 minutes for 2 hours.
8. The sacrificial anode electrode removed after (2 hours), the sacrificial anode electrode cleaned, washed with distilled water. After rinsing with ethanol, it was dried and then re-weighted.
9. Repeat these steps for different solutions, distances and alloys.

Calculation of Current Output of Sacrificial Anodes

The current output of sacrificial anode is calculated from the following equation

$$Total\ Weight\ Loss\,(g) = \frac{Wt.I.t}{n(96500)} \qquad (1).$$

Where:

Wt = atomic weight of the metal or alloy (sacrificial anodes);

I = current in Ampere;

t = time duration of current flow in sec;

n = valance electron of the metal or alloy;

To find atomic weight for sacrificial anode alloys [14], use

$$Wt = \frac{100}{\frac{C_1}{Wt_1} + \frac{C_2}{Wt_2}} \qquad (2).$$

Wt = atomic weight for alloy (g/mole);

C_1, Wt_1 = weight percent and atomic weight for Al respectively;

And, C_2, Wt_2 = weight percent and atomic weight for second alloying element respectively.

-a- -b-

Fig-2 a: The Saturated Calomel Elec, b: Sacrificial cathodic protection system

Determine Life and Capacity of Anode

The sacrificial anode capacity of a galvanic anode is calculated from the equation [14, 15].

$$A_C = \left[\frac{A_L \times I \times 8760}{A_W \times U_F} \right] \quad (3).$$

Where:

A_C = anode capacity (A. hrs/kg);
A_L = anode Life (year);
A_L = mass of sacrificial anode/ consumption rate;
Consumption rate = weight loss / time (kg/hr);
I = discharged current (Ampere);
A_W = anode weight (Kg);
U_F = utilization factor = 0.9;
And, 8760 = total hours in a year.

Linear Polarization Test

This method is used to estimate the corrosion current and corrosion potential. The tester consists of electrochemical cell and electrodes. The cell is made of glass and the shape of the cell was spherical with1 liter volume.

The cell contains three electrodes:

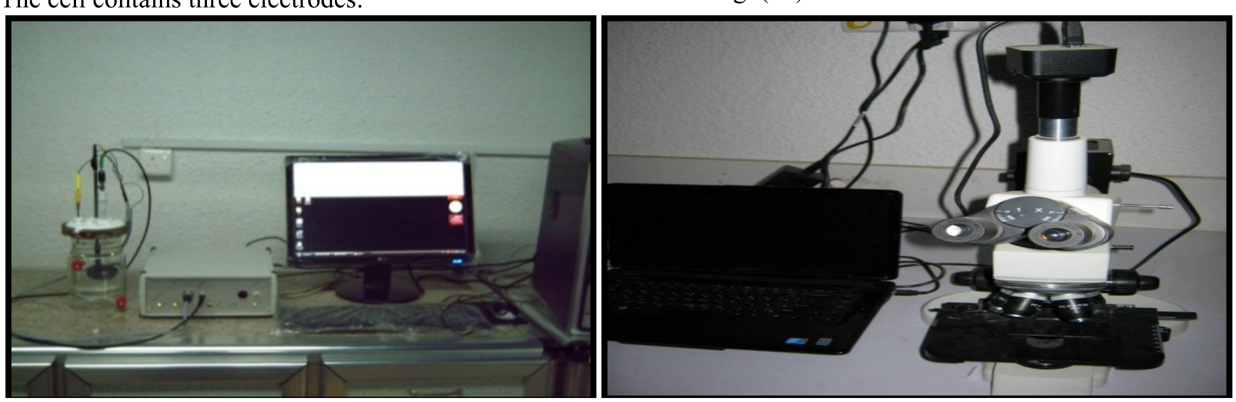
1. Reference electrode: saturated calomel electrode.
2. Auxiliary electrode: platinum electrode.
3. Working electrode: testing electrode (sample used).

In this study, a (2.5% NaCl) solution was used. To draw the polarization curves, the anode and cathode were controlled by a computer which communicated simultaneously with a potentionstat using Bank-Elechtionies programme. The Tafel tester was (MLab 100, power 35 W) type to test electrochemical corrosion as shown in Fig.(3a).

Microstructural Examination

Final stage after polishing for Microstructural examination, the samples tested were etched. This involved a short treatment for (15-20) sec in (Keller's Reagent) prepared as follows:

(1%HF, 1.5% HCl , 2.5%HNO_3 and 95%H_2O) . After etching, The samples were washed with distilled water, rinsed with ethanol, and finally dried. The microstructures of samples were observed by using (SIMRAN optical microscope made in USA) as shown in fig. (3b).



-a- -b-

Fig-3 a: The Tafel tester to test electrochemical corrosion, b:Light Optical Microscopy (LOM).

3. Results and Discussion

Potential Protection

The potential was measured every 3minutes for 120 minutes. The figures (4 to 6) indicate that the protection potential increases in the negative direction when the percentage of tin increases in alloy and the resistivity of solution decreases, weight losses from sacrificial anode are calculated after 2 hours, as shown in Table (5).

Table -5 the Potential Protection and Current from the Sacrificial Cathodic Protection to Protect Sample With Area 5.6 cm^2

Alloy type	Solution type	Distance (cm)	Weight loss(g)	Potential (-mv)	Current (µA)
Al-4% Zn	Al-Qasim	10	0.0005	665	266
Al-4% Zn	Al-Qasim	30	0.0005	672	275
Al-4% Zn-0.4% Sn	Al-Qasim	10	0.0005	871	101
Al-4% Zn-0.4% Sn	Al-Qasim	30	0.0003	866	105
Al-4% Zn-0.5% Sn	Al-Qasim	10	0.0003	910	90
Al-4% Zn-0.5% Sn	Al-Qasim	30	0.0004	900	96

Table -6 Shows the Anode Life and Anode Capacity for all Sacrificial Anode Alloys

Sacrificial anode	Solution type	Distance (cm)	Current output(µA)	Anode life (hr)	Anode capacity A.hr/Kg
Al-4% Zn	Al-Qasim	10	727.62	8472	28328708.73
Al-4% Zn	Al-Qasim	30	727.62	9337.2	28328708.73
Al-4% Zn-0.4% Sn	Al-Qasim	10	725.26	9251.2	28236732.41
Al-4% Zn-0.4% Sn	Al-Qasim	30	435.16	16445.33	28236726.68
Al-4% Zn-0.4% Sn	Al-Qasim	10	434.84	1594.7	28214647.45
Al-4% Zn-0.4% Sn	Al-Qasim	30	580.21	11430	28216209.37

Cathodic Polarization Protection

Cathodic Protection at Al-Qasim Solution

Fig. (4 to 6) represent the relationship between potential and time for various distances. The protection potential for steel in sea water and soil when using saturated calomel electrode is -800mv [14, 16].

The protection potential in fig. (4) for (Al-4% Zn) alloy is more than -800 mv. Therefore this selected sacrificial anodes do not protect the steel sample because their potential is more than the desired value.

The protection potential in figs. (5 and 6) for (Al-4%Zn-0.4% Sn , Al - 4%Zn-0.5%Sn) alloys is lower than protection potential of steel which was -800mv. Therefore these alloys can be used successfully as sacrificial protection electrode.

Current Output of Sacrificial Anodes

The current output of sacrificial anode is calculated from equation (1)

W_t Al =26.98 g/mol, Wt Zn = 65.41 g/mol and W_tSn =118.710 gm/mol

Table (6) shows the current output for all sacrificial anode alloys.

Life and Capacity of Anode

The sacrificial anode capacity of galvanic anode is calculated from equation (3).

Table (6) shows the anode life and anode capacity for all sacrificial anode alloys

The Best Selection of Sacrificial Anode

The best selection of sacrificial anodes used in this work depends on:

1. Potential: the potential of anode must be more negative value than the structure potential.
2. Anode life: the higher the anode life the better it is.

From the above, we can conclude the best selected anode in Al-Qasim Region is alloy Al-4%Zn-0.4%Sn at 30 cm from the structure which gives and anode life of 16445.33 hrs with anode capacity of 28236726.68 A.hr/kg.

Linear polarization Tests

Linear polarization of (Al-4%Zn) Alloy

Fig. (7) Shows the polarization data of the sacrificial anode (Al-4% Zn) alloy. The polarization curves as shown below, show that the corrosion potential in the conditions of as cast (Al-4% Zn) alloy, the corrosion potential is (-652.4mV) and the corrosion current icorr=1.51µA/cm. However, it should be noted that the corrosion potential was small.

Linear polarization of (Al-4% Zn-0.4% Sn)Alloy

Fig. (8) Shows the polarization data of the sacrificial anode (Al-4% Zn-0.4% Sn) alloy. The polarization curve shows that the i_{corr} of alloy is equal to (7.13µA/cm²). ($E_{corr.}$) = (-840.4mV) which is higher than that of (Al-4% Zn).

Linear polarization of (Al-4% Zn-0.5% Sn)Alloy

Fig. (9) Shows the polarization data of the sacrificial anode (Al-4% Zn-0.4% Sn).The polarization curve shows that the icorr of alloy is equal to (4.63µA/cm²). (Ecorr.) = (-869.5mV) which is higher than that of (Al-4%Zn and Al-4% Zn-0.4% Sn) alloys.

As observed, the polarization behavior of all (Al-Zn-Sn) alloys exhibits an active behavior compared with (Al-Zn) alloy, the corrosion potential takes more negative value than (AL-Zn) alloy. This behavior is attributed to the presence of Sn as an alloying element leading to electrochemical activity of alloy due to modification in the chemistry of the film leading to the active dissolution of Al [17]. It is clear from the polarization curves the extent of activation increases with increase in Sn content concentration.

Microstructure Observations of Prepared Aluminum Alloys

Fig. (10a to 11a) represent the microstructures of some specimens prior to exposure to the environment. Fig. (11b to 12b) represent the microstructures of some specimens after exposure to the environment. From these shapes we have noted that all the sacrificial anodes were subjected to uniform corrosion.

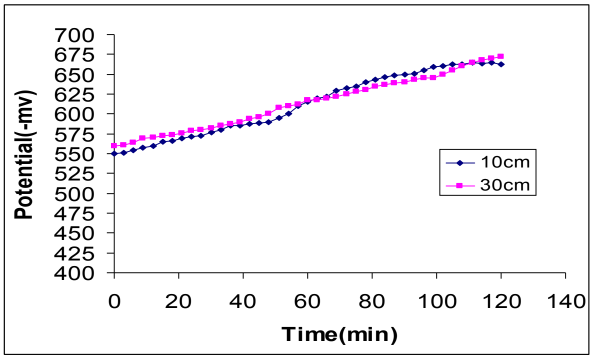


Fig-4 Potential vs. Time for sacrificial cathodic protection system to (Al – 4%Zn) in Al-Qasim solution

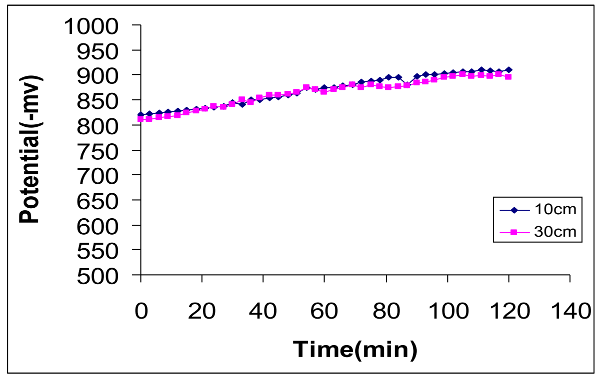


Fig-6 Potential vs. Time for sacrificial cathodic protection system to (Al – 4%Zn-0.5%Sn) in Al-Qasim solution

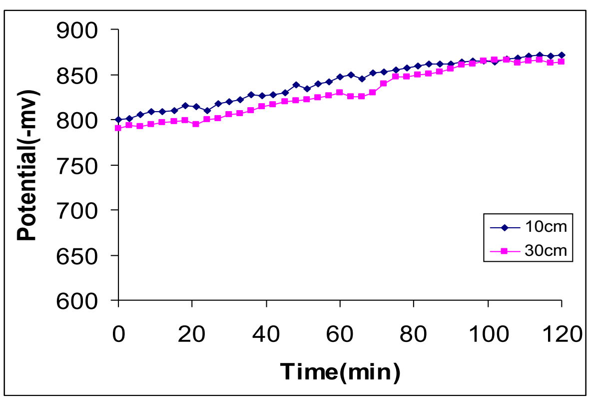


Fig-5 Potential vs. Time for sacrificial cathodic protection system to (Al – 4%Zn-0.4%Sn) in Al-Qasim solution

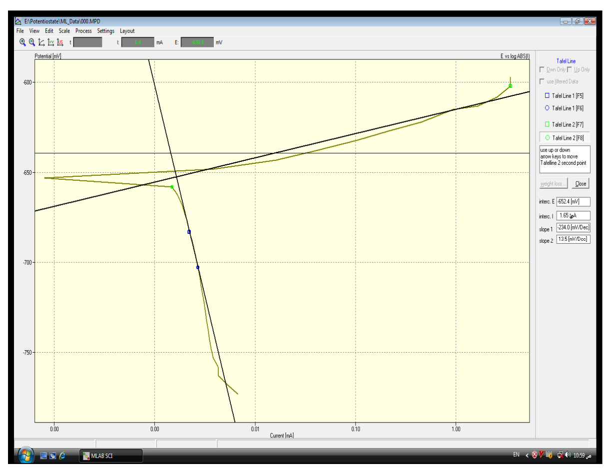


Fig-7 Polarization curve for (Al-4%Zn) alloy

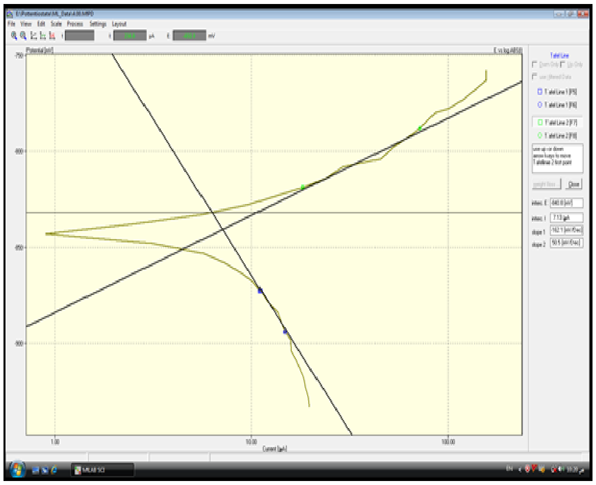


Fig -8 Polarization curve for (Al-4% Zn-0.4% Sn) alloy

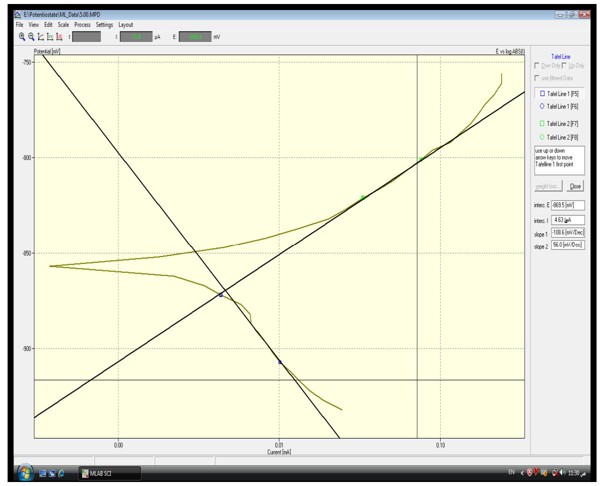
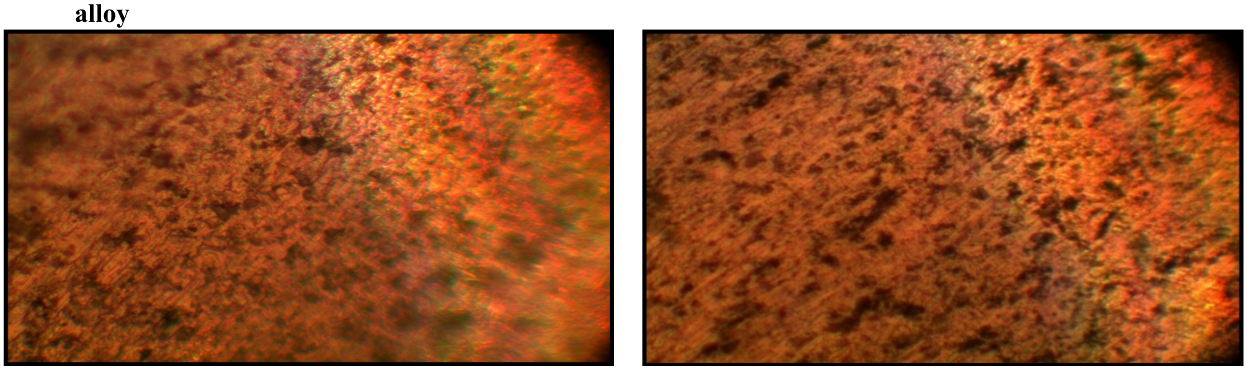
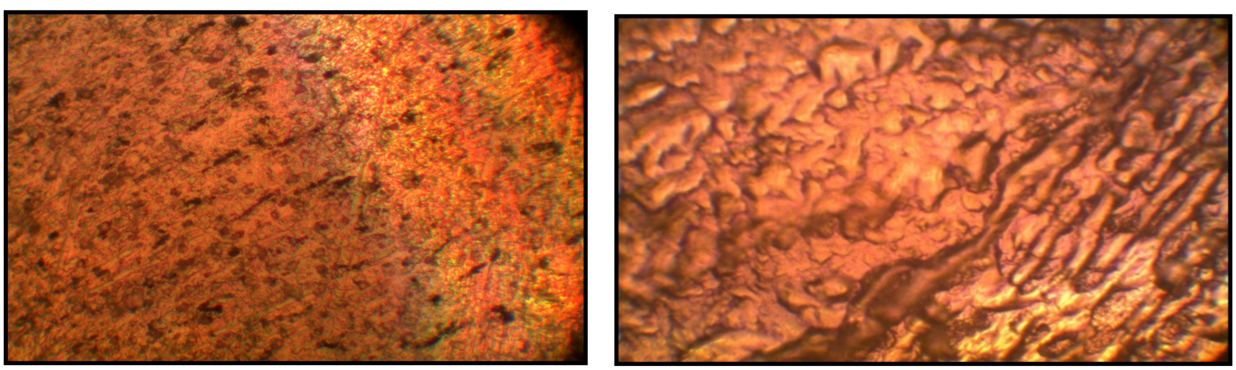


Fig-9 Polarization curve for (Al-4%Zn-0.5%Sn) alloy



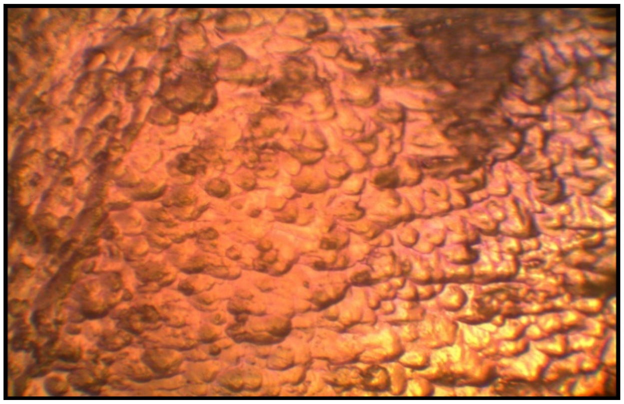
-a- -b-

Fig-10 a: The microstructure of (Al – 4% Zn) alloy before immersion, 400X
b: The microstructure of(Al – 4% Zn-0.4%Sn)alloy before immersion, 400X



-a- -b-

Fig-11 a: The microstructure of(Al– 4% Zn-0.5%Sn)alloy before immersion, 400X
b: The microstructure of(Al – 4% Zn) alloy after immersion, 400X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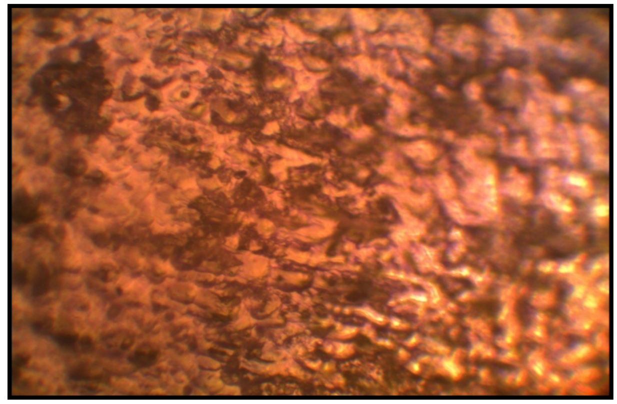
-b-

Fig-12 a: The microstructure of (Al – 4% Zn -0.4%Sn)alloy after immersion, 400X
b:The microstructure of (Al – 4% Zn-0.5%Sn)alloy after immersion, 400X

Conclusions

According to the results of present study, the following can be concluded:

1. It is possible to produce Al-alloys as sacrificial anodes candidates for the protection of the oil pipes Al-Qasim region.
2. The performance of Al anodes is strongly influenced by the type and concentration of the alloying elements; even if a small amount of Sn in Al-Zn alloy is introduced it is very beneficial.
3. The addition Sn produced activation of (Al-Zn) alloy and the extent of activation increases with increase in Sn content.
4. The polarization curves show the corrosion potential of (Al-Zn) alloys with Sn shifts to less negative direction in comparison to (Al-Zn) alloys.
5. The parameters (solution resistivity, distance between protected sample and sacrificial anode, and different alloys) have significant effect on the cathodic protection current.
6 .The best selection of sacrificial anode was Al-4% Zn-0.4% Sn) alloy at 30cm in Al-Qasim region.

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