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Corrosion Behavior Evaluation of Prepared (Aluminum -Zinc-Magnisum) Alloys as Sacrificial Anode in Cathodic Protection

A Thesis

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(استاذ مساعد)

(2009) م

بسم الله الرحمن الرحيم

وَلو أنّما في الارضِ مِن شَجَرةٍ
أَقلامُ والبَحرُ يَمدُّهُ مِن بَعدِهِ
سَبعةُ أبحرٍ ما نَفِدَت كَلِماتُ
اللهِ إنّ الله عزيزٌ حَكيم

صَدقَ الله العظيم
سورة لقمان
آيه (27)

Dedicated

" For Every One
Who Lighted a Candle
Brightening My Way "

بسم الله الرحمن الرحيم

ولو أنَّما في الارضِ مِن شَجَرَةٍ
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ABSTRACT

Sacrificial anode cathodic protection is one of the most methods that uses in protection of buried oil pipe lines against the corrosion damages. In the present work, a series of Aluminum alloys have been prepared as candidate sacrificial anodes materials to be used in the protection of oil pipelines that pass through AL-FAO region area in Southern of Iraq. This region is enriched with the chlorides ions and has an aggressive nature. The preparation of these alloys consists of alloying the molted pure Aluminum with different weight percentages of Zn and Mg. The alloying of Aluminum with these elements develops multi types of intermetallic phases (α, β, τ) that play an important role in the corrosion behavior of the prepared alloys.

These prepared alloys were microstructurally and electrochemically characterized to evaluate their performance as Al-sacrificial anodes for cathodic protection of oil pipes that exposed to aggressive environments. Knowing that, the criteria for choosing sacrificial anode material is" The anode must be dissolved uniformly with maximum available current density development".

Generally all the prepared Al-alloys provide the protection for steel pipes with different efficiencies at lower current density ranging from (1.51-12.36 $\mu A/cm^2$) in comparison with the used Mg-alloy (67.08 $\mu A/cm^2$). The prepared (C-alloy) with chemical composition (Al-10%Mg-5.5%Zn) is clearly satisfied the above mentioned criteria in comparison with other prepared alloys (A, B, D & E) with chemical compositions (Al-6%Zn), (Al-8%Mg-5.5%Zn), (Al-15% Zn -12% Mg)

,(Al-12% Zn -9.2% Mg) respectively, where a uniform weight loss rate accompanied with a noticeable current density (i.e. 12.36 µA/cm^2). The development of the two intermetallic phases (β and τ) in specified amounts throughout the microstructure of C-alloy is the reason behind the better performance of this alloy in comparison with the reference (E-alloy) and other prepared alloy. The specific amounts of these phases was found to play an important role in breaking down the protective oxide film that can form on the Al-alloys surface as well as gives high corrosion current density. As a result, the effectiveness of C-alloy as a sacrificial anode was developed by a uniform increasing of dissolution with time. The other prepared alloys behave differently from that obtained in C-alloy where the percentages of Zn and Mg are different. These alloys are found to develop a less uniform time dependent weight loss with a minimum corrosion current density. This work shows that the prepared (C-alloy) can be used in cathodic protection of oil pipelines in Southern of Iraq in AL-FAO region.

الخلاصة

الحماية الكاثودية بالتضحية هي من اكثر الطرق المستخدمة لحماية انابيب النفط المدفونة من اضرار التآكل.

في البحث الحالي تم تحضير مجموعة من سبائك الالمنيوم كمواد تستخدم كأقطاب تضحية لحماية انابيب النفط التي تمر في منطقة الفاو في جنوب العراق .هذه المنطقة غنية بايونات الكلوريدات وتكون هذه المنطقة ذات طبيعة تاكلية قاسية . يتضمن تحضير هذه السبائك سبك منصهر الالمنيوم مع نسب وزنية مختلفة من الخارصين والمغنيسيوم . إن سبك الالمنيوم مع تلك العناصر يؤدي الى تكوين أنواع عديدة من الأطوار المعدنية (α, β, τ) والتي تلعب دور مهم في السلوك التآكلي لهذهِ السبائك .

تم دراسة خواص السبائك المحضرة مجهرياً وكهروكيميائياً لتقييم أداء تلك السبائك كأقطاب انودية مضحية في اسلوب الحماية الكاثودية لأنابيب النفط التي تتعرض الى أوساط قاسية . مع العلم إن معايير إختيار مواد أقطاب التضحية هي"انحلال المادة بشكل منتظم مع اعلى قيمة لكثافة التيار".

بصورة عامة كل سبائك الالمنيوم المحضرة توفر الحماية لأنابيب النفط الفولاذية وبكفاءة مختلفة وعند قيم كثافة تيار منخفضة تتراوح بين$\mu A/cm^2$ (1.51-12.36) بالمقارنة مع سبائك المغنيسيوم ذات قيمة كثافة تيار ($67.08 \mu A/cm^2$).

السبيكة (C) ذات التركيب الكيميائي (Al -10%Mg - 5.5%Zn) حققت المعايير المذكورة أعلاه بالمقارنة مع السبائك (A , B, D & E) ذات التركيب الكيميائي

(Al - 6%Zn), (Al - 8%Mg - 5.5%Zn), (Al- 15% Zn - 12 % Mg),

(Al-12% Zn -9.2% Mg) , من حيث معدل الفقدان بالوزن المنتظم والمصاحب بكثافة التيار والتي تبلغ (($12.36 \mu A/cm^2$)). ان وجود الطورين ($\beta(Al_2Mg)$, $\tau(Mg_{32}(Al,Zn)_{49}$) وبكمية منتظمة خلال بنية السبيكة (C) يعد السبب في الاداء

الخلاصة

الافضل لهذه السبيكة بالمقارنة مع [Reference(E) alloy] والسبائك الاخرى المحضرة. ان النسب المنتظمة لهذه الاطوار تلعب دورا مهماً في كسر طبقة الاوكسيد الحامية التي تتكون على سطح سبائك الالمنيوم بالاضافة الى دورها في زيادة قيمة كثافة تيار التآكل. إن ذلك يؤدي الى تحسن كفاءة السبيكة (C) من خلال الزيادة المنتظمة في إنحلال السبيكة (زيادة التآكل) مع الزمن. السبائك المحضرة الاخرى تسلك سلوك مختلف عن سبيكة (C)حيث إن نسبة (الخارصين والمغنيسيوم) تكون مختلفة, قيمة الفقدان بالوزن في هذه السبائك تكون اقل انتظاماً مع الزمن وقيمة كثافة التيار تكون اقل.كما وجد في هذا البحث ان السبيكة (C) (المنيوم- 10 % مغنيسيوم-5.5 % خارصين) يمكن ان تستخدم في حماية انابيب النفط الموجودة في جنوب العراق في منطقة الفاو.

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NOTATIONS

SYMBOL	DEFINITION	UNIT
Wt%	Weight Percent	%
At%	Atomic Percent	%
α	Solid Solution of Al	---
β	Intermetallic Phase of (Al_2Mg)	
τ	Intermetallic Phase of ($Mg_{32}(Al,Zn)_{49}$)	---
E	Electrode Potential	volt
R(mpy)	Corrosion Rate	Mil/year
pH	Hydrogen Content	---
ρ	Resistivity of Electrolyte	Ohm.cm
V	Valence Electron of the Metal	---
t	Time	hour
i	Current	μ A
A	Atomic Weight	---
C.C	Current Capacity	A.hr/kg
η	Overpotential	mv
θ	Bragg Angle	^{o}
V	Voltage	kv
Ω	Ohm	
Ecorr	Corrosion Potential of Electrode	mv
icorr	Corrosion Current	μ A
DC	Direct Current	A
I	Intensity	
$+\Delta W/A_0$	Specific Weight Loss $(W_1-W_2)/A_0$	mg/cm^2
$-\Delta W/A_0$	Specific Weight Gain $(W_1-W_2)/A_0$	mg/cm^2

Appendix A

Figure shows
Optical micrograph of E -alloy
Magnification X 800
Using AL-FAO soil solution as etching solution for 5 minutes

Appendix B

Table shows The Chemical Analysis of AL-FAO Soil for 14th Days

Date(Days)	Chemical Analysis			
	Cl^-	So^{3-}	Moisture Content%	pH
1	1.5	5.54	20	8.5
2	1.5	5.5	20	8.48
3	1.5	5.54	20	8.45
4	1.5	5.54	20	8.5
5	1.5	5.54	20	8.5
6	1.5	5.54	20	8.5
7	1.5	5.54	20	8.5
8	1.5	5.54	20	8.48
9	1.5	5.54	20	8.5
10	1.5	5.54	20	8.5
11	1.5	5.54	20	8.5
12	1.5	5.54	20	8.5
13	1.5	5.54	20	8.5
14	1.5	5.54	20	8.5

CHAPTER ONE

" GENERAL INTRODUCTION & LITERATURES SURVEY "

CHAPTER TWO

"THEORETICAL BACKGROUND"

CHAPTER THREE

"EXPERIMENTAL WORK"

CHAPTER FOUR

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CHAPTER FIVE
" CONCLUSIONS & RECOMMANDATIONS "

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CHAPTER ONE

INTRODUCTION & LITERATURE SURVEY

1.1. INTRODUCTION

Corrosion is the deterioration of a material through reaction with its environment [1]. Also it can be defined as an electrochemical process in which a current leaves a structure at the anode site, passes through an electrolyte, and reenters the structure at the cathode site as shown in figure (1.1). For example, one small section of a pipeline may be anodic, and now because it is in a soil with low resistivity compared to the rest of the line, the current would leave the pipeline at that anode site, pass through the soil, and reenter the pipeline at a cathode site. That is, the anode potential is the driving force for the corrosion. The total system including anode, cathode, electrolyte, and metallic connection between anode and cathode in a pipeline system shown in figure (1.1) below is termed a corrosion cell [2] [3].

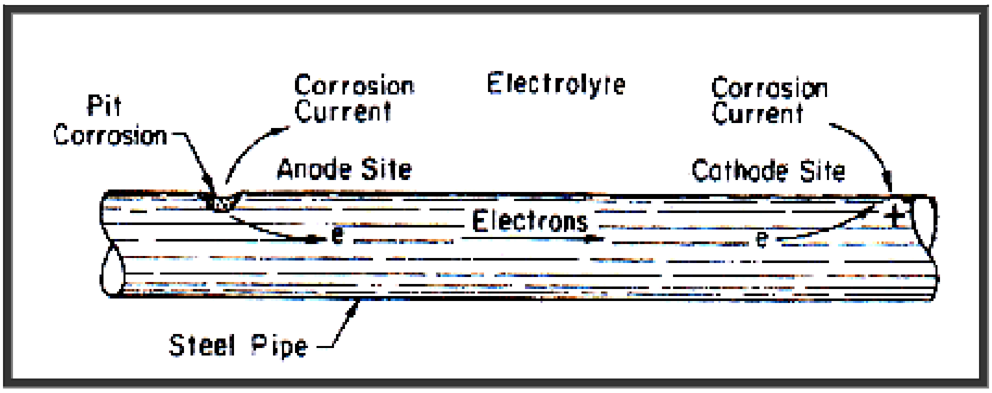


Fig. (1.1)

Corrosion of pipeline due to the localized anode and cathode [2] [3]

It is widely recognized[4, 5, 6, 7].that the placement of metallic materials below ground can result in a continuous process of corrosion. The surfaces of these buried metallic structures are attacked through the migration of ions from the surface, resulting in a reduction in the wall thickness of the structure and over time, a reduction in the structural capacity of the element. Ultimately, if the extent of corrosion is significant enough, the element may fail. Corrosion is one of the key factors in limiting the life expectancy of steel foundation structures[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 movement[8].

Also Pipeline failures, due to internal and external corrosion, have resulted in both monetary and human losses [9].

An extensive network of buried steel pipelines is used throughout the world to transport natural gas and liquid petroleum products. In Iraq alone, there are over 10,000 kilometers of pipes used to transport natural gas and petroleum products, while in the United States there are 2.1 million kilometers of pipes used to transport natural gas and 28980 kilometers gas pipeline network related facilities in Italy [10]. Failure to prevent external corrosion of pipelines can have disastrous consequences [11] [12].

The corrosion-related cost to the transmission pipeline industry is approximately $5.4 to $8.6 billion annually. This can be divided into the cost of failures, capital, operations and maintenance (O&M) at 10, 38, and 52 percent, respectively[13].

In order to mitigate underground pipelines corrosion, the principal methods are [14]:-

1. Coatings.
2. Cathodic Protection (CP).

In the first method, the aim of applying a coating to the buried metal such as a pipeline is to prevent an electrical contact with an electrolyte such as soil and/or water [15] .

Cathodic protection is an electrical method of mitigating corrosion on structures that are exposed to electrolytes such as soils and waters. Cathodic protection was used mainly to prevent further corrosion after repair of damaged structures, but recently, cathodic protection has been incorporated in new constructions in an effort to prevent corrosion from starting [16][17]. There are two types of cathodic protection systems. One involves the use of current that is produced when two electrochemically dissimilar metals or alloys are metallically connected and exposed to the electrolyte. This is commonly referred to as a sacrificial or galvanic cathodic protection system. The other method of cathodic protection involves the use of a direct current power source and auxiliary anodes, which is commonly referred to as an impressed current cathodic protection system[2][3]. The latter method is out of this work.

1.2 LITERATURE SURVEY:

Cathodic protection is the reduction of corrosion rate by shifting the corrosion potential of the electrode toward a less oxidizing potential by applying an external electromotive force. Cathodic protection (C.P.) is one of the several techniques that are employed mainly in many industries and marine environments to control corrosion. Sacrificial anode cathodic protection is greatly employed to protect oil pipelines, marine, and some domestic structures [18]. The electrochemical behavior of sacrificial anode materials is of vital importance for the reliability and efficiency of cathodic protection systems for seawater exposed structures [19].

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[18][20]. 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 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 [18] [21].

A study of electrochemical efficiency, as a function of composition, for various aluminum alloy galvanic anodes was given by many researchers as shown below:-

- **U.S. Pat. No. 4,141,725 to Murai et al.1979 [22]**

Provide an improved Al-Zn-In alloy for a galvanic anode to be used for a cathodic protection of steel structures in sea-water of which the anode potential becomes less noble in a very short period of time even in sea-water at a low temperature of up to about 10° C, and which exhibits excellent galvanic performances including a stable anode current efficiency similar to those available in sea-water at a temperature of over about 10° C, also the anode potential becomes noble only at a very slight rate even in service for a long period of time and which exhibits excellent galvanic performances including a stable anode current efficiency.

They assume that causes of scattering in the anode potential in (Al-Zn-In)aluminum alloys that are used for the cathodic protection of steel structures in sea-water are considered due to the adverse effects of the low-temperature sea-water acting on the structure of the active surface of the galvanic anode as well as on the rate of dissolving reaction.It is evident that these adverse effects are related with the indium content in the alloy: a higher indium content in the alloy results in an improved structure of the active surface and a rate of dissolving reaction, and permits achievement of a less noble anode potential even in low-temperature sea-water of up to about 10° C. however, a higher indium content in the alloy causes an increase in the amount of self-corrosion of the galvanic anode, and results in a serious problem of the remarkable reduction in the anode current efficiency.

The Al-Zn-In aluminum alloy used in that work consists of the elements shown in table (1.1) below.

Table (1.1)

Chemical composition of (Al-Zn-In) alloy [22]

Element	Wt%
Zinc	0.5 to 10.0
Indium	0.005 to 0.050
Calcium	0.005 to 0.50
Magnesium	0.1 to 4.0

- **S.F. Daily. (1998) [23]**

A new alloy has been developed as a sacrificial anode for cathodic protection of concrete. The anode consists of Aluminum-Zinc- Indium (Al-Zn-In) wire, *Arc Sprayed Aluminum-Zinc-Indium* thermally sprayed onto concrete .The improved performance of the Al-Zn-In alloy is attributed to an indium activating agent, which tends to reduce the passivation effect of the anode. Test results from field trials and laboratory studies are very encouraging and show a significant increase in current output as compared to pure zinc.

- **J. A. Juarez-Islas and J. Genesca. 2000[19]:-**

Studied the corrosion mechanism during electrochemical testing, and this involved electrochemical testing of Al sacrificial anodes, where the evaluation of an Al-Zn-Mg-Li alloy as a potential candidate for Al-sacrificial anode was studied. The effect of Li additions on superficial activation of the anode by means of precipitation of AlLi type compounds was also examined.

The resulting Al-Zn-Mg-Li alloy showed two kinds of species in the interdenderitic spacing. These corresponded, to a eutectic of $Al_2Zn_3Mg_3$, and precipitates of Mg_7Zn_3. The results also showed that despite the improvement in electrochemical efficiency of the Al-anode, it was apparent that research must be focused on the role played by the τ-$Al_2Zn_3Mg_3$, Mg_7Zn_3 and δ -AlLi compounds in the α -Al matrix, and on the effect of the decay of eutectic and particles in interdenderitic regions. This will result in the prevention of the formation of a continuous, adherent, and protective oxide film by particle precipitation leading to a uniform dissolution of the Al-anode.

- **U.S. Army Corps of Engineers. 2001[24].**

Produce Al –alloys limited to use in seawater or very brackish water use (must have more than 1000 ppm chloride ion concentration for Indium alloyed material and 10,000 ppm Cl- for Mercury alloyed material) Al-alloys consist of (Aluminum- Zinc - Silicon- Mercury -Indium), they found that Aluminum Anode operated at approximately 95% efficiency yielding approximately 1250 amp-hrs-lb or a consumption rate of approximately 6.8 lbs. /amps-yr in seawater applications only. This efficiency may drop in half or more in brackish waters.

- **Watanabe, Kunio . 2004[25].**

Studied an alloy for a sacrificial anode which is suitable for corrosion protection of reinforcement in a structure built of reinforced concrete; namely, an alloy which enables a sacrificial anode formed to have a sufficiently low potential and to cause generation of a sufficiently large amount of electricity. These alloys are***:***

1. (Al-Zn- In).
2. (Al-Zn-Si-In).
3. (Al- Zn- In- Ce).
4. (Al- Zn-In - Ti- B)**.**

In the first alloy, both (Zinc and Indium) used so as to restrict self dissolution of the alloy thus increasing the amount of electricity generated. The second alloy which contain Silicon, Si has the same function as (Zn and In).The third alloy, which contain Cerium (Ce), Ce, used so as to prevent hole-type corrosion of the alloy thus increasing the amount of electricity generated. In the last alloy both Ti and B function so as to prevent hole-type corrosion and groove-type corrosion (corrosion occurring in the form of a groove leaving two sides of the groove uncorroded) of the alloy by making the crystals of the alloy microscopic grains instead of large pillars thus increasing the amount of electricity generated .

- **S.M.A. Shibli and V.S. Gireesh. 2005[26]**

They explored the feasibility of effective aluminum activation by selenium incorporation. The selenium incorporated anode showed an improved galvanic efficiency of around 70%. High performed anodes were developed by incorporating other activators of Sn and Bi along with Se in aluminum alloy anodes.

The best activator combination was found to be 0.5%Se + 0.1%Sn + 0.1%Bi. This combination of activator in aluminum alloy anodes shows a galvanic efficiency of 90%.

- **R. Orozco, et al. 2005[27].**

Studied the effect of Mg content on the performance of (Al-Zn-Mg) sacrificial anodes that using in cathodic protection of structures exposed to marine environments (sea water). In this study samples of (Al-5.3 at. % Zn (12 wt. %) -x at. % Mg (X= (5.5-11.3at %) (4.6-9.2wt %) alloys were microstructurally and electrochemically characterized to evaluate their performance as Al sacrificial anodes for cathodic protection of structures exposed to marine environments. It is shown that by increasing Mg content an improvement of electrochemical properties of Al-alloy such as current capacity and then electrochemical efficiency can be obtained. As-cast Al-5.3Zn-Mg alloys showed a microstructure that consisted of α-Al dendrites and eutectic (α+ τ) in interdenderitic regions. This alloy reached values of electrochemical efficiency up to 75%.Magnesium addition helps in improving the anode current capacity when present to the extent of 8.5% at.

- **S.M.A. Shibli, et al. 2006 [28]**

Incorporated metal composites of alumina and zinc oxide into Al + 5% Zn alloy and the reinforced alloys were used as efficient sacrificial anodes for cathodic protection of steel objects. ZnO was not only used to reinforce the alloy matrix and improve the metallurgical characteristics but also to yield effective activation of the sacrificial anodes. High galvanic efficiency (83%) was achieved when 0.5% ZnO was incorporated into the anode matrix.

- **L.E. Umoru and O.O. Ige. 2007[18].**

They investigated the effect of tin composition on Al-Zn-Mg alloy as sacrificial anode in seawater. Corrosion experiments were mounted to determine the optimal effect of tin on the efficiencies of the aluminum alloy anodes. The results obtained showed that the anode efficiency of (Al-Zn-Mg Sn) alloy increased with tin concentration. The (Al-Zn-Mg-0.1Sn) gave the best anode efficiency. The microstructures of the (Al-Zn-Mg-Sn) alloys revealed increased distribution of tin globules and a breakdown of passive alumina film network on the anodes surfaces and thus improving the anode efficiencies. The sample with 0.1% Sn is advocated for use because of its high output current capacity and is enhanced by better microstructural features.

1.3 AIMS OF THE PRESENT WORK:-

The objectives of the present work can be summarized as follows:

1. Preparation of new aluminum alloys with different chemical compositions basis on Zn and Mg addition in different percentages to be used as a candidate sacrificial anodes in

cathodic protection of oil pipe lines in southern of Iraq (Al-FAO region).

2. Evaluation of the prepared Al alloys by being subjected them to a set of electrochemical tests such as Tafel extrapolation and weight loss tests of the sacrificial anodes in addition to the direct current measurement that passes between the anode and cathode.
3. Using of Mg-alloy that is used originally in cathodic protection in the area of AL-FAO region to compare the performance of multi prepared alloys.
4. Using real conditions in the process of evaluation the prepared alloys by using the AL-FAO soil, AL-FAO soil solution, same pH and also the same material of the pipe to be protected.
5. A study of the phases that is developed during the solidification of prepared alloys by using an optical microscopy under the supporting of x-ray diffraction examinations.
6. Selection of the best Al-alloy to be used as a sacrificial anode material that satisfies the requirements of sacrificial cathodic protection that gives a uniform dissolution rate to predict the sacrificial anode operating life.

CHAPTER TWO
THEROTICAL BACKGROUND

2.1 DEFINITION OF CORROSION:-

Corrosion: is a chemical or electrochemical reaction that causes degradation of a material[1]. The corrosion process involves the release of electrons (oxidation) of the metal [Equation (1)] and the consumption of those electrons by some other reduction reaction, such as oxygen or water reduction [Equations (2) and (3), respectively] [14] [29] [30]:

$$Fe \rightarrow Fe^{+2} + 2e^{-} \quad \ldots (2.1).$$

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \quad \ldots (2.2).$$

$$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-} \quad \ldots (2.3).$$

The oxidation reaction is commonly called the anodic reaction and the reduction reaction is called the cathodic reaction. Both electrochemical reactions are necessary for corrosion to occur. The oxidation reaction causes the actual metal loss but the reduction reaction must be present to consume the electrons liberated by the oxidation reaction, maintaining charge neutrality [31]. Otherwise, a large negative charge would rapidly develop between the metal and the electrolyte and the corrosion process would cease. The oxidation and reduction reactions are sometimes referred to as half-cell reactions and can occur locally (at the same site on the metal) or can be physically separated. When the electrochemical reactions are physically separated, the process is referred to as a differential corrosion cell [14].

2.2 Polarization

When two complementary processes such as those illustrated in Fig (2.1) occur over a single metallic surface, the potential of the material will no longer be at an equilibrium value. This deviation from equilibrium potential is called *polarization.* Electrodes can also be polarized by the application of an external voltage or by the spontaneous production of a voltage away from equilibrium. The magnitude of polarization is usually measured in terms of overvoltage, which is a measure of polarization with respect to the equilibrium potential E_{eq} of an electrode. This polarization is said to be either anodic, when the anodic processes on the electrode are accelerated by changing the specimen potential in the positive (noble) direction, or cathodic, when the cathodic processes are accelerated by moving the potential in the negative (active) direction. There are three distinct types of polarization in any electrochemical cell, the total polarization across an electrochemical cell being the summation of the individual elements as expressed in Eq. (2.4):

$$\eta_{total} = \eta_{act} + \eta_{conc} + iR \quad .... (2.4)$$

Where:

η_{act} : Activation overpotential, a complex function describing the charge transfer kinetics of the electrochemical processes. act is predominant at small polarization currents or voltages.

η_{conc} : Concentration overpotential, a function describing the mass transport limitations associated with electrochemical processes. conc is predominant at large polarization currents or voltages.

iR: Ohmic drop. *iR* follows Ohm's law and describes the polarization that occurs when a current passes through an electrolyte or through any other interface, such as surface film, connectors, etc[14]. .

2.2.1. ***Types of polarization***

1. ***Activation Polarization***:

In the case of activation polarization, the rate of the corrosion reaction is limited by the electron transfer reaction at the metal surface. This electron transfer process has associated activation energy and the rate of this process is exponentially related to the free energy change. Since the free energy is directly related to the potential, and the rate is directly related to the electrical current, the relationship becomes as the following[14]:

$$\Delta I \propto e^{(\eta/RT)} \quad .... (2.5)$$

in which:

I: is the corrosion current

R: is the gas constant.

T: is the absolute temperature.

Upon taking the log of both sides of the equation, the relationship becomes as the following:

$$\mathrm{Log}(\Delta I) \propto \eta / RT \quad ....(2.6)$$

2. ***Concentration Polarization*:**

Another type of polarization commonly observed is concentration polarization. A definition of concentration polarization is "The portion of the polarization of a cell produced by concentration changes resulting from passage of current through the electrolyte." Concentration polarization is most commonly associated with the reduction reaction[14].

3. *Combined polarization*

Both activation and concentration polarization usually occur at an electrode. At low reaction rates, activation polarization usually controls, while at higher reaction rates concentration polarization becomes controlling. The total polarization of an electrode is the sum of the contributions of activation polarization and concentration polarization[14]:

$$\eta^{T} = \eta^{A} + \eta^{C} \qquad \text{……….} (2.7)$$

Where η^T: is total overvoltage. During anodic dissolution, concentration polarization is not a factor as mentioned above, and the equation for the kinetics of anodic dissolution is given by:

$$\text{…………} (2.8) \quad \eta^{diss} = \beta \log \frac{i}{i_o}$$

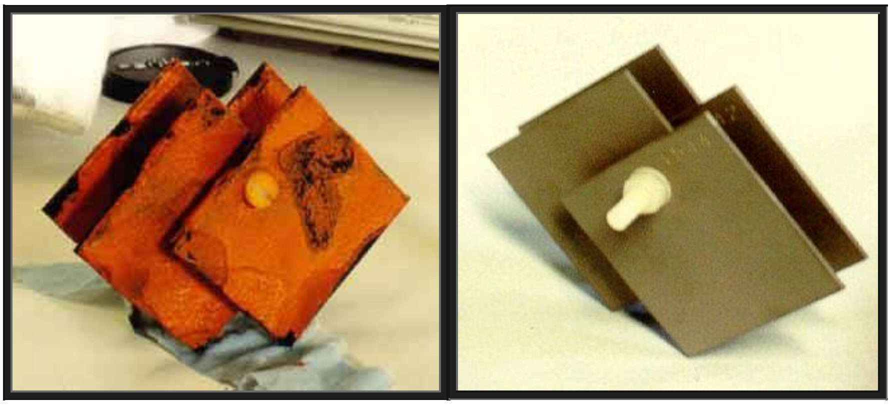
During reduction process such as hydrogen evolution or oxygen reduction, concentration polarization becomes important as the reduction rate approaches the limiting diffusion current density. The overall reaction for a reduction process in given by combining equations 2.6 and 2.8 with appropriate signs[14]:

$$\text{…………..}(2.9) \quad \eta^{red} = -\beta \log \frac{i}{i_o} + 2.3\frac{RT}{ZF}\log\left(1 - \frac{i}{i_L}\right)$$

2.3 <u>Forms of Corrosion</u>:-

1. ***Uniform Corrosion:-***This is also called general corrosion. It is the most common form of corrosion where current flows between

different sites on a single metal, causing a wide area of metal to be progressively corroded[32] .Figure (2.1)shows an example on the uniform corrosion



(a) (b)

Fig. (2.1)

(a) Shows a steel coupon corroded (rusted) uniformly over its entire surface after immersion in oxygen aerated water[33].
(b) The same batch of coupons exposed to deaerated water retained their metallic appearance with no visible corrosion (rust) [33].

2. ***Galvanic Corrosion:*** Galvanic corrosion can result when a metal is in contact with another *dissimilar* metal. In order for galvanic attack to take place there must be four things present. First, there must be an *anode*. This is the material, which corrodes (e.g., the formation of rust takes place if the metal is iron). Second, there also must be another electrode called the *cathode*. Third, an *electrical connection* must exist between the *anode* and *cathode* through which electrons can flow. Finally there must be an *electrolyte* through which chemical ions can flow as shown in figure (2.2). This is generally an aqueous (water) solution yet even damp soil can make an excellent electrical conductor. The arrangement of these four specific components is always

necessary for an electrochemical chemical cell to function. However in the case of galvanic corrosion, the anode, and cathode are clearly dissimilar metals, copper and zinc, iron and brass, or mild steel and cast iron, for examples[34].

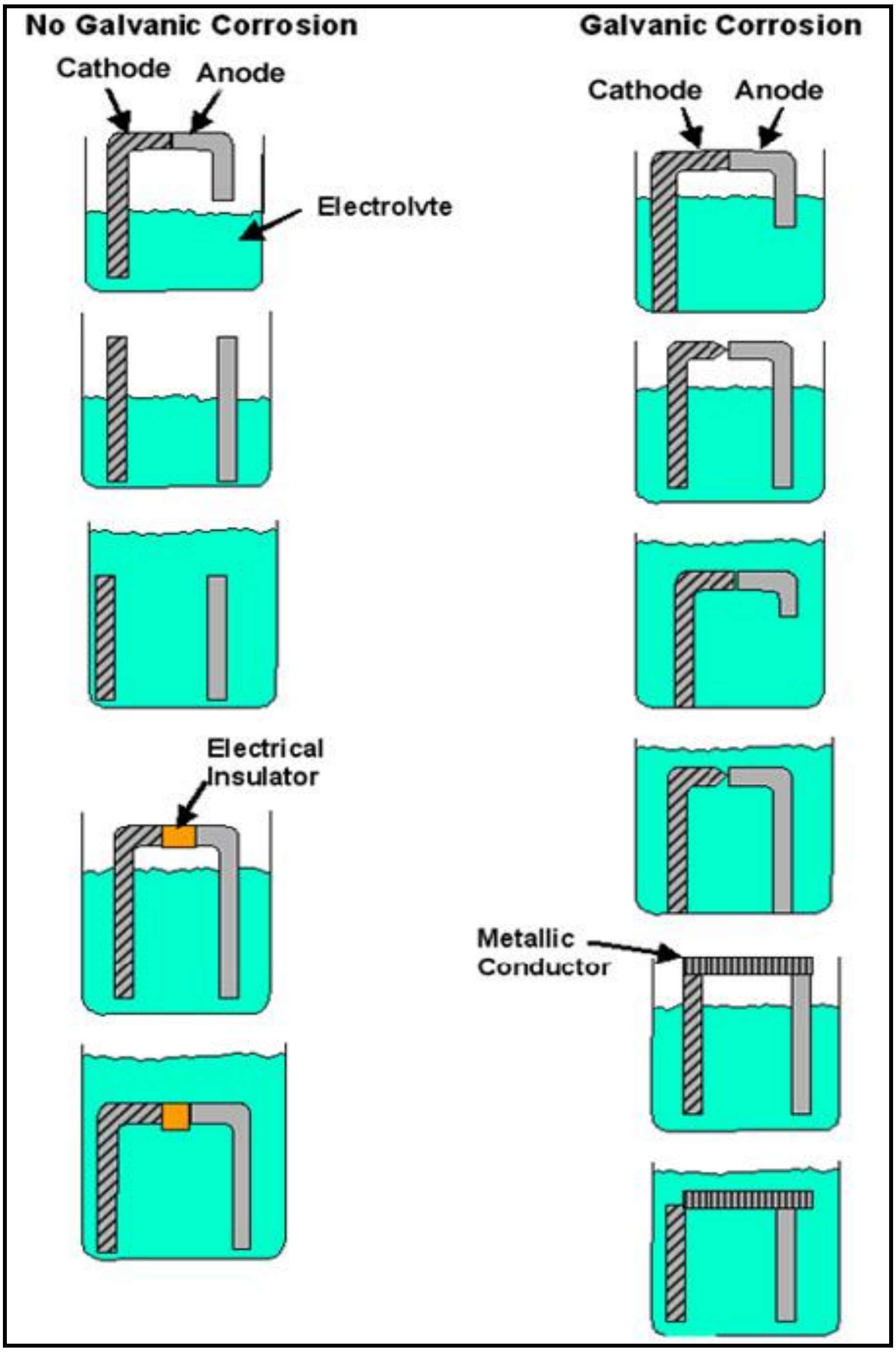
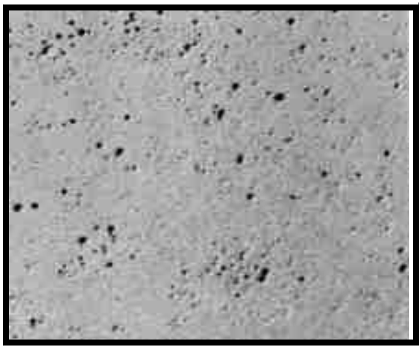


Fig .(2.2)

Example on Galvanic Corrosion[34]

3. ***Pitting Corrosion:* -** Pitting corrosion is a localized corrosion that occurs at microscopic defects on a metal surface. The pits are often found underneath surface deposits caused by corrosion product accumulation as shown in figure (2.3). Some materials are more subject to *pitting* than others[35]



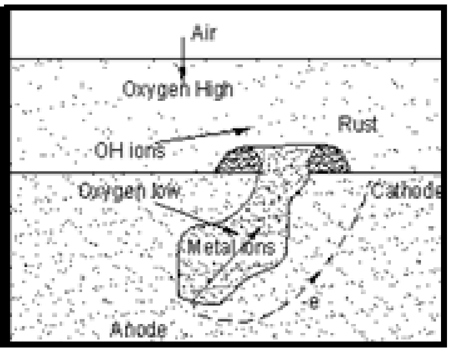


Fig. (2.3)
Example on Pitting Corrosion [34]

4. ***Fretting corrosion*:-** The rapid corrosion that occurs at the interface between contacting, highly loaded metal surfaces when subjected to slight vibratory motions is known as fretting corrosion[35]
5. ***Crevice Corrosion:-*** the attack which occurs because part of a metal surface is in shielded or restricted environment, compared to the rest of the metal which is exposed to a large volume of electrolyte thus ,crevice corrosion is very much associated with the geometry of structures such as riveted plates ,welded structures and threaded components; contact of metal with non-metallic solids such as plastics, rubber and glass; or deposits of sand, dirt or corrosion products[34] .

6. ***Dealloying Corrosion*:-** Dealloying is a rare form of corrosion found in copper alloys, gray cast iron, and some other alloys. Dealloying occurs when the alloy loses the active component of the metal and retains the more corrosion resistant component in a porous "sponge" on the metal surface [35]

7. ***Fatigue* Corrosion**: - Corrosion fatigue is a special case of stress corrosion caused by the combined effects of cyclic stress and corrosion [35].

8. ***Erosion Corrosion*:-** Erosion corrosion is the result of a combination of an aggressive chemical environment and high fluid-surface velocities [35]

9. ***Hydrogen Embrittlement*:-** Hydrogen embrittlement is a problem with high-strength steels, titanium, and some other metals. Control is by eliminating hydrogen from the environment or by the use of resistant alloys [34]**.** Figure (2.4) shows an example on this type**.**

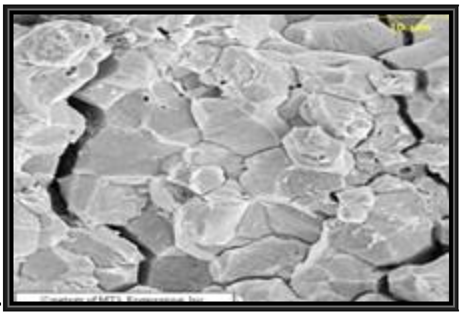


Fig. (2.4)
Example on Hydrogen embrittlement [34]

10. ***Microbial Corrosion*:-** Microbial corrosion (also called microbiologically) influenced corrosion or MIC) is corrosion that is caused by the presence and activities of microbes.

Microbial corrosion can take many forms and can be controlled by biocides or by conventional corrosion control methods [35].

11. ***Intergranular Corrosion:***

Intergranular corrosion occurs when a grain boundary area is attacked because of the presence of precipitates in these regions. Grain boundaries are often the preferred sites for the precipitation and segregation processes observed in many alloys [34].Figure (2.5) shows an example on this type.

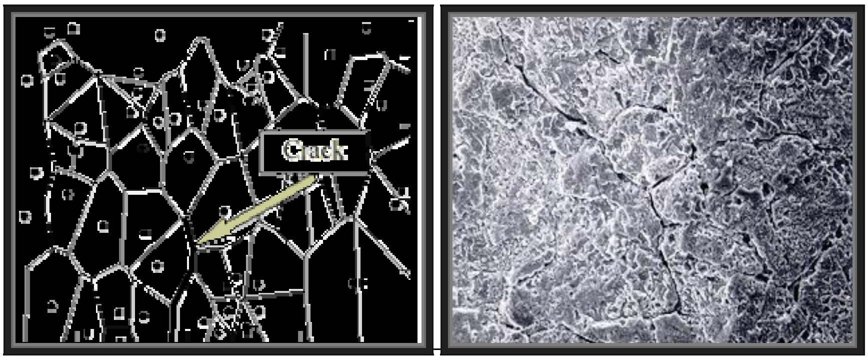


Fig . (2.5)
Example on Intergranular corrosion [34]

***12. Stress Corrosion Cracking*:**

The simultaneous effects of tensile stress and a specific corrosive environment cause stress corrosion cracking (SCC). Stresses may be due to applied loads, residual stresses from the manufacturing process, or a combination of both[34].Figure (2.6) shows example on Stress Corrosion Cracking.

Fig .(2.6)
Example on Stress Corrosion Cracking[34]

2.4 Corrosion Control

The most common methods to prevent corrosion are by[1]:

1. Cathodic protection.
2. Anodic protection.
3. Protective coating such as paint.
4. Corrosion-resistant metals and alloys.
5. Addition of inhibitors.
6. Very pure metals.
7. Design.

The selecting method depends on many factors such as cost, availability, contamination of environment with corroding metal.etc [36] [37].

2.5 Corrosion of Underground Steel Pipelines:-

Underground corrosion of pipelines and other structures is often the result of differential corrosion cells of which a variety of different types exist. These include differential aeration cells, where different parts of a pipe are exposed to different oxygen concentrations in the soil, and cells created by differences in the nature of the pipe surface or the soil chemistry. Galvanic corrosion is a form of differential cell corrosion in which two different metals are electrically coupled and exposed in a corrosive environment [14]

2.5.1. ***Differential Corrosion Cells***

1. ***Differential Aeration Cell*:-**

The differential aeration cell is probably the most common corrosion cell found on Pipelines or other underground structures. The upper parts of the structure are exposed to higher concentrations of oxygen, become the cathodes in the cell while the lower Parts of the structure are oxygen deficient, and become the anodes [14].

2. ***Galvanic Corrosion:-***

The differential aeration cell is one example of a differential corrosion cell. Galvanic corrosion is another example. In the case of galvanic corrosion, the potential difference is created by the presence of different metals. Referring to the galvanic series described below in table (2.1) where each material has a different corrosion potential in a given environment. When these metals are electrically coupled, the metal with the most positive corrosion potential is cathodically polarized, reducing its corrosion rate, while the more negative member of the couple is anodically polarized, increasing its corrosion rate. Galvanic corrosion can be very detrimental to an underground structure. Examples include the corrosion of iron in contact with copper or stainless steel fittings. However, galvanic corrosion can be used as an effective means of CP [14] [38].

Table (2.1)

Standards Electrochemical Series for Some Common Metals and Reactions [14]

3. *New and Old Pipe:-*

A condition closely related to dissimilar metal corrosion occurs when new steel pipe, as shown in Figure (2.7) is intermixed with old steel pipe. This has often been found in older distribution piping systems where a section of pipe has been replaced because of corrosion damage. The new piece of pipe, exposed to the same corrosion

	Reaction	Standard Reduction Potential V (SHE)
	$Au^{3+} + 3e^- = Au$	+1.4
Noble↑	$Pt^{2+} + 2e^- = Pt$	+1.200
	$Pd^{2+} + 2e^- = Pd$	+0.987
	$Ag^+ + e^- = Ag$	+0.799
	$Hg^{2+} + 2e^- = 2Hg$	+0.788
	$O2 + 2H_2O + 4e^- = 4OH-$	+0.401
	$Cu^{2+} + 2e^- = Cu$	+0.337
	$2H^+ + 2e^- = H_2$	0.000
	$Pb^{2+} + 2e^- = Pb$	-0.126
	$Sn^{2+} + 2e^- = Sn$	-0.136
	$Ni^{2+} + 2e^- = Ni$	-0.250
	$Co^{2+} + 2e^- = Co$	-0.277
	$Cd^{2+} + 2e^- = Cd$	-0.403
	$Fe^{2+} + 2e^- = Fe$	-0.440
	$Cr^{3+} + 3e^- = Cr$	-0.744
	$Zn^{2+} + 2e^- = Zn$	-0.763
	$Al^{3+} + 3e^- = Al$	-1.662
	$Mg^{2+} + 2e^- = Mg$	-2.363
Active↓	$Na^+ + e^- = Na$	-2.714
	$K^+ + e^- = K$	-2.925

conditions, logically would be expected to last as long as the original section. However, the new section will usually fail sooner than expected unless it is electrically insulated from the remainder of the system. This is simply an application of the practical galvanic series of Table (2.2) which shows that the potential of bright new steel is markedly different

Potential		Metal V(CSE)[1]
Carbon, Graphite, Coke		+0.3
Platinum		0 to -0.1

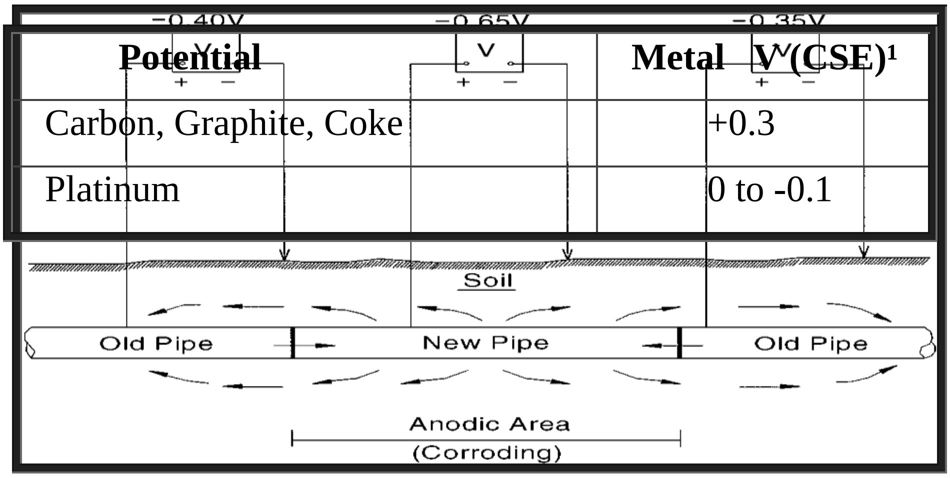


Fig. (2.7)
Schematic showing a differential corrosion cell created by replacement of a section of pipe [14]

from that of old rusted steel. The new steel is anodic and corrodes more rapidly than the old rusted steel. A similar corrosive condition can occur if, during work on an existing piping system, tools cut or scrape the pipe and expose areas of bright steel. These bright spots will be anodic and can result in accelerated corrosion in low resistivity soils [14].

Table (2.2)

Practical Galvanic Series for Metals in Neutral Soils and Water [14]

Mill Scale on Steel	- 0.2
High Silicon Cast Iron	-0.2
Copper, Brass, Bronze	-0.2
Mild Steel in Concrete	-0.2
Lead	-0.5
Cast Iron (Not Graphitized)	-0.5
Mild Steel (Rusted)	-0.2 to -0.5
Mild Steel (Clean and Shiny)	-0.5 to -0.8
Commercially Pure Aluminum	-0.8
Aluminum Alloy (5%Zinc)	-1.05
Zinc	-1.1
Magnesium Alloy (6% Al, 3% Zn, 0.15% Mn)	-1.6
Commercially Pure Magnesium	-1.75

[1]Typical potentials normally observed in neutral soils and water, measured in relation to copper sulfate reference electrode.

4. Dissimilar Soils:-

A steel pipeline passing through dissimilar soils can establish corrosion cells in much the same manner that corrosion cells can be established with dissimilar metals. This is illustrated by Figure (2.8) which shows a pipeline passing through two dissimilar soils. The potential of the pipeline in soil A is slightly different from the potential in soil B. As it is known, the corrosion, or native potential of a metal can vary with differences in the environment. This causes the potential difference illustrated and satisfies the conditions necessary to establish a differential corrosion cell. In the figure (2.8) the pipe in soil A is anodic to that in soil B and is corroding as indicated by the current discharge. This behavior is sometimes made strikingly apparent when excavating an old bare pipeline in which some areas (cathodic) are in excellent condition but other areas (anodic) only a few feet away are severely corroded. The middle voltmeter illustrates that the potential difference between soil types can be measured. This type of measurement is used during pipeline surveys [14] [38] .

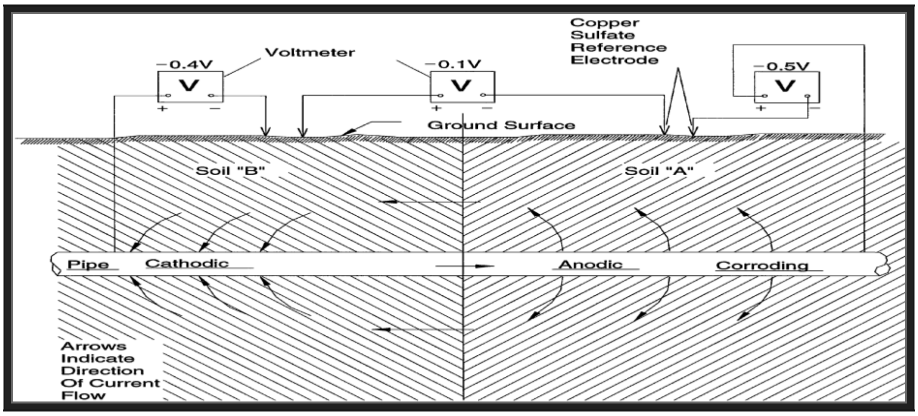


Fig.(2.8)
Schematic showing differential corrosion cell created by dissimilar soils [14].

5. Relative Size of Anodic and Cathodic Areas:-

An understanding of the effect of differences in area relationships is important for an appreciation of why, for example, a dissimilar metal combination can cause very rapid corrosion under certain area relationships and relatively little in others[14].

Figure (2.9) demonstrates the effect of anode to cathode area ratio on galvanic corrosion [14].

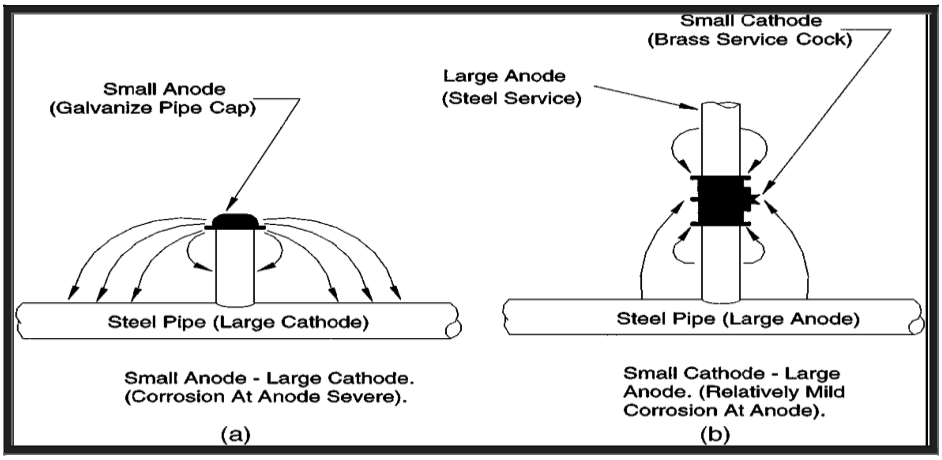


Fig. (2.9)
Schematic showing the effect of anode to cathode area ratio on galvanic corrosion [14].

Major interrelated factors that affect underground corrosion are as follows[39]:-

1. Soil Resistivity: - depends on natural ingredients, the amount of salts dissolved in soil, and the moisture content. The corrosivity increases with the reduction of soil resistivity. Table (2.3) provides the relationship between soil resistivity and corrosivity.

Table (2.3)

Soil Resistivity and Corrosion [39]

Soil Resistivity Class (ohm-meter)	Typical Corrosion Rate (mils/year)
Less than 25	Severely Corrosive (> 13)
26 – 50	Moderately Corrosive (9 -12)
51 – 100	Mildly Corrosive (4 – 9)
Greater than 100	Very Mildly Corrosive (< 4)

2. pH value of soil affects the corrosion process greatly. The more acidic the soil is the higher the corrosion rate. pH value ranges generally from 5 to 10 in soil; a value of 7 indicates neutrality (lower values, acidity; and higher values, alkalinity). The general relationship between the pH values and the corresponding corrosion is shown in Table (2.4).
3. Moisture contents depend on season, location, soil type, particle size, and ground water level. The degree of wetness contributes to the corrosion by dissolving
4. Soluble salts thereby changes the soil composition. Generally, corrosion increases with higher moisture contents (for normal ranges). Aeration is a measure of the availability of oxygen to the metal. Aeration characteristics of a soil are dependent

primarily on particle size and distribution. Corrosion decreases with the increase in aeration. Miscellaneous factors are those that are difficult to classify because they are a combination of one or more of the above and include the effect of temperature, bacterial, or interference current effects. These factors typically contribute no more than 10% to the total corrosion rate and are usually neglected.

Table (2.4)

pH Values and Corrosion [39][40]

Soil characteristics	PH Values	Corrosion Rate
Extremely Acid	Below 4.5	Highest Corrosion
Strongly Acid	5.1 - 5.5	
Medium Acid	5.6 – 6.0	
Slightly Acid	6.1 – 6.5	Least Corrosion
Neutral	6.6 – 7.3	
Mildly Alkaline	7.4 – 7.8	
Moderately Alkaline	7.9 – 8.4	
Strongly Alkaline	8.5 – 9.0	Higher Corrosion
Very Strongly Alkaline	9.1- Higher	

2.6. Corrosion Damage:-

Corrosion is the degradation of a material through environmental interaction .The environment plays an important role in the extent, type, and severity of corrosion. Underground corrosion involves structures that are buried or otherwise surrounded by soil for example, storage tanks, and pipelines. Often, these structures store and transport oil, gas, and other hazardous substances, which if released to the environment, can cause substantial damage. 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 movement. The direct cost of corrosion in the United States was estimated in 2001 to be $279 billion annually, while the direct cost of corrosion associated with underground storage tanks (USTs) alone was estimated to be $2.5 billion annually14[41].

2.7. Corrosion Control of Underground Steel Pipelines:-

External corrosion control must be a primary consideration during the design of a piping system. Materials selection and coatings are the first line of defense against external corrosion. Because perfect coatings are not feasible, cathodic protection must be used in conjunction with coatings [2] .

2.7.1. *Material Selection*:-

There are no materials that are immune to corrosion in all environments. Material selection refers to the selection and use of corrosion-resistant materials such as stainless-steel, plastics, and special alloys to enhance the lifespan of the structure such as pipeline. It is limited when all aspects of safety, structural integrity, operating life and economic considerations are taken into account and acted upon. Material selection needs to be addressed during project design [42] [43]. Most transportation of crude oil and gas by land from production area to distribution terminal pipelines are made up of low carbon steel allied with C-Mn. Low carbon steel, although susceptible to corrosion is widely used because of its low cost, high strength and the ease of field make up by welding. Crude oil and gas pipelines are usually protected externally by coating couple with a cathodic protection system [44].

2.7.2. ***External Coatings***:-

External coatings is used to control corrosion by isolating the external surface of the underground or submerged piping from the environment, to reduce cathodic protection current requirements, and to improve current distribution[15].External coatings must be properly selected and applied and the coated piping carefully handled and installed to fulfill these functions. Various types of external coatings can accomplish the desired functions. These may be organic coating such as paint, a variety of different plastic, tape, bitumen, epoxy coating [14][45] .

Desirable characteristics of external coatings include the following[14]:

1. Effective electrical insulator.
2. Effective moisture barrier.
3. Application to pipe by a method that does not adversely affect the properties of the pipe.
4. Application to pipe with a minimum of defects.
5. Good adhesion to pipe surface.
6. Ability to resist development of holidays with time.
7. Ability to resist damage during handling, storage, and installation.

8. Ability to maintain substantially constant electrical resistivity with time.
9. Resistance to disbonding.
10. Resistance to chemical degradation.
11. Ease of repair.
12. Retention of physical characteristics.
13. Nontoxic to the environment.

2.7.3. *Cathodic Protection*:-

In the constructing process of the underground pipeline, since the partial damages of coating by the various reasons are unavoidable, a cathode protection method is used to protect corrosion in the partially damaged positions of the pipe [46].

2.7.3.1. *Cathodic Protection Systems*:-

Cathodic protection is an electrochemical method used to prevent or control corrosion of buried or submerged metallic structures .CP systems are active systems that rely on the application of electric current to control corrosion. If current is interrupted, corrosion will progress at a normal rate for the material/environment combination; if supplied current is inadequate for complete protection, corrosion will progress at a reduced rate[47].

All cathodic protection systems require an anode, a cathode, an electric circuit between the anode and cathode, and an electrolyte. Thus, cathodic protection will not work on structures exposed to air environments. The air is a poor electrolyte, and it prevents current from flowing from the anode to the cathode [40].

2.7.3.2. ***History of Cathodic Protection:-***

The first reported practical use of cathodic protection is generally credited to Sir Humphrey Davy in the 1820s. Davy's advice was sought by the Royal Navy in investigating the corrosion of copper sheeting used for cladding the hulls of naval vessels. Davy found that he could preserve copper in seawater by the attachment of small quantities of iron, zinc, or tin. The copper became, as Davy put it, "cathodically protected". It was quickly abandoned because by protecting the copper its antifouling properties became retarded, hence reducing the streamline of the ships, as they began to collect marine growths. The most rapid development of cathodic protection was made in the United States of America and by 1945. The method was well established to meet the requirements of the rapidly expanding oil and natural gas industry, which wanted to benefit from the advantages of using thin-walled steel pipes for underground transmission [15].

In the United Kingdom, where low-pressure, thicker-walled cast iron pipes were used extensively, very little cathodic protection was applied until the early 1950s. The increasing use of cathodic protection in modern times has arisen, in part, from the initial success of the method as used from 1952 onwards to protect about 1000 miles of wartime fuel-line network. The method is now well established and is used on a wide variety of immersed and buried facilities and infrastructure, as well as reinforced concrete structures, to provide corrosion control[30] .

2.7.3.3. *Principle of Cathodic Protection*:-

The principle of cathodic protection is in connecting an external anode to the metal to be protected and the passing of an electrical DC current so that all areas of the metal surface become cathodic and therefore do not corrode. The external anode may be a galvanic anode, where the current is a result of the potential difference between the two metals or it may be an impressed current anode where the current is impressed from an external dc power source. In electro-chemical terms, the electrical potential between the metal and the electrolyte solution with which it is in contact is made more negative by the supply of negative charged electrons, to a value at which the corroding (anodic) reactions are stifled and only cathodic reactions can take place[42][48].

2.7.3.4. *Advantages and Uses of Cathodic Protection*:-

The main advantage of cathodic protection over other forms of anti-corrosion treatment is that it is applied simply by maintaining a dc circuit and its effectiveness may be monitored continuously. Cathodic protection is commonly applied to a coated structure to provide corrosion control to areas where the coating may be damaged. It may be applied to existing structures to prolong their life. Specifying the use of cathodic protection initially will avoid the need to provide a “corrosion allowance” to thin sections of structures that may be costly to fabricate. It may be used to afford security where even a small leak cannot be tolerated for reasons of safety or environment. Cathodic protection can, in principle be applied to any metallic structure in contact with a bulk electrolyte (including concrete). In practice, its main use is to protect steel structures buried in soil or immersed in water. It cannot be used to prevent atmospheric corrosion on metals. However, it can be used to protect atmospherically exposed and buried reinforced concrete from corrosion, as the concrete itself contains sufficient moisture to act as the electrolyte. Structures that are commonly protected by cathodic protection are the exterior surfaces of[2][30]:

- Pipelines
- Ships' hulls
- Storage tank bases
- Jetties and harbor structures
- Steel sheet, tubular and foundation pilings
- Offshore platforms, floating and subsea structures

Cathodic protection is also used to protect the internal surfaces of [2][30]:-

- Large diameter pipelines
- Ship's tanks (product and ballast)
- Storage tanks (oil and water)
- Water-circulating systems.

2.7.3.5 .*Theoretical Basis of Cathodic Protection*:-

The CP principle is illustrated in figure (2.10) for a buried pipeline, with the electrons supplied to the pipeline by using a DC source and an ancillary anode. In the case of a coated pipeline, it should be noted that current (using the conventional direction) is flowing to the areas as the coating is defective. The nonuniform current flux arising from the particular geometry in figure (2.10) is also noteworthy. Furthermore, it should be noted that an electron current flows along the electric cables connecting the anode to the cathode, and ionic current flows in the soil between the anode and cathode to complete the circuit [49].

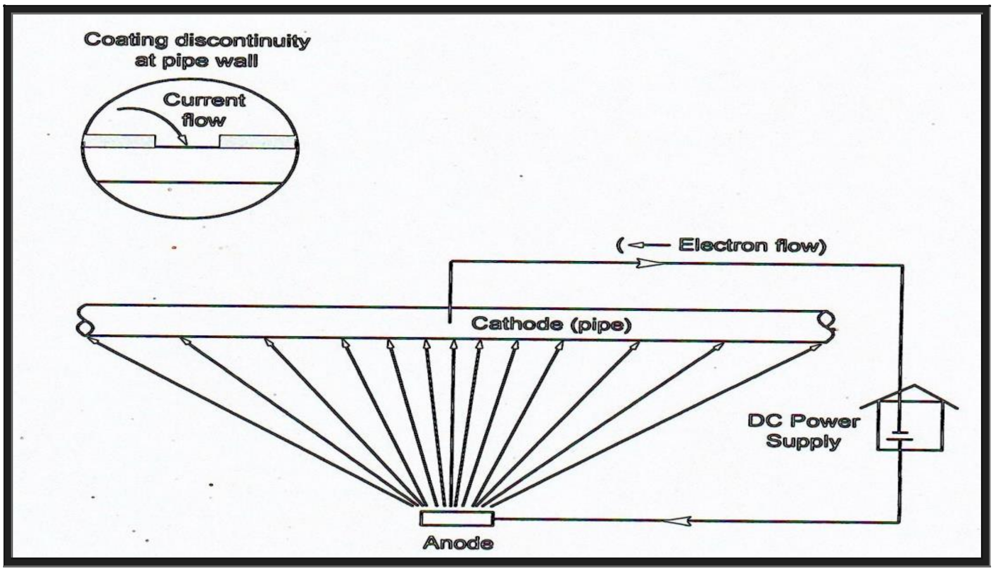


Fig. (2.10)

Schematic shows current flow and distribution in cathodic protection of a pipeline [49].

- Note: the current flow for a coated pipeline at a coating discontinuity.

In anaerobic, acidic environments the hydrogen evolution reaction tends to occur at the cathodically protected structure, whereas oxygen reduction is a likely cathodic reaction in aerated, near-neutral environments [49].

$$2H^{+} + 2e^{-} \rightarrow H_2 \quad \text{.....(2.10)}$$

(Anaerobic, acidic environments).

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \quad \text{.... (2.11)}$$

(Near-neutral environments).

The production of hydroxide ions, leading to alkaline surface conditions, should be noted in the oxygen reduction reaction. The balancing anode reactions depend on the material of the anode and the environment. The following are examples of reactions at the anodes of a CP system[49]:

$$M \rightarrow M^{n+} + ne^{-} \quad \text{.... (2.12)}$$

(For a consumable anode).

$$2H_2O \rightarrow O_2 + 4H^{+} + 4e^{-} \quad \text{... (2.13)}$$

(Inert anode).

$$2Cl^{-} \rightarrow Cl_2 + 2e^{-} \quad \text{. ... (2.14)}$$

(Inert anode in brackish environment).

2.7.3.6. *Types and Choice of Cathodic Protection*:-

There are two types of cathodic protection: sacrificial anode, and impressed-current. Both types are widely used. Sacrificial anode systems are simpler. They require only a material anodic to the protected steel in the environment of interest. The type of cathodic protection system to be applied (i.e. sacrificial anodes or impressed current) shall be as indicated on the requisition. If not specified, the contractor will select the type of cathodic protection and shall justify his choice in his basic design. The following factors should be considered when making the selection [2] [50]:-

1. Soil resistivity
2. Total current demand
3. Economic considerations
4. Presence of stray currents
5. Availability of power supply

6. Site layout
7. Presence of other conductors
8. Maintenance
9. Possibility to use existing, principal owned cathodic protection systems.

2.7.3.6.1. ***Impressed Current Systems:-***

In impressed current systems cathodic protection is applied by means of an external power current source figure (2.11). In contrast to the sacrificial anode systems, the anode consumption rate is usually much lower. Unless a consumable "scrap" anode is used, a negligible anode consumption rate is actually a key requirement for long system life.

Impressed current systems typically are favored under high-current requirements and/or high-resistance electrolytes. The following advantages can be cited for impressed current systems[49]:

- High current and power output range
- Ability to adjust ("tune") the protection levels
- Large areas of protection
- Low number of anodes, even in high-resistivity environments
- May even protect poorly coated structures.

The limitations that have been identified for impressed current CP systems are:

- Relatively high risk of causing interference effects.
- Lower reliability and higher maintenance requirements.
- External power has to be supplied.

- Higher risk of overprotection damage.
- Risk of incorrect polarity connections (this has happened on occasion with much embarrassment to the parties concerned).
- Running cost of external power consumption.
- More complex and less robust than sacrificial anode systems in certain applications.

The external current supply is usually derived from a transformer rectifier (TR), in which the ac power supply is transformed (down) and rectified to give a dc output. Other power sources include fuel- or gas-driven generators, thermoelectric generators, and solar and wind generators. Important application areas of impressed current systems include pipelines and other buried structures, marine structures, and reinforcing steel embedded in concrete[49]:

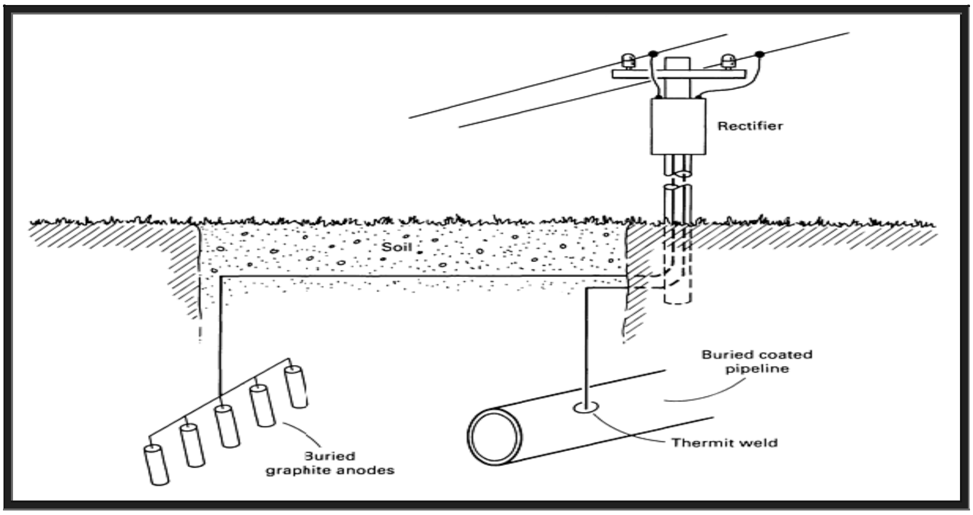


Fig. (2.11)
Impressed-current cathodic protection of a buried pipeline using graphite anodes[40]

2.7.3.6.2 *Sacrificial Anode CP Systems*:-

Cathodic protection can be applied by connecting sacrificial anodes to a structure. Basically, the principle is to create a galvanic cell, with the anode representing the less noble material that is consumed in the galvanic interaction[45], as shown in figure (2.12) .The consumption rate depends on the magnitude of current generated as well as the material of which the anode is made of and is given by Farady's Second Law of Electrolysis [39]:-

Total Weight Loss (gm) = A. i. t / V (96,500) … (2.9)

Where:

V =Valence Electron of the Metal.

t =Time duration of Current Flow in Sec.

i= Current in A.

A =Atomic Weight of the Metal.

When the protected structure and the electrically connected sacrificial anode are both disposed within the same electrolytic environment (e.g., soil or water containing ions), a galvanic cell is formed in which the protected structure is the cathode. Metal atoms on the exposed surface of the sacrificial anode are ionized by the surrounding electrolyte and go into solution with the electrolyte, thereby corroding the sacrificial anode. Due to the difference in electrical potential between the cathodically protected metal and the sacrificial anode [table (2.1)], electrons produced by the electrochemical corrosion reaction of the anode flow as an electrical current through the electrical connection between the sacrificial anode and the protected structure. When electrons reach the protected structure, they combine with positive ions (such as hydrogen ions) or dissolved oxygen in the electrolyte at the surface of the protected structure. The protected structure does not corrode since the positive ions or oxygen would otherwise initiate a corrosion reaction at the surface of the protected structure [22]. In practice pure metals are never used as sacrificial anodes. There is variety of reasons for this, which includes the need for [15]:

1. A reliable, reproducible and negative operating potential for the anode.
2. A high and reproducible capacity (Ah/kg) for the anode.
3. Uniform dissolution of the anode so that all metal is consumed usefully in providing cathodic protection and not wastefully by mechanical loss.
4. Freedom from any loss of activity by the anode due to passivation.

In practical applications a number of anodes usually have to be attached to a structure to ensure overall protection levels. The electrochemical behavior of sacrificial anode materials is of vital importance for the reliability and efficiency of cathodic protection systems for seawater exposed structures [18] .The following advantages are associated with sacrificial anode CP systems[49] :

- No external power sources required.
- Ease of installation (and relatively low installation costs).
- Unlikely cathodic interference in other structures.
- Low-maintenance systems (assuming low current demand).
- System is essentially self-regulating.
- Relatively low risk of overprotection.
- Relatively uniform potential distributions.

Unfortunately, these relatively simple systems also have some limitations such as[49]:-

- Limited current and power output.
- High-resistivity environments or large structures may require excessive number of electrodes. Maximum resistivity of 6000 to 10,000 Ω.cm is generally regarded as the limit, depending on coating quality.
- Anodes may have to be replaced frequently under high current demand.
- Anodes can increase structural weight if directly attached to a structure.

Typical applications include buried tanks, underground pipelines, buried communication and power cables, water and gas distribution systems, internal protection of heat exchangers and hot water tanks, ships, and marine structures [18] [48] .

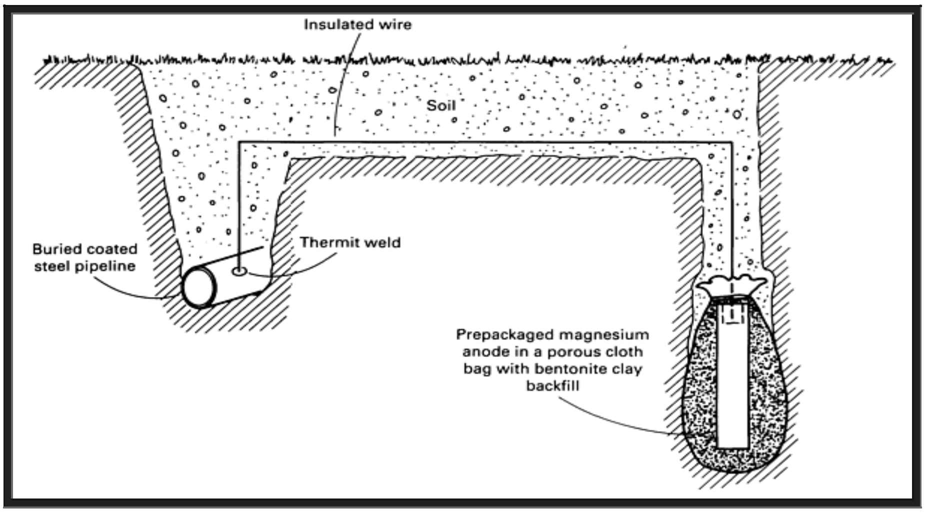


Fig. (2.12)
Cathodic protection of buried pipeline using a buried magnesium anode [40]

2.7.3.6.2.1 *Sacrificial Anode Materials*

Whilst cathodic protection 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). In a cathodic protection system the sacrificial anode must be more electronegative than the structure. There is, therefore, a limited range of suitable materials available to protect carbon steel. The range is further restricted by the fact that the most electronegative metals (Li, Na and K) corrode extremely rapidly in aqueous environments. Thus, only magnesium, aluminum, and zinc are viable possibilities. These metals form the basis of the three generic types of sacrificial anode. [15] [51] .

1. Magnesium Anodes:-

   Magnesium-based alloys are used in soil and fresh water application .Magnesium anodes are also used for the protection of the interiors of water tanks and heaters, heat exchangers and condensers, and waterfront structures[52]. Magnesium anodes are available as castings and extrusions weighing from 0.45 kilograms to over 90.72 kilograms (1 to over 200 pounds) and in a wide variety of shapes [40] [1]

   Magnesium-based alloys have characteristics of[20] [24]:

   a) Highest operating voltage of all common galvanic anodes but has the lowest efficiency and highest cost per ampere year of current flow.
   b) Typically used in soils and waters with resistivities higher than 1500 ohm-cm, because of their theoretical low half-cell potential, as well as the possibility of high current capacity.

2. Zinc Anode:

Zinc Anodes are used for cathodic protection in freshwater and marine water. Zinc is especially well suited to cathodic protection on ships that move between salt water and harbors in brackish rivers or estuaries. Zinc anodes are also used to protect ballast tanks, heat exchangers, and many mechanical components on ships, coastal power plants, and similar structures[40][1].They are, however, occasionally used in the protection of buried structures when special circumstances are encountered, usually in soil resistivities below 2,000 ohm centimeters with extremely well coated structures. Zinc anodes are commonly available in the form of plates, bars, and rods[1][52] .

3. Aluminum Anode:-

Aluminum galvanic anodes are a more recent development than either zinc or magnesium alloys. Their primary use is in the protection of structures in seawater. However, they have occasionally been used in fresh water or in soil. When the original anodes used are aluminum alloy and their performance has been satisfactory, they should be replaced by anodes of the same type[53] .

Aluminum galvanic anodes are used for corrosion protection of pipeline, crude oil tanks, condensers, water boxes, heat exchangers, boilers, and various marine structures such as offshore platforms, ship hulls, etc, from corrosion in marine, saline mud and fresh water environment in both ambient and high temperatures[27] [53] .

2.8 Introduction to Aluminum-Alloys:-

A unique combination of properties makes aluminum one of the most versatile engineering and construction materials. Just a mere recital of its characteristics is impressive. It is light in mass, yet some of its alloys have strengths greater than that of structural steel. It has high resistance to corrosion under the majority of service conditions and no colored salts are formed to stain adjacent surfaces or discolor products with which it comes in to contact . When aluminum surfaces are exposed to the atmosphere a thin invisible oxide skin forms immediately that protects the metal from further oxidation. This self-protecting characteristic gives aluminum its high resistance to corrosion. Unless exposed to some substance or condition, which destroys this film, the metal remains fully protected against corrosion. Alkalis are among the few substances that attack the oxide skin and therefore are corrosive to aluminum [54]. Pure aluminum is soft, ductile, and corrosion resistant and has a high electrical conductivity, as shown in table (2.5). In consequence it is widely used for foil and conductor cables, but alloying with other elements is necessary to provide the higher strengths needed for other applications [55]

Table (2.5)

Typical Properties for Aluminum [55]

Property	Value
Atomic Number	13

Atomic Weight (g/mol)	26.98
Valency	3
Crystal Structure	Face centered cubic
Melting Point (°C)	660.2
Boiling Point (°C)	2480
Mean Specific Heat (0-100°C) (cal/g.°C)	0.219
Thermal Conductivity (0-100°C) (cal/cms. °C)	0.57
Co-Efficient of Linear Expansion (0-100°C) (x10-6/°C)	23.5
Electrical Resistivity at 20°C (μΩ.cm)	2.69
Density (g/cm^3)	2.6898
Modulus of Elasticity (GPa)	68.3
Poisson's Ratio	0.34

2.8.1 ***Aluminum Alloys***

The main alloying elements are copper, zinc, magnesium, silicon, manganese, and lithium. Small additions of chromium, titanium, zirconium, lead, bismuth, and nickel are also made and iron is invariably present in small quantities. There are over 300 wrought alloys with 50 in common use. They are normally identified by a four figure system, which originated in the USA and is now universally accepted. Table (2.6) describes the system for wrought alloys. Cast alloys have similar designations and use a five digit system (Table 2.6) [55].

Table (2.6)

Designations for alloyed wrought and cast aluminum alloys [55]

Major Alloying Element	Wrought	Cast
None(99%+Aluminum)	1XXX	1XXX0
Copper	2XXX	2XXX0
Manganese	3XXX	
Silicon	4XXX	4XXX0
Magnesium	5XXX	5XXX0
Magnesium + Silicon	6XXX	6XXX0
Zinc	7XXX	7XXX0
Lithium	8XXX	

2.8.2 ***Effects of Alloying Elements on Aluminum***

1. Magnesium: - is the major alloying element in the 5xxx series of alloys. Resistance to corrosion by sea water and marine atmosphere of cold-worked alloys is improved by the addition of magnesium. However, high percentage reduces the hot- and cold-working properties and so a compromise must be made in deciding the amount to be added [55][56].

2. Zinc**: -** The aluminum-zinc alloys have been known for many years, but hot cracking of the casting alloys and the susceptibility to stress-corrosion cracking of the wrought alloys curtailed their use. Aluminum-zinc alloys containing other elements offer the highest combination of tensile properties in wrought aluminum alloys [55] [56]. Figure (2.13) shows the binary phase diagram of (Al-Zn)

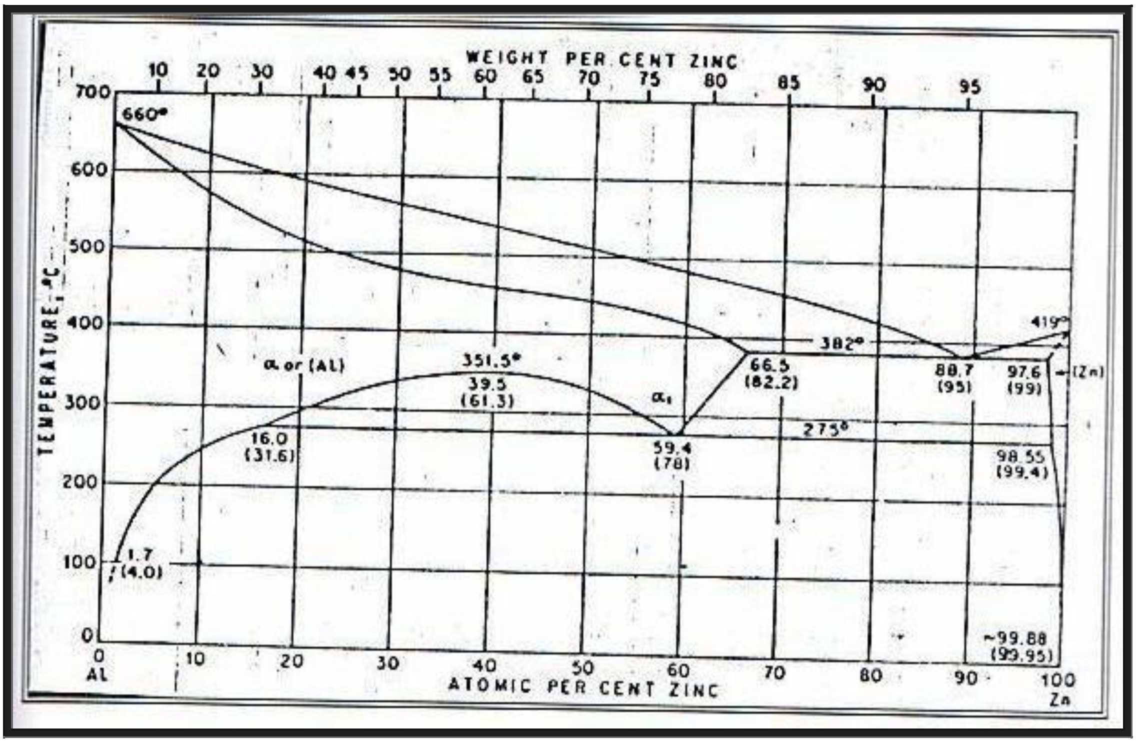


Fig.(2.13)
Phase diagram of binary (Al-Zn) alloy [57]

3. (Zinc-Magnesium):- The addition of magnesium to the aluminum-zinc alloys develops the strength potential of this alloy system, especially in the range of 3 to 7,5% Zn. Magnesium and zinc form $MgZn_2$, which produces a far greater response to heat treatment than that which occurs in the binary aluminum-zinc system. The strength of the wrought aluminum-zinc alloys also is substantially improved by the addition of magnesium [55] [56]. Figure (2.14) shows ternary phase diagram of (Al-Zn-Mg) at 20ºC.

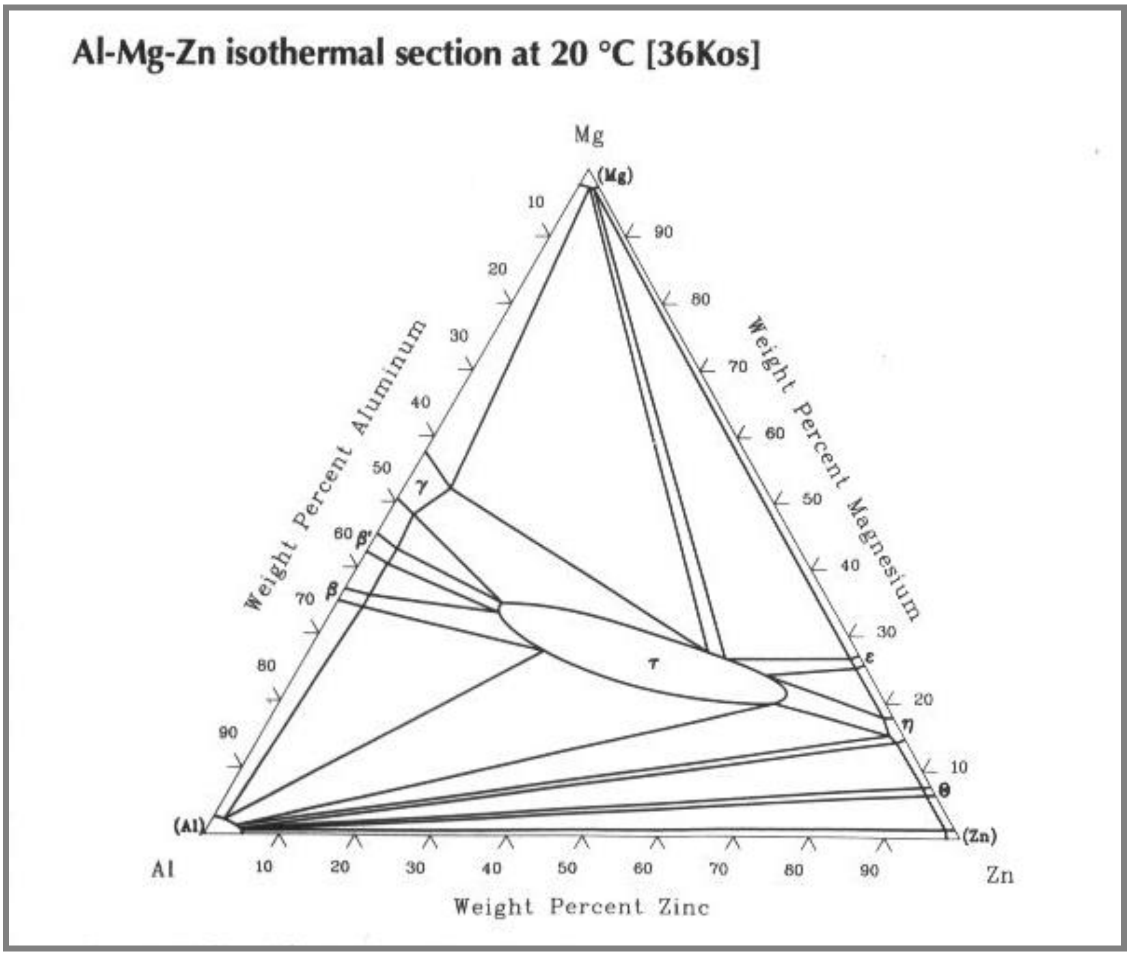


Fig. (2.14)

Ternary phase diagram of (Al-Mg-Zn) alloy [57]

2.8.3.<u>Using of Aluminum Alloys in Cathodic Protection</u>

For protecting structures made from ferrous metals such as iron and steels, the sacrificial anodes are generally magnesium, aluminum, or zinc. Aluminum is a preferred material for controlling and preventing corrosion in marine environments, due to its relatively low price, low density, and high theoretical electrical capacity (due to formation of a trivalent cation) [22].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. 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 [58]. 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 the following ones: gallium (Ga), titanium (Ti) and thallium (Tl) which are rarely used [18],[21].

Aluminum galvanic anodes are used for corrosion protection of pipeline, crude oil tanks, condensers, water boxes, heat exchangers, boilers. and various marine structures such as offshore platforms, ship hulls, etc, from corrosion in marine, saline mud and fresh water environment in both ambient and high temperatures[27],[53] Aluminum anodes are not suitable for low chloride environments which would lead to passivation [15] .

CHAPTER THREE

EXPERIMENTAL WORK

3.1 INTRODUCTION

Experimental work was carried out to evaluate the performance of Al-alloys that are prepared especially to be used as a sacrificial anodes in the protection of underground steel pipelines of Basra (Southern of Iraq) especially in AL-FAO region against corrosion damages .The soil of AL-FAO region has remarkable characteristics like containing a high percentage of chlorides (~1.5% of Cl^-) in addition to high content of moisture .

The prepared alloys in this work have been chosen after studying many literatures and also after many visits to the Iraqi southern oil company. These alloys are prepared with high attention during melting of aluminum, addition of alloying elements and sampling with minimum defects. The target of such alloys option is based on the requirements to get required intermetallic phases such as (τ, ß, and α-phases). It is thought that, these phases play an important role in the process of corrosion protection.

Furthermore, the alloy in literature [27] is reprepared at the same composition and other conditions, and then it is subjected to the same procedure of evaluation that is adopted in this work in order to be used as a reference alloy for comparing the results obtained above.

The comparison is also done with the Mg-alloy that is already used originally by the Southern Oil Company in AL- FAO region. So, the following main steps are adopted in order to accomplish the targets of the present work:-

1. Preparation of the steel pipe samples & Mg –alloy samples.
2. Choosing & preparation of new aluminum alloys with different

composition, including; melting, alloying, and sampling.

3. Re-preparing of the alloy that is used in reference no [27] in order to be used as a reference alloy for comparisons.
4. A careful study of the resulted phases those evolutes in prepared alloys by using X-ray diffraction analysis and optical microscopy.
5. A study of corrosion behavior of steel pipe material, prepared aluminum alloys and Mg alloy (that is already using by Southern Oil Company in AL- FAO region), through a sets of experiments includes :
   - Tafel extrapolation test.
   - Weight loss test for steel samples.
   - Sacrificial anode weight loss test.
   - Microstructure observation.
   - Current measurement of sacrificial anode system (i.e. galvanic cell).

Figure (3.1) shows the experimental procedure as a block diagram for the main steps that followed in this work.

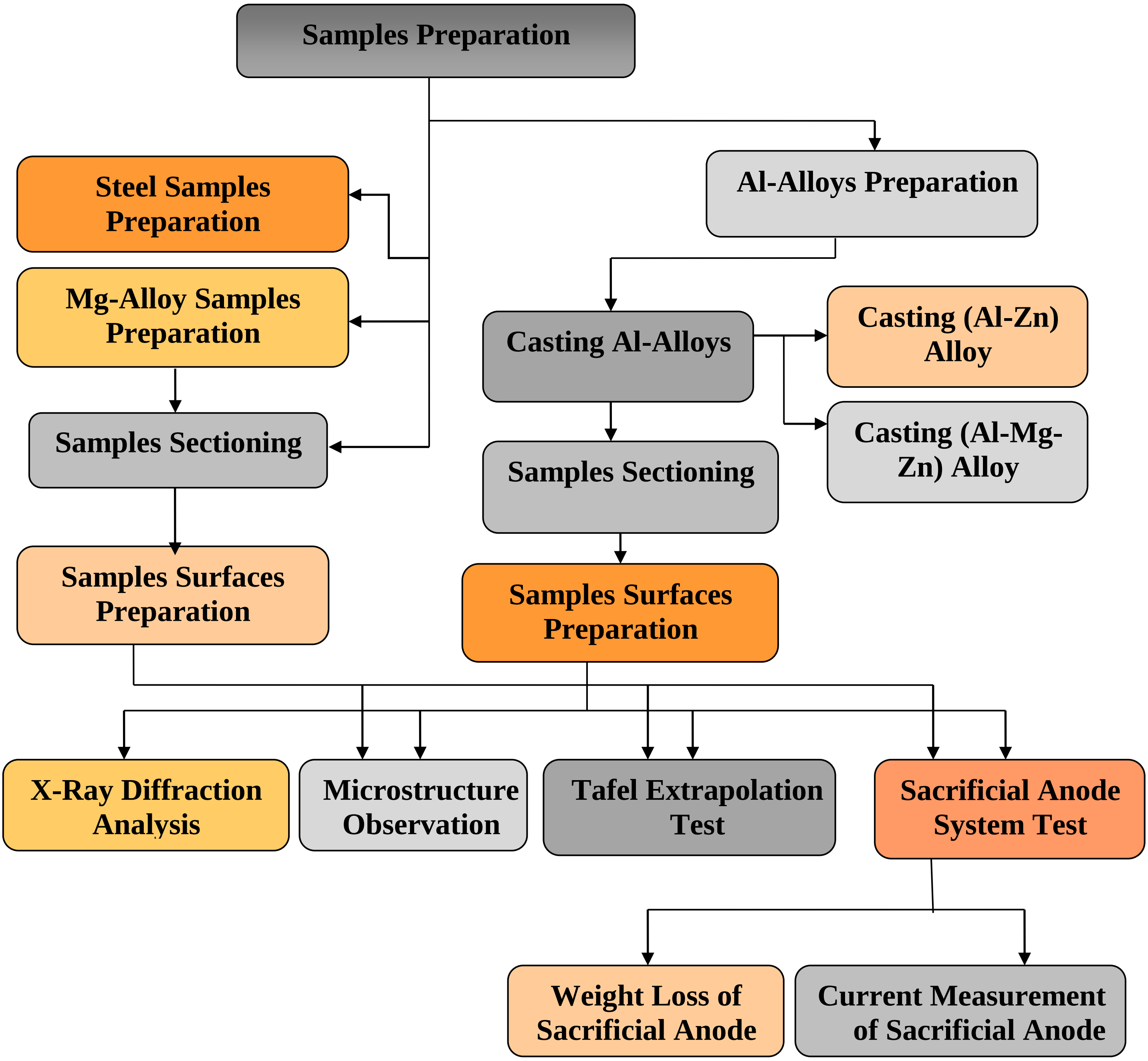

Samples Preparation
Steel Samples Preparation
Al-Alloys Preparation
Mg-Alloy Samples Preparation
Casting Al-Alloys
Casting (Al-Zn) Alloy
Casting (Al-Mg-Zn) Alloy
Samples Sectioning
Samples Sectioning
Samples Surfaces Preparation
Samples Surfaces Preparation
X-Ray Diffraction Analysis
Microstructure Observation
Tafel Extrapolation Test
Sacrificial Anode System Test
Weight Loss of Sacrificial Anode
Current Measurement of Sacrificial Anode

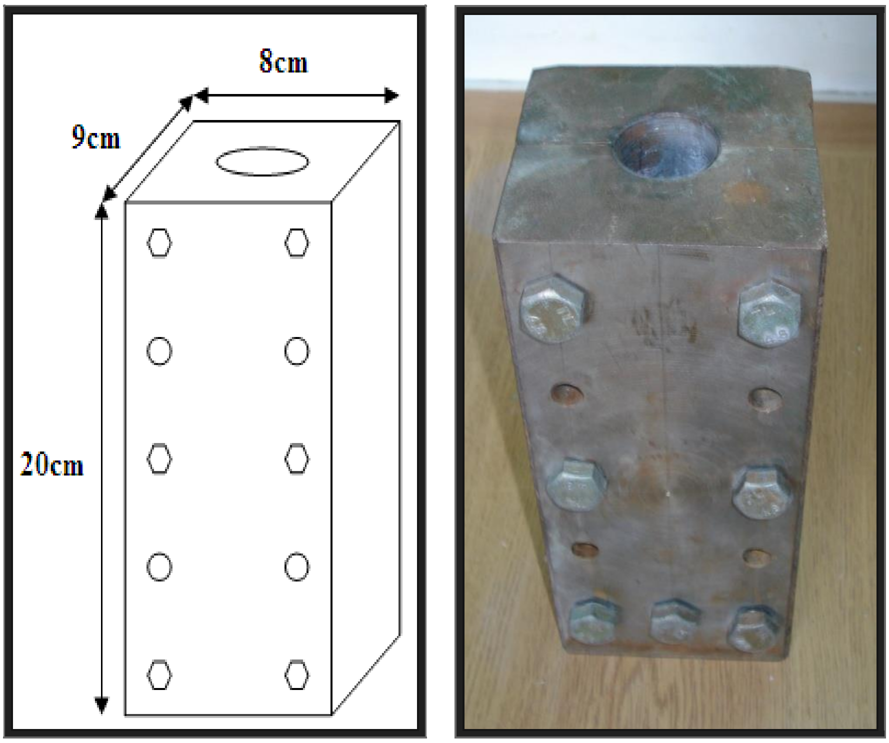
Figure (3.1)

The experimental procedure as a block diagram for the main steps that follow in this work

3.2 Preparation of Aluminum alloys

Following is a list of apparatus and tools that are used foundry process of aluminum alloys that are adopted in this work:

1. Multi-Silicon Carbide (SiC) crucibles with a size of (2000 gm.) capacity.
2. An electric resistance furnace type (REC TRADE UAR) used for melting practices.
3. Portable thermocouple (k-type) used for pouring temperature monitoring.
4. A Steel mold with a cylindrical cavity having the dimensions as shown in figure (3.2) used for alloys sampling as ingots.



(a) (b)

Fig(3.2)
a. Steel mold with it's dimensions.
b. Photo picture of steel mold.

3.2.1. *Materials Used*:-

1. Aluminum with (99.5 % purity) from local market as a wire form.
2. Pure Magnesium with (99.7% purity).
3. Pure zinc of (99.9%purity) in the form of thick plate.

3.2.2. *Preparation of Aluminum and Alloying Elements for Foundry Process:*

1. Aluminum wires were cut into small pieces to facilitate their weighting and melting.
2. Zinc plates were cut, grind by using emery paper (180-grade) to remove the oxide film and also to remove any surface impurities. The zinc samples are washed with distilled water rinsed in ethanol and kept in dissector contains silica gel until using.
3. Mg foils and zinc samples are packing now with Al-foils to ensure minimum losses in their weight percentages during foundry process.

3.2.3. *Alloys Preparation Procedure*: -

The following procedure was adapted during melting, alloying of aluminum to get a samples of (Al-Zn-Mg) alloys:-

1. Al, Mg, and Zn are predetermined in required weights.
2. Preliminary melting of aluminum was done in an electric resistance furnace (type REC TRADE UAR). The melt was cleaned from drosses and dirts, and then superheated to 750ºC.
3. Now, the alloying elements are ready for addition in the required weight percentages.
4. A continuous mixing by using a graphite stirring rode to ensure a best mixing and dissolution of alloying elements and to avoid segregation defects.

5. Degassing treatment was done by an addition of suitable amount of degasser to the mix, to avoid the existence of (gas porosity's defect) in casting alloys composition.
6. Cleaning the melt from inclusions, contaminations that occur on the mix surface alternatively.
7. The uniformly mixed emulsion of aluminum, zinc, and magnesium was then poured into the mold with minimum agitations. .
8. Avoidance of turbulence during pouring to minimize drossing and hydrogen pick-up.

The process described above was repeated for the various aluminum base alloys employed in this work. The chemical composition of prepared alloys are tested systematically after each heating in (*The Ministry of Sciences and technology/*, then any deviations from the required composition would be repeated or adjusted to meet the chemical composition requirements. The average chemical composition of prepared alloys is as indicated in table (3.1).

Table (3.1)

Average chemical composition of preparing Al-alloys (wt %)

Al alloys coding	**Zn%**	**Mg%**	**Al%**
Alloy(A)	6	--------	Balance
Alloy(B)	5.5	8	Balance
Alloy(C)	5.5	10	Balance
Alloy(D)	15	12	Balance
Reference alloy(E)	12	9.2	Balance

3.3. Samples Preparation:-

Two kinds of corrosion testing are used to evaluate the preparing alloys efficiency in the protection process of steel pipe samples as shown:

1. Tafel testing.
2. Sacrificial anode tests.

3.3.1. *Samples Used in Tafel Test:*

These samples are categorized into three groups:

a. Steel samples: A piece of steel pipe of (48cm diameter) as received from (Southern Oil Company) having a chemical composition as shown in table (3.2).The chemical composition was measured in the *"General Company of Mechanical Manufactures*" using *"Spectrum Analysis of Metals*" method. The steel samples are now machined to the required dimensions of (20X20) mm, 3mm thickness. The samples are now washed with distilled water, rinsed with ethanol, dried and kept in dissector contains silica gel.

Table (3.2)

The analytical chemical composition of Mild carbon steel pipe (CK 35)

C%	P%	Mn%	Si%	S%	Fe%
0.340	0.035	0.640	0.400	0.035	BALANCE

b. Aluminum Alloys Samples: Al-alloys ingots were machined into a disc shape samples with the dimensions of (20mm diameter, 3mm thickness) , washed with distilled water, rinsed with ethanol dried and kept in dissector contains silica gel.

c. Mg Alloy Samples: Mg alloy with chemical composition as shown in table (3.3) as was received from (Southern Oil Company) with a dimensions of (75cm length, 15cm width and 15cm height), weighted (22) kg, as in figure (3.3), these alloy was machined for sampling into rods of 20mm diameter and 150mm length ,then it was machined again to samples of 20mm diameter and 3m thickness, washed with distilled water, rinsed with ethanol dried and kept in dissector which contains a silica gel.

Fig (3.3)
Mg alloy used in AL- FAO as a sacrificial anode for cathodic protection of steel pipelines

Table (3.3)
Chemical composition of Mg alloy (wt %)

Al%	Zn%	Ni%	Cu%	Mn%	Fe%	Mg%
5.5	3	0.003	0.08	0.2	0.005	Balance

3.3.2. *Samples Used in Sacrificial Anode System Tests:-*

The same method used in preparation of steel, Al-alloys and Mg alloy samples are repeated except the drilling of a hole of (2mm diameter) in each sample for the purpose of suspension in the used media (i.e. AL-FAO soil).

Each one of steel samples in each type of test, are subjected to annealing practices at (600ºC) for one hour and furnace cooled to room temperature in order to remove residual stresses.

3.3.3 *Surface Preparations of Samples:-*

All Samples used in this work were grinded by an emery papers with (180, 400, 600, 800, 1000, 1200 grit size) respectively by using a rotary grinding wheel (type-Hergon-mp 200V). After each stage the samples were washed with distilled water rinsed with ethanol, dried, and kept in dissector contains silica gel until using.

3.4. X-Ray Diffraction Analysis:

X-ray diffraction analysis was used for Al-alloys in order to estimate:-

1. The phases exist in cast Aluminum alloys.
2. Amount of these phases in each alloy.

The test carried out through scanning the specimen continuously within Bragg angle (2θ) range (30º-60º) using Cu target at voltage of 40 *kV* and 30 *mA* of current with continuous scan mode, range (30.000-60.000) degree.

In order to identify all phases present in each alloy , the value of d-spacing, which can be calculated from the value of 2θ (using brag equation) of the resulting peaks (for alloy), is matching with the value of d-spacing for phases present in x-ray data files that are published by (N 1997 JCPDS-International Centre for Diffraction Data).

3.5 Microstructural Examination:-

The aim of using microstructural examination is to show the existence, amount, and distribution of phases in cast Al-alloys that are prepared in this work. All the samples of Al-alloys prepared previously were polished through using alumina suspension. The samples were etched by immersion in an etching solution for (60 sec). The solution consists of:-

10% perchloric acid ($HClO_4$) in ethanol (CH_3CH_2OH) [27]

In this work it is shown that AL-FAO soil solution can be used as etching solution for (Al-Mg-Zn) alloys .The microstructure of alloys was observed using an optical microscopy (Union / ME-3154) type.

3.6 <u>Tafel Extrapolation Test:</u>

This method is used to estimate the corrosion current and corrosion potential .This test is carried out for steel, Mg alloy, and Al-alloys. The resulting behavior for steel is compared with each alloy of Mg &Al-alloys. The results of this test which is carried out in the (*Ministry of Sciences and technology/chemical research office*) using potentiostat apparatus, which consist of:-

A. Electronic processor.

B. Electrochemical cell, which consists of glass cell of 1 liter in volume and three electrodes:-

1. Reference electrode: saturated calomel electrode.
2. Auxiliary electrode: platinum electrode.
3. Working electrode: testing electrode (sample using) that will be steel, Mg alloy, Al-alloy respectively in each test.

3.6.1. *Corrosion Test Solution:-*

Standard soil solution used as an electrolyte in Tafel Extrapolation Test due to the difficulty and limitations of using soil as a test solution in this apparatus. The solution was prepared under high attention according to the chemical analysis of AL-FAO soil as shown in table (3.4). This test is carried out in Babylon University / Civil Engineering College / Soil & Sanitary Laboratories. The composition of simulated solution as prepared is shown in table (3.5).

Table (3.4)

Chemical Test of AL-FAO Soil

Cl^- %	SO_3%	Gyp%
1.5	5.54	11.92

Table (3.5)

Chemical Composition of a Prepared AL-FAO Soil Solution

Sodium chloride (NaCl)%	**Na_2SO_3 %**	**Gypsum ($CaSO_4$)%**
2.5	8.7%	11.92%

pH value of AL-FAO soil solution= (8.45), Resistivity of this solution is (13.38) Ω.cm, which measured through the measuring of conductivity of solution using Microprocessor Conductivity Meter HANA instrument, and the test was carried out at room temperature.

3.6.2 Testing Procedure:

The glass cell is filled with standard soil solution(i.e. test solution) , also the bridge tube is filled with the test solution , then reference electrode, auxiliary electrode, and working electrode that are previously prepared(with surface area 1 cm^2) are immersed in solution as shown in figure (3.4).In order to estimate the open circuit potential (opc), the auxiliary electrode is closed(current=0)and estimate potential for 30 minute , corrosion potential (E_{corr}) can be found where : $E_{corr} \approx$ opc.

In order to measure the passage current and voltage between the auxiliary electrode and working electrode a voltage with a range of (±250 mV) above &under open circuit potential is applied, with scanning rate(3mv/sec) for each 10 mV. The value of passage current can be found for each value of voltage in the range of (±250 mV). The program using in this test is *ELECTROCHEMICAL SeI* program

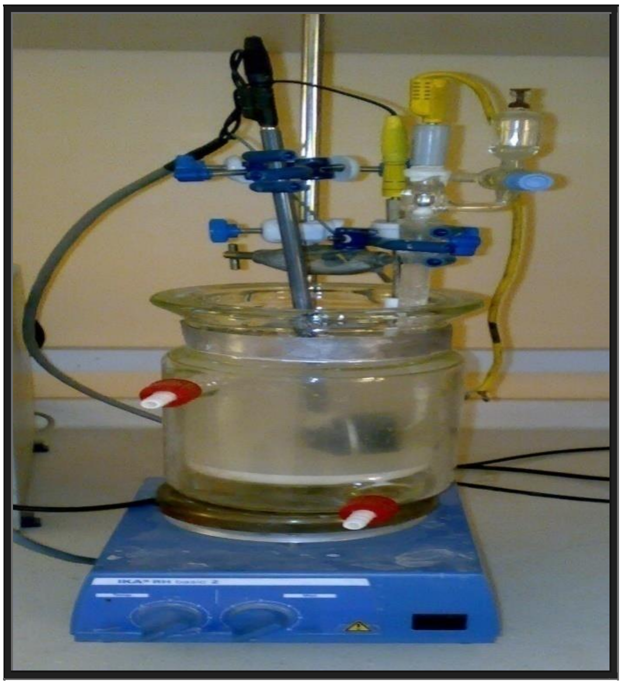


Figure (3.4) (a)

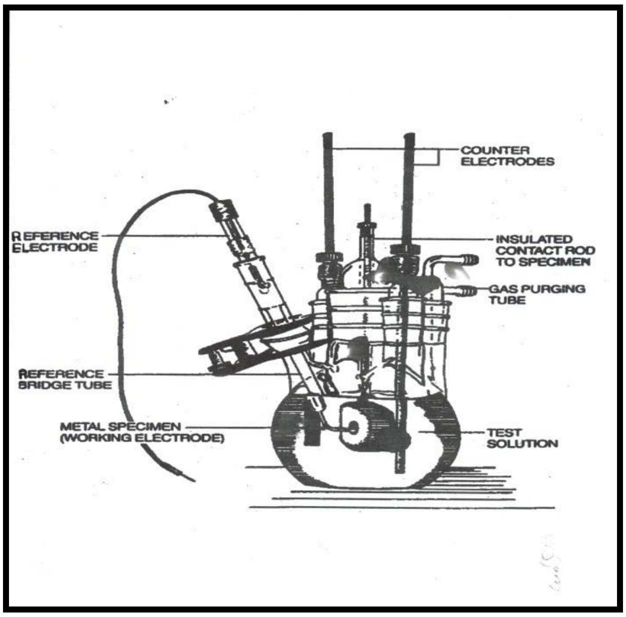


Figure (3.4) (b)

(a). Photo picture shows the use of the electrochemical cell in drawing polarization curves.

(b).Schematic sketch shows the use of the electrochemical cell in drawing polarization curves.

3.7 Weight Loss Test:-

Another vital method for estimating corrosion rate that is adopted in this work is using simple immersion test. This test has been implemented to estimate the corrosion rate for the steel and sacrificial anode system.

3.7.1. *Preparation of Electrolyte Used in Weight Loss Test:-*

AL- FAO soil with chemical composition mentioned in table (3.4) is used in this test as an electrolyte. This choice is adopted for the following reasons:

1. In order to avoid the problem of any deposition of anode reaction products on the steel surface samples (Cathode) in the case of using liquid solution.
2. It is more reliable to use a real media than using a simulated media.
3. Using soil with identical properties gives the produced results an excellent verification.
4. It is possible to use the results of the work under such conditions directly in the design and selection of sacrificial anode system in the petroleum industry (especially in AL- FAO region).

For each (1000 gm) of soil a (200ml) of distilled water is added to obtain the nominal value moisture percentage in soil. The (pH) value of resulting AL-FAO soil is found a (8.5), and electrical conductivity was found (13.736 Ω.cm) at room temperature.

The prepared soil is put in plastic container with dimension (15x15x30) cm.

3.7.2 *Testing Procedure:-*

3.7.2.1 *Steel Pipe:-*

This test is carried out in order to study the behavior of mild steel pipelines samples in AL- FAO soil as follows:-

a. Samples of steel pipe that were previously prepared and kept with high attention are now re-washed with distilled water, rinsed with ethanol and dried. A precise weighing process is now carried out to record the initial weight of samples.

b. The steel samples are connected with an insulated wire and immersed completely in the electrolyte (i.e. the prepared soil).
c. Steel samples are re-weighed after each day (i.e. 24 hrs.). The process of re-weighing is carried out under high attention by a perfect cleaning of samples by using distilled water and rinsing in ethanol with sufficient drying. The process of re-weighing is repeated every day for 14 days maximum
d. The purpose of re-weighing process is to determine the weight loss as referred to by ($\Delta W/A_0$) in results and findings.

The moisture content of soil used in this work is subjected to decreasing alternatively due to the summer atmospheric conditions in the laboratory. This problem was solved by adding a round (10ml) of distilled water in every day to the mud. The process of water addition is monitored alternatively by checking the moisture content in Soil Laboratory .Micrograph picture was taken before and after the 14 day of exposure time for steel sample.

3.7.2.2 *Sacrificial Anodes:*

After studying the corrosion behavior of steel pipe sample, it is possible now to study the behavior of each one of Al-alloys and Mg-alloy as sacrificial anodes in the protection of steel pipe samples by its electrically connection together(i.e. steel samples with these alloys) . This system consists of the following items:

A. *Electrodes*: - Cathode: a sample of steel pipe.
B. Anode: Represented by the prepared and received alloys that includes (Al-alloys, Mg alloy).
C. *Electrolyte*: - AL- FAO soil used as an electrolyte in this work. It was prepared by the addition of (200ml) of distilled water to each (1000g) of

AL-FAO soil in order to obtain moisture in soil as it was mentioned previously.

D. *Metallic conductor*: - Copper cable with 2mm diameter is used as a conductor between anode and cathode is used to transfer the current (electrons). The insulated copper wire was chosen due to its high electrical conductivity (59.6 × 10^6 ($S \cdot m^{-1}$) (copper come after Silver which has the highest electrical conductivity among any known metals) [64]. The high conductivity is very important to conduct an electric current between anode and cathode.

E. *Thermometer*: The thermometer was placed in the electrolyte to measure temperature up to 100 ̊ C.

F. *Plastic container:* Plastic container of (15X15X30) cm dimensions is used to as a container for each, the electrolyte, and the samples of cathode and anode.

Figure (3.5) shows the sacrificial anode system used in this work.

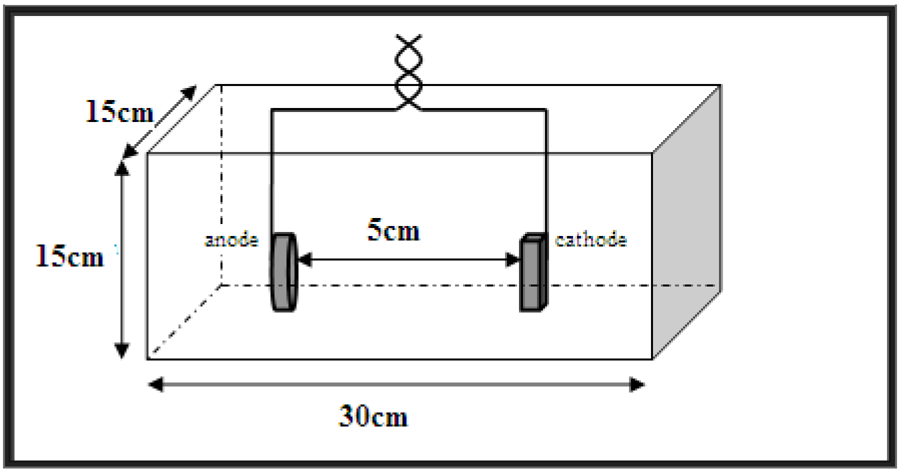


Fig (3.5) (a)

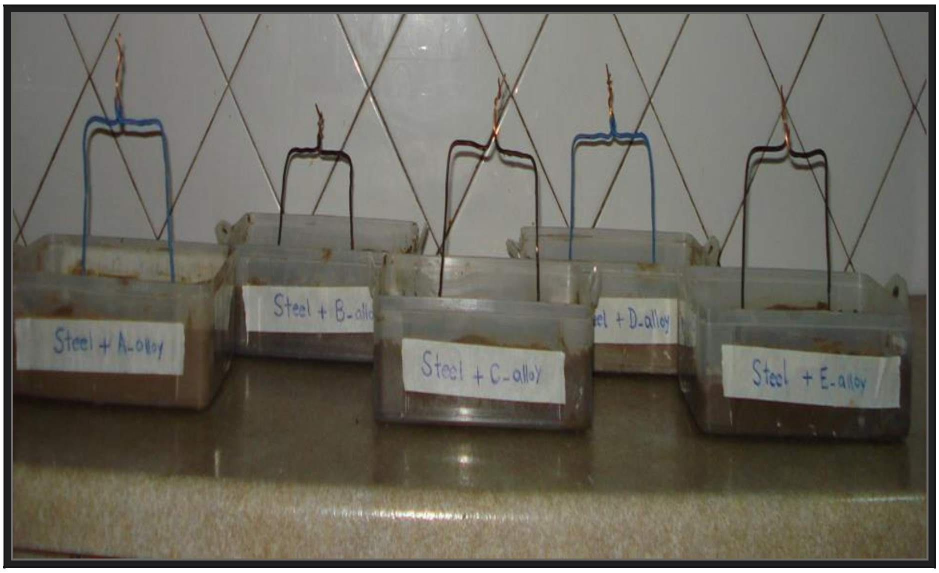


Fig (3.5) (b)

(a).schematic sketch shows the dimensions of plastic container and galvanic cell.

(b).photo picture for the electrochemical cells (galvanic cells) used in this work.

The procedures for carrying out weight loss test of sacrificial anodes include:

1. Preparation of Samples Used in Sacrificial Anode System Tests:-

Two types of samples have been prepared, the anode sample (Al-alloy or Mg alloy), and cathode sample (steel pipe). These samples are now electrically connected to each other by one end of copper wire. The application of epoxy is now important to the outer surface of connecting assembly. Keep in mind that the contact surface between the wire and samples is still free of epoxy. The process of connecting samples to the wire is very important to get the following requirements:

A. An excellent contact must be achieved between the sample surface and the connecting wire.

B. This contact must be ensuring a perfect transferring of DC current between the samples.

C. The using of epoxy above the connecting assembly is highly recommended to prevent moisture from reaching the region of contact and also to prevent the so expected galvanic corrosion that appears in these conditions.

The following picture (figure (3.6)), shows the sample method of connection.

(a) (b)

Fig (3.6)

(a). Anode (Alloy specimen) electrically connects with copper cable.
(b). Cathode (steel) electrically connects with copper cable.

2. Weight loss test of sacrificial anodes

The following procedures are adopted in this work:

A. Each specimen of anode and cathode that connect to cable are weighted initially.

B. Each specimen of anode that (electrically connect with copper cable) electrically connect to a specimen of cathode (that electrically connect to copper cable also) from the other ends for anode and cathode then immersing completely in soil as shown in fig (3.5).

C. Specimens removed after (1 day), this lased for 14 days, the specimens cleaned, washed with distilled water. After rinsed with ethanol respectively dried and then re-weighed to determine the weight loss ($\Delta W/A_0$) in each cell (cathode and anode).

- Note: - In order to keep the same average of moisture content distilled water (10ml) is added every day to the cell) as it was mentioned .

  Micrograph picture was taken before and after the 14 days of exposure time for steel samples (i.e. cathode) and sacrificial anodes samples.

3.7.3 *Current Measurement of Sacrificial Anode System*:-

During weight loss test the current pass in cell was measured using μ Ampere .This measurement is useful for estimating efficiency for each alloy in sacrificial anode system.

CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 INTRODUCTION:-

Sacrificial anode is one of the most important methods used in the protection of multi types of structures and pipelines against corrosion damages. Petroleum pipelines are subjected frequently to the corrosion because its pass through a multi types of soils and Medias. Many types of metals and alloys are used as a sacrificial anode as can be seen in theoretical background and literature survey. In the present work a set of aluminum alloys are prepared with a high attention in order to be used as candidate sacrificial anodes for the protection process of petroleum pipelines that pass through southern of Iraq. The research is focusing on the protection of petroleum pipelines that pass through the AL-FAO region in Basra governorate. Petroleum pipelines are passed through an aggressive and wet soil, where, the chlorides percentages is about (1.5%) as it was measured (see chapter three).

Magnesium-alloy is used now in the region of AL-FAO as a sacrificial anode. Knowing that, that alloy is imported completely from the outside of Iraq, production and design of such alloys is very restricted by the production company. So that it is hoped to produce a sacrificial anode produced from aluminum alloys with corrosion properties equal or higher than that gained from the imported Mg-alloy.

Finally the results are compared with the Mg-alloy and the alloy in paper [27] that is reprepared and tested in AL-FAO soil. For that, the research has two phases:-

1. Preparation of aluminum alloys with different chemical compositions by melting and alloying aluminum.
2. Evaluation of corrosion characteristics for the prepared alloy through a set of electrochemical tests such as Tafel extrapolation, weight loss test, microstructure observation and current measurement test.

The behavior of prepared alloys in the protection of steel petroleum pipes are discussed in details with the combination of metallurgical aspects and corrosion affinity. The experiments focused on the effect of alloying elements addition on the electrochemical behavior such as (Zn & Mg).

4.2 Preparations of Aluminum Alloys:-

The technique that is described in the experimental work (see chapter three) has led to the preparation of aluminum alloys where the Zinc and Magnesium are added in different percentages as described in table (3.1). The pure aluminum was melted, alloyed systematically with the zinc and magnesium elements. Mixing and pouring temperature are sustained at (700ºC).This temperature has found very reasonable where the mixing practicing takes about (20minutes).The additions of alloying element with the high mixing velocity causing an excessive dross formation that must be removed frequently to avoid the problem of structure coarsening as revealed under microscopy.

The produced mixture of alloys are molded quickly to overcoming the problem of hydrogen dissolution and left to cool under the conditions of laboratory conditions, where the temperature is (35ºC) as it was measured. The alloys as produced were found to be macroscopically sound and almost free of gas defects.

4.2.1 Microstructure Observations of Prepared Aluminum Alloys & X-Ray Analysis:

Microstructure observations of Aluminum-base alloys under the conditions that are adopted in this work show that all alloys consist mainly of large dendrites (α-Al) with interdenderitic phases surrounded it. The dendritic structure comes as a result of slow cooling rate during the solidification process of prepared alloys.

Now, in order to make an accurate description of the evaluated microstructures of prepared alloys, it must support the optical microscopy observations with the x-ray diffractions examinations. The x-ray diffraction examinations for the prepared alloys, showed the intensity of constituent phases that developed after the solidification of prepared alloys. The following is a detailed description of the microstructures evolution of the prepared alloys:-

A. Microstructure of A-alloy:-

In order to describe the microstructures of the alloys at the conditions adopted in this work, it must take the following points into consideration:-

1. During alloying of pure aluminum with the zinc element a fast recovery (i.e. melting and dissolution) of zinc in a short time has been expected. That recovery coming as a result of the low melting temperature of zinc (419.5 ^{o}C) in comparison with aluminum (660 ^{o}C) [59] [60] .
2. A segregation problem is so expected also due to the large difference in densities between zinc and aluminum (7.14 g/cm^{3})for zinc and (2.6898 g/cm^{3}) for Al) [59] [60].

Zinc atoms do not tend to form an intermetallic phases with Aluminum atoms, which means that the interactions of Al-Zn is rather weak. The microstructure of A-alloy as can be seen in figure (4.1) consists mainly of large aluminum dendrites surrounded by interdenderitic and the phase ($Al_{0.71}Zn_{0.29}$) as it was revealed by the x-ray diffraction peaks (see figure (4.2) & table (4.1) that attached with the x-ray diffraction peaks)

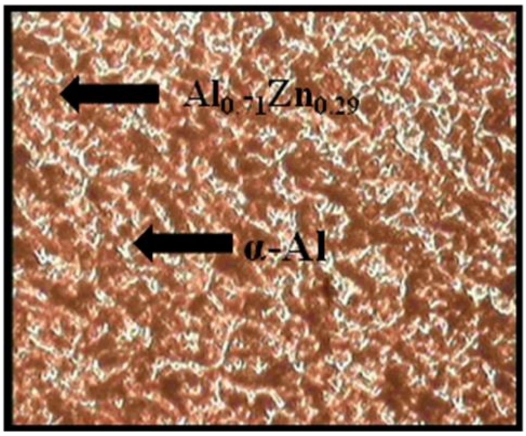


Figure (4.1)
Optical micrograph of A-alloy. Magnification x (400)

2θ (degree)	d-spacing(A°)	Constituent Phase	Intensity
38.253	2.352	α-Al	83
38.530	2.334	$Al_{0.71}Zn_{0.29}$	2

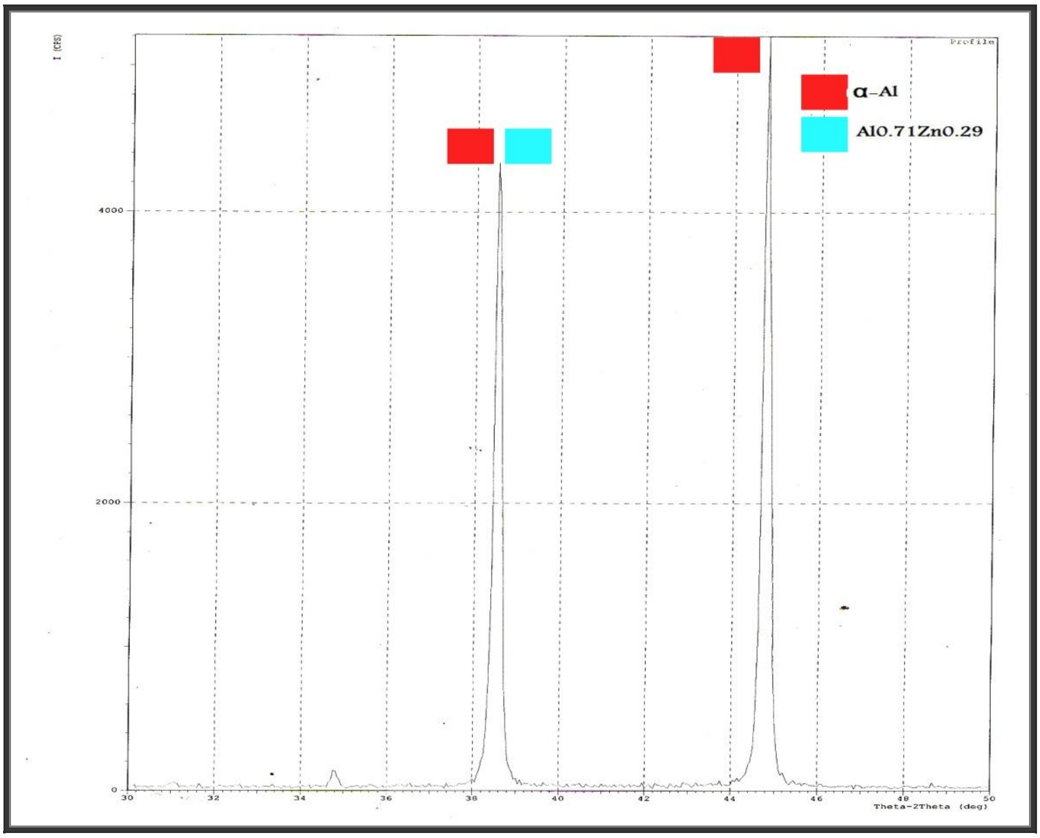


Fig (4.2)
X-ray diffraction analysis of A-alloy

Table (4.1)

Types of phases appeared in A-alloy according to the X-ray diffraction measurement

44.759	2.023	α-Al	100

As could be seen in the x-ray diffraction analysis, the developed phases consist of the products of the binary reactions between Zn and Al that occurs within the microstructure. The products of these reactions form a network that surrounds the (α-Al) phase as shown in the microstructure as shown in figure (4.1) above.

B. Microstructure of B-alloy:-

Recently, it has been pointed out to the Al-Mg-Zn system as a potential candidate to be used as an alloy for cathodic protection of structures that exposed to marine environment, paying special attention to the effect of the (τ-phase) in α-Al solid solution.

Now, it is known that, the as-cast microstructure of solidified alloy consists mainly of dendrites with eutectic between dendritic arms.

The addition of magnesium enhanced the refinement of dendritic structure of (α-Al). These refinements come as a result of supporting the growth of interdenderitic intermetallic phases by the Magnesium additions.

Following is a figure shows the optical micrograph of B-alloy. Figure (4.3) has been supported by an x-ray diffraction analysis of the same sample. The x-ray diffraction peaks as shown in figure (4.4) which shows a set of phases that are developed during the solidification process of the alloy under the adopted conditions in present work. These phases as it is revealed in table (4.2) that are attached with the x-ray diffraction peaks are mainly consist of ß(Al_2Mg)-phase in addition to the τ($Mg_{32}(Al,Zn)_{49}$)-phase that is presented in small amount . ß (Al_2Mg)-

phase also can be noted as dark spots around the major phase α-Al as can be seen in figure (4.3).

The predicted solidification sequence could be described as follows; the first phase candidate for growth is the α-Al phase that represents the major dendritic patterns .Now the liquid material that interfaces with the dendritic arms of α-Al phase is enriched with the zinc and magnesium solute of atoms. The results of x-ray diffraction analysis supporting the Al-Mg-Zn ternary phase diagram as shown in figure (4.4), where the ß (Al_2Mg)-phase is the dominant phase.

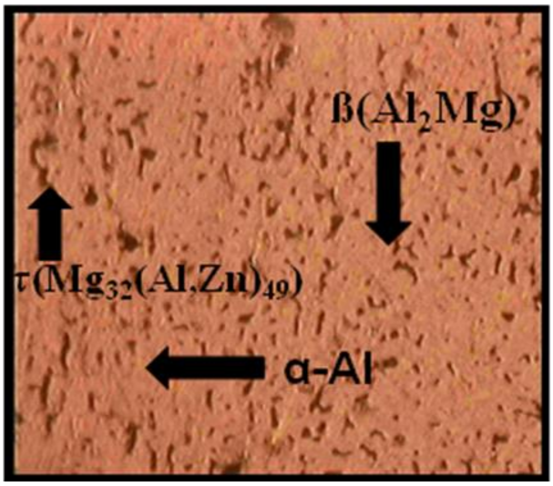


Figure (4.3)
Optical micrograph of B-alloy
Magnification X 400

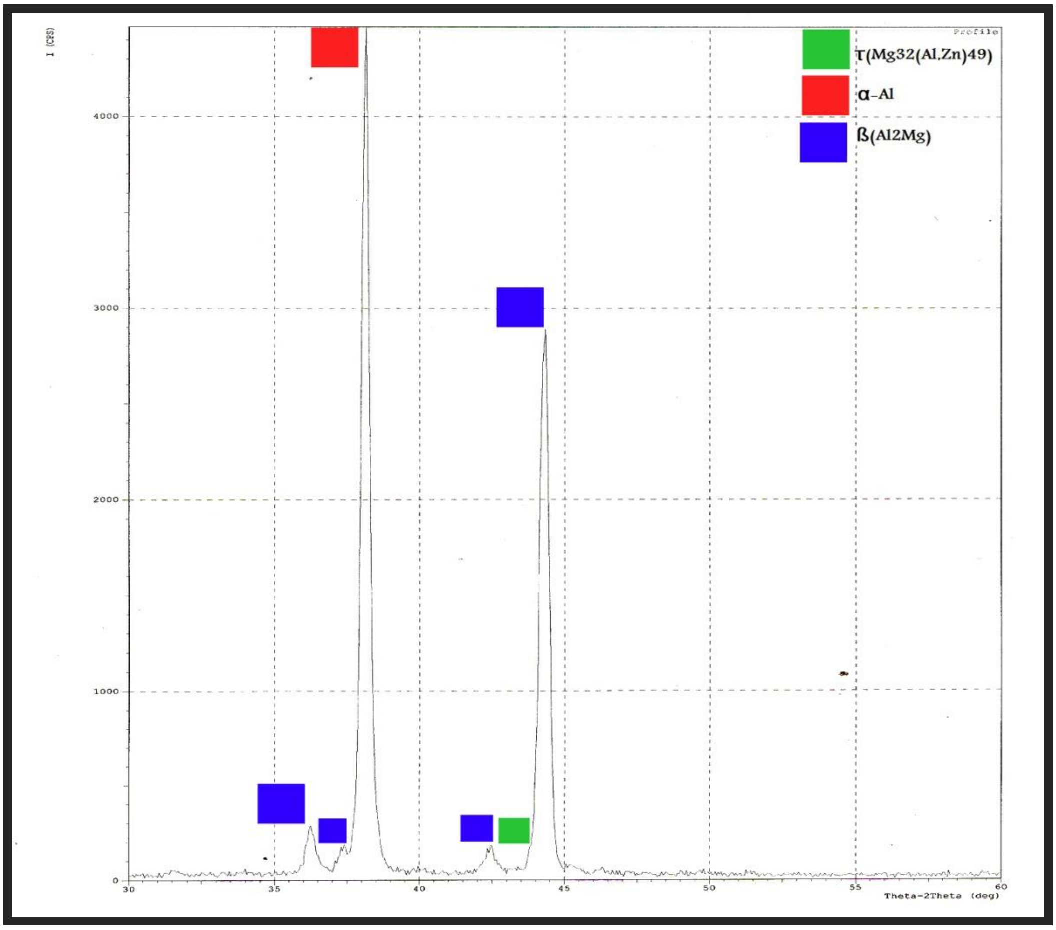


Fig (4.4)
X-ray diffraction analysis of B-alloy

Table (4.2)

Type of phases appeared in B-alloy according to the X-Ray diffraction measurement

2θ (degree)	d-Spacing(A°)	Constituent Phase	Intensity
36.25	2.475	ß(Al_2Mg)	6
37.41	2.403	ß(Al_2Mg)	5
38.128	2.358	α-Al	100
38.58	2.331	α-Al	5
42.30	2.134	ß(Al_2Mg)	3.71
42.44	2.128	τ($Mg_{32}(Al,Zn)_{49}$)	2.18

44.291	2.043	ß(Al_2Mg)	64

C. Microstructure of C-alloy:-

The chemical composition of this alloy shows that, the alloy contains the same amount of zinc as in B-alloy with an increasing in Mg content, so that it is possible to study and monitoring the effect of Mg increasing on the behavior of (Al-Mg-Zn) alloys to be used as sacrificial anode in the process of oil pipelines protection against corrosion damages.

Microstructure observation of this alloy as shown in figure (4.5) shows large dark region as well as dark spots around the major phase α-Al ,a large dark region represents τ($Mg_{32}(Al,Zn)_{49}$)-phase and small dark spots represents ß(Al_2Mg)-phase. Figure (4.5) has been supported by an x-ray diffraction analysis of the same sample.

Figure (4.6) represents the x-ray diffraction peaks of C-alloy, the phases that are developed in this alloy during the solidification process as it was revealed in table (4.3) that is attached with the x-ray diffraction peaks consist mainly of ß(Al_2Mg)-phase in addition to the τ($Mg_{32}(Al,Zn)_{49}$)-phase that is exist in a larger amount this time as compared with τ($Mg_{32}(Al,Zn)_{49}$)-phase that developed in B-alloy. This can be seen clearly in figure (2.14) which shows that an increasing in Mg content with the same amount of Zn content will cause an increment in the amount of τ(Mg32(Al,Zn)49)-phase in alloy.

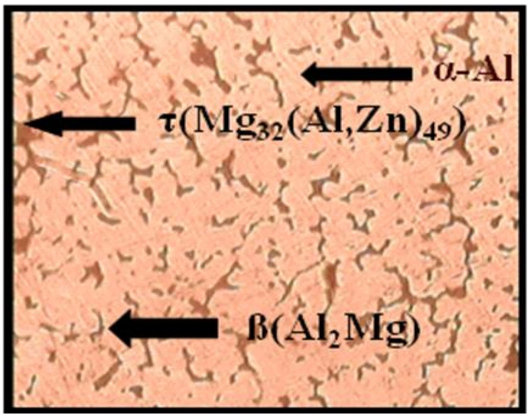


Fig (4.5)
Optical micrograph of C-alloy (Magnification X 400)

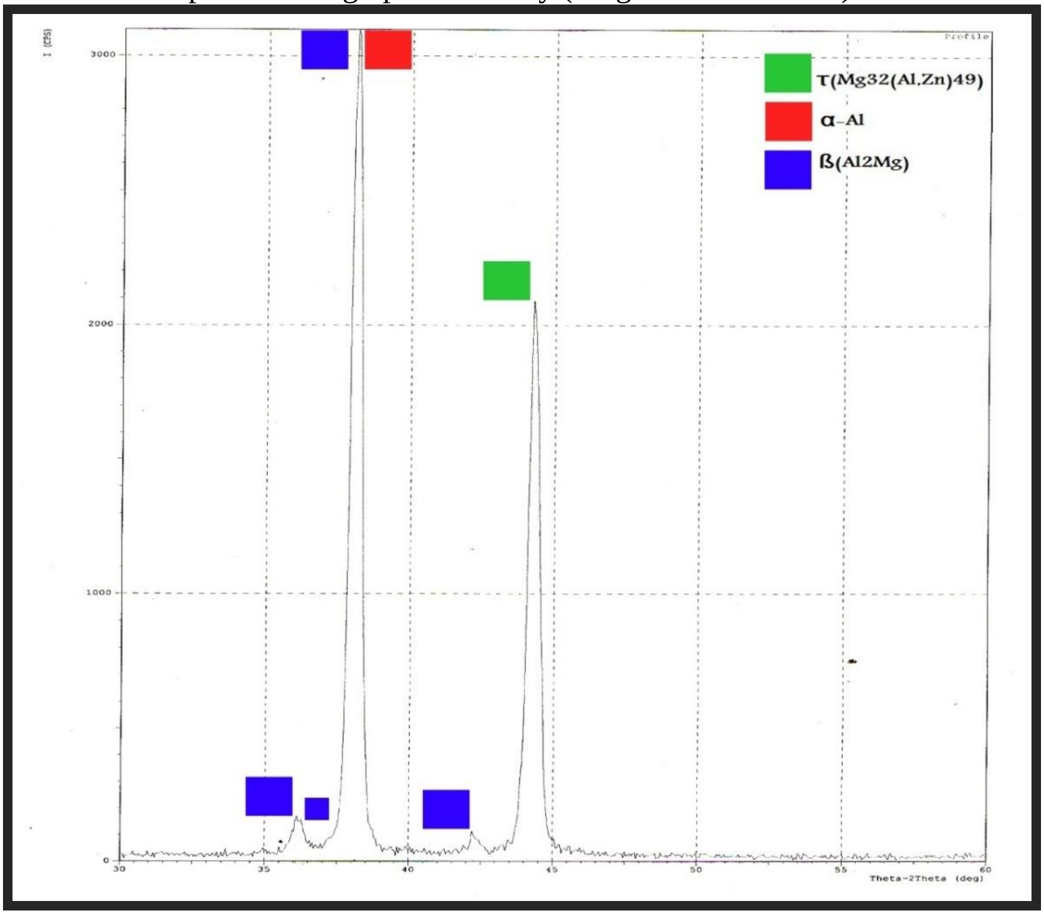


Fig (4.6)
X-ray diffraction analysis of C-alloy

Table (4.3)

Type of phases appeared in C-alloy according to the x-ray diffraction measurement

D. Microstructure of D-alloy:-

Chemical composition of this alloy shows an obvious increasing in Mg and Zn contents as compared with previous produced alloys i.e. (A, B, and C). This increasing will affect directly the resulting phases that are developed during the solidification of this alloy. The as-cast microstructure as shown below in figure (4.7) of the solidified alloy consists mainly of dendrites arms with intermetallic phases between the arms.

Figure (4.8) represents the x-ray diffraction peaks of D -alloy, the developed phases in this alloy as it is revealed in table (4.4),which consists mainly of τ (Mg_{32} (Al, Zn) $_{49}$) phase and small amount of (Mg_2Zn_3) phase. The τ (Mg_{32} (Al, Zn) $_{49}$) phase can be noted as a large dark regions surround the major (α-Al) phase as shown in figure (4.7).

2θ (degree)	d-Spacing(A°)	Constituent Phase	Intensity
36.261	2.478	ß(Al2Mg)	5
37.3	2.408	ß(Al2Mg)	5
38.152	2.356	α-Al	100
38.534	2.130	ß(Al2Mg)	5
42.39	2.130	ß(Al2Mg)	4
44.32	2.041	τ(Mg32(Al,Zn)49)	23

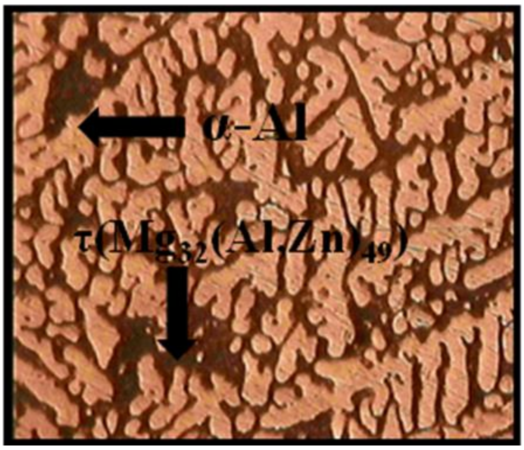


Fig (4.7)
Optical micrograph of D -alloy .Magnification X 400

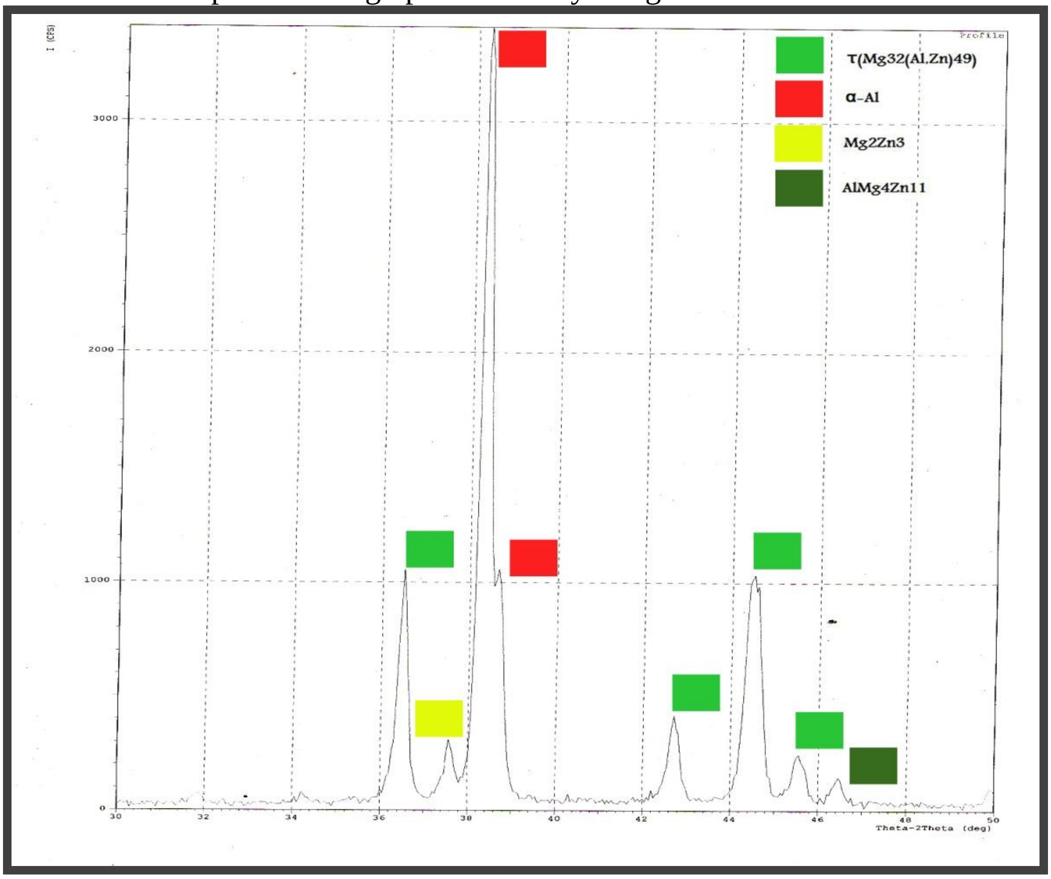


Fig (4.8)
X-ray diffraction analysis of D-alloy

Table (4.4)

Type of Phases Appeared in D-Alloy According to the X-Ray Diffraction Measurement

2θ (degree)	d-Spacing(A°)	Constituent Phase	Intensity
36.50	2.45	τ(Mg32(Al,Zn)49)	40
37.58	2.39	Mg2Zn3	7
38.312	2.347	α-Al	100
38.68	2.325	α-Al	18
42.707	2.115	τ(Mg32(Al,Zn)49)	11
44.494	2.034	τ(Mg32(Al,Zn)49)	29
45.551	1.989	τ(Mg32(Al,Zn)49)	6
46.427	1.95	AlMg4Zn11	3

E. Microstructure of E-alloy:-

E-alloy represents the reference alloy in this work. It was the same alloy that is used in reference [27] and now it is reprepared for comparing the results of present work. It was originally contains a suitable amount of Zn and Mg. The as-cast microstructure of solidified alloy consists mainly of dendrites arms with interdenderitic phases that are developed during the solidification of alloys between arms as shown in figure (4.9).

X-ray diffraction analysis as shown in figure (4.10) shows a set of phases that were developed as it was stated above during the solidification process of alloy. These phases as it is revealed in table (4.5) consist of τ (Mg_{32} (Al, Zn) $_{49}$) and Mg_2Zn_3 phases as well as a reasonable amount of ß (Al_2Mg) and $AlMg_4Zn_{11}$ phases. Now according to the table (4.5) it can be noted that τ (Mg_{32} (Al, Zn) $_{49}$) phase occurs in smaller amount than in D-alloy and this is shown in figure (4.9) which shows the existence of large dark region of τ (Mg_{32} (Al, Zn) $_{49}$) phase around the major phase α-Al phase.

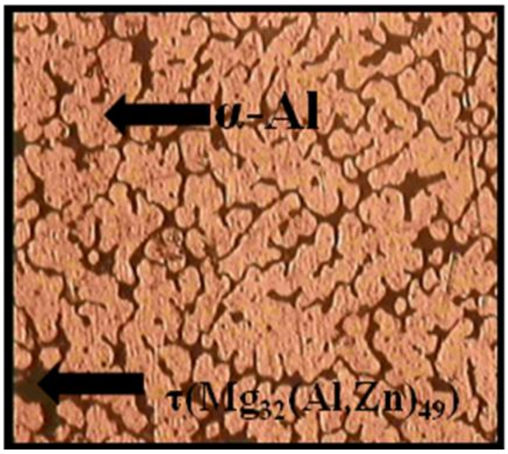


Fig (4.9)
Optical micrograph of E -alloy
Magnification X 400

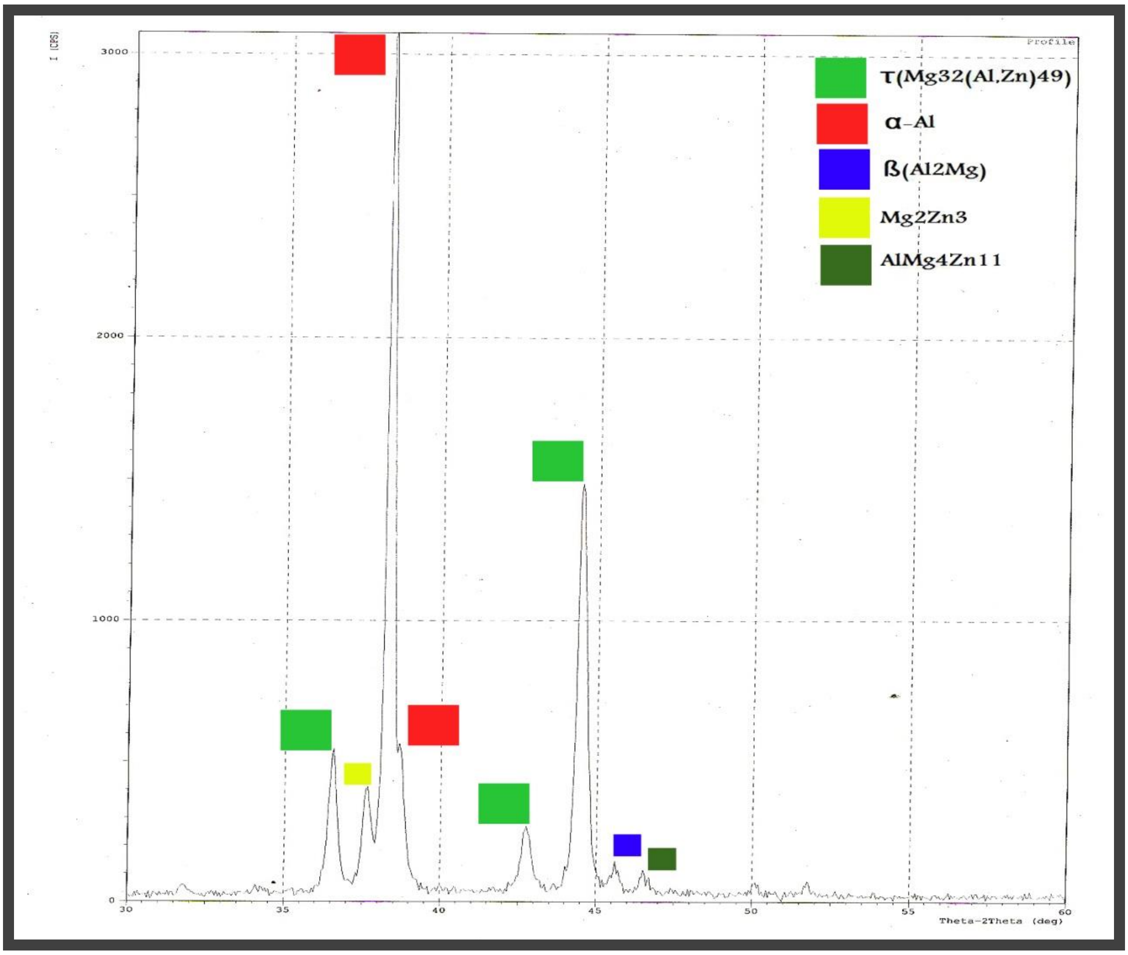


Fig (4.10)
X-ray analysis of E-alloy

Table (4.5)

Type of Phases Appeared in E-Alloy According to the X-Ray Diffraction Measurement

2θ (degree)	**d-Spacing(A°)**	**Constituent Phase**	**Intensity**
36.54	2.456	τ($Mg_{32}(Al,Zn)_{49}$)	15
37.64	2.387	Mg_2Zn_3	11
38.29	2.348	α-Al	100
38.78	2.319	α-Al	13
42.752	2.113	τ($Mg_{32}(Al,Zn)_{49}$)	7
44.47	2.035	τ($Mg_{32}(Al,Zn)_{49}$)	48
45.52	1.993	ß(Al_2Mg)	4
46.55	1.946	$AlMg_4Zn_{11}$	3

4.2.2 Microstructure Observation of Pipeline Material

Steel pipeline is manufactured essentially from an alloy of iron and carbon (0.34wt %) which also contains manganese and a variety of residual elements. These residual elements were present within the raw materials used in the production process. The appearance of pure iron is so clear during the ferrite phase with the bright fields a long the microstructure shown below in figure (4.11). The dark parts represent the constituent containing the carbon.

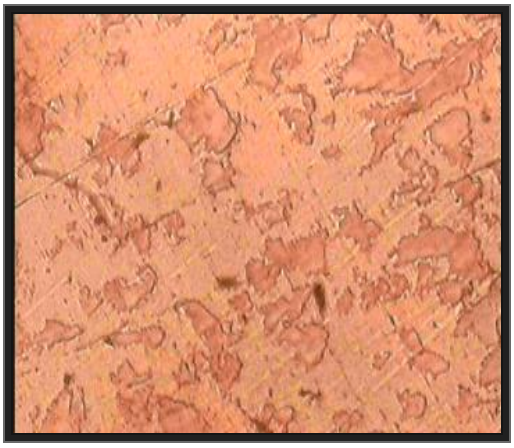


Fig (4.11)
Microstructure of steel

Magnification X 400

4.2.3. *Microstructure Observation of Mg-alloy:-*

It is known that, the properties of Mg can be improved by adding suitable alloying and the alloys in use find extensive application in many engineering fields. The addition, of manganese is to raise the corrosion resistance and weld ability of alloy. Figure (4.12) shows the microstructure of this alloy.

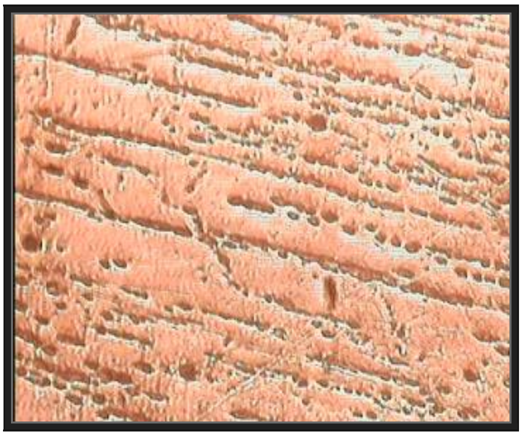


Fig (4.12)
Microstructure of Mg-alloy
Magnification X 400

4.3 Tafel Extrapolation Results Discussion:-

Polarization experiments were carried out in simulated conditions that were adopted in this work. The solution has the same characteristics of AL-FAO soil. These tests are carried out to determine the corrosion potential and corrosion current density for each prepared alloy and the steel pipe material. The polarization curves and its discussions for different alloys are given as follows:

4.3.1 *Tafel Extrapolation of Steel Pipe Sample*

Polarization curves of steel pipe sample shown in figure (4.13) below shows E_{corr} and i_{corr}, where E_{corr} value is (-735.9mV) and i_{corr} (14.73µA/cm²).The corrosion current for steel as can be seen from the figure below is high.

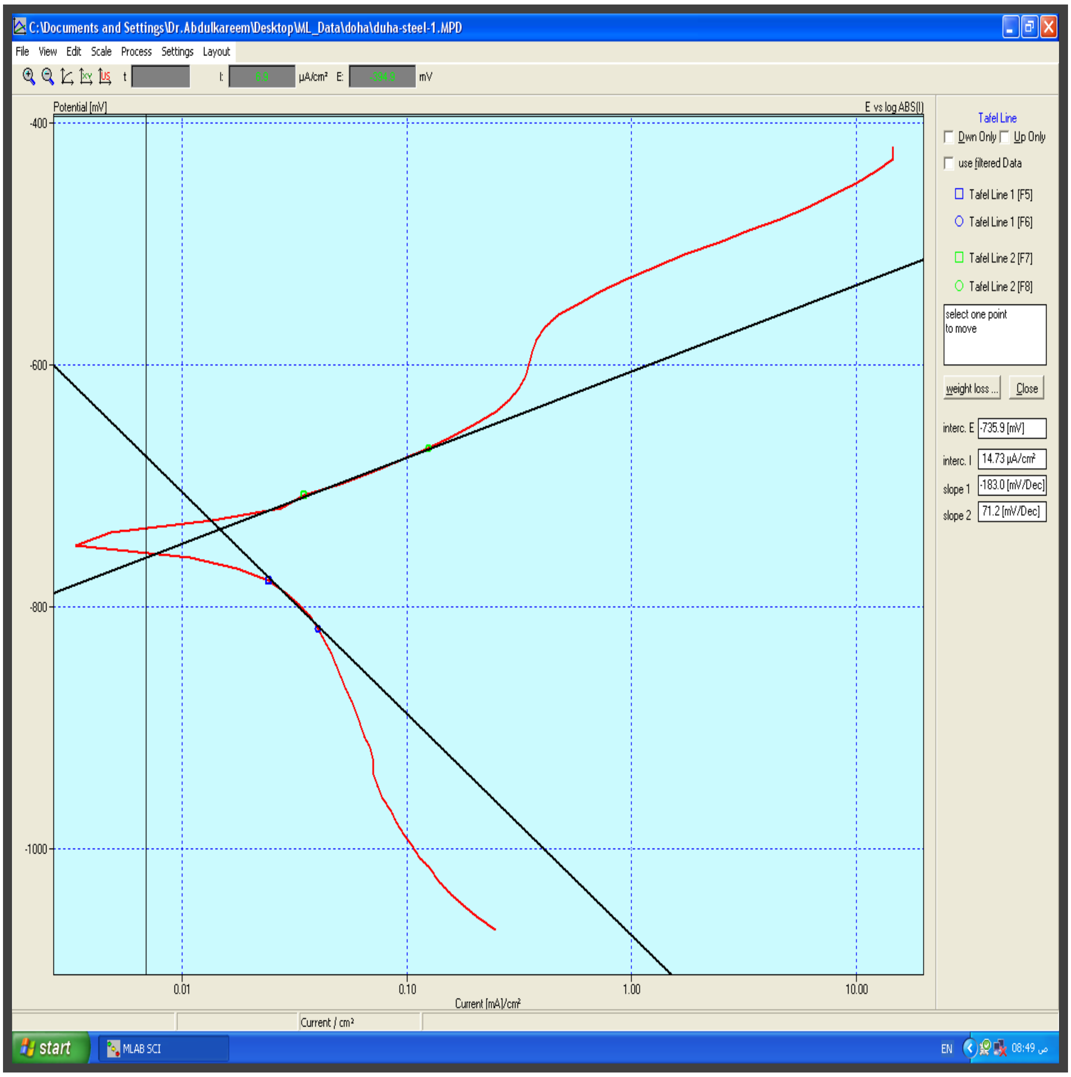


Fig (4.13)

Polarization curves of steel pipe sample immersed in AL- FAO soil solution.

The steel pipe sample is connecting to auxiliary electrode (platinum) (i.e. steel will work as an anode).

4.3.2 *Tafel Extrapolation Test Results of A-Alloy*

The application of a sacrificial anode (A-alloy) serves to reducing the corrosion rate of cathode (steel pipe sample) as the present work is objected. Figure (4.14) shows, the polarization data of the sacrificial anode (A-alloy) at the assumption conditions that are adopted in this work, where the solution is the simulated solution of AL-FAO soil as it was mentioned in the experimental work.

The polarization curves as shown below, show that the corrosion potential in the conditions of as cast A-alloy ,the corrosion potential is (-977.3mV) and the corrosion current i_{corr}=1.51µA/cm. However, it should be noted that the current density passed in this experiment was small (i.e. 1.51 µA/cm^2).

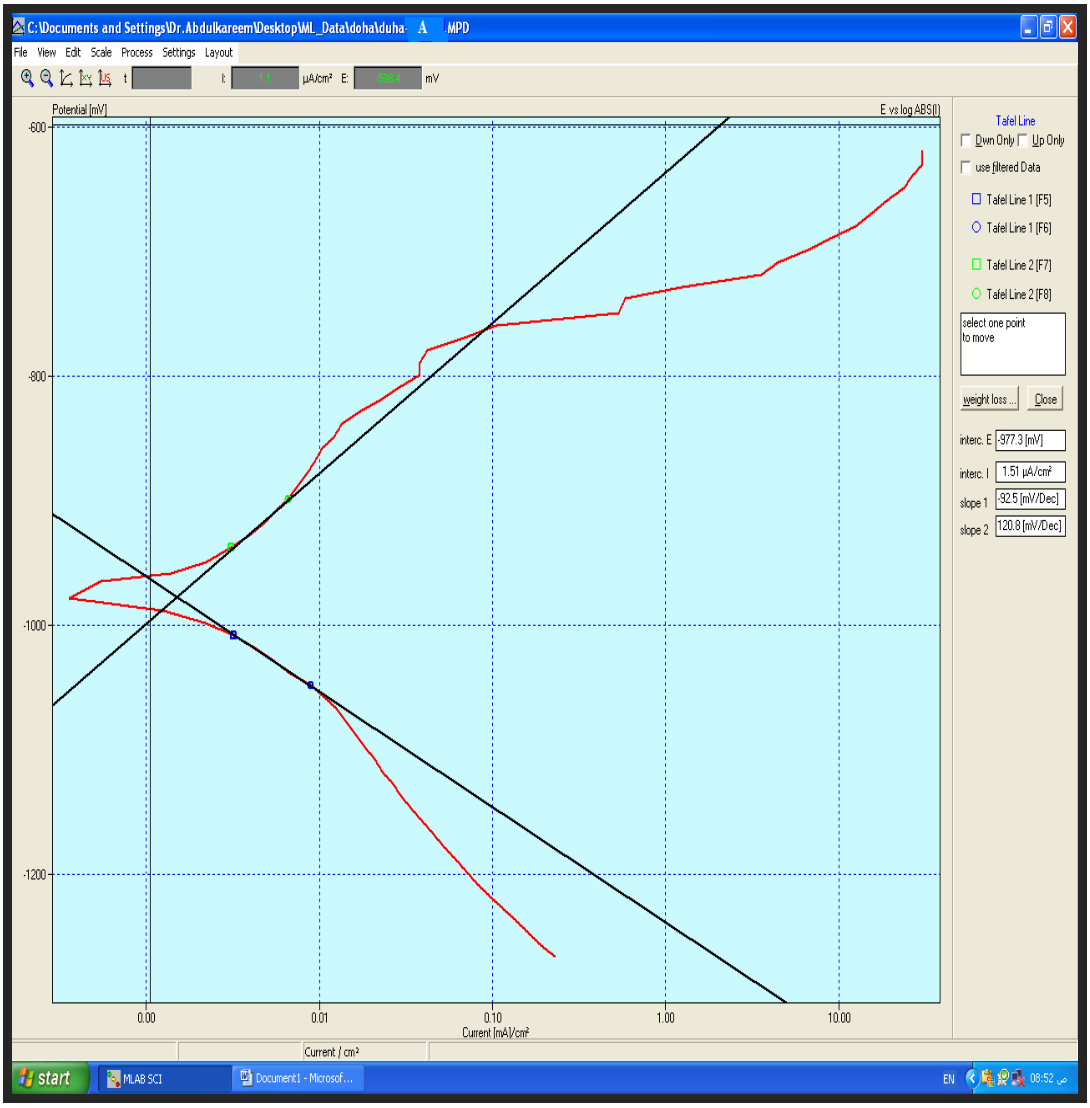


Fig (4.14)
Polarization curves for (A-alloy) sample immerse in Al- FAO soil solution

4.3.3 ***<u>Tafel Extrapolation Test of B-Alloy</u>***

The polarization curves of B-alloy are shown in figure (4.15) below. The behavior of this alloy was different to some extent from that seen in A-alloy. The first different, B-alloy is less negative ($E_{corrosion}$) = (-909.7mV) and higher corrosion current (i_{corr}=8.9µA/cm^2).

The chemical composition of B-alloy is different from that of A-alloy; the Magnesium which is the second constituent element in addition to the Zinc content that is presented in (8%wt).These alloy constituent (i.e. Mg and Zn) with these weight percentages play an important role in producing a set of intermetallic phases that in turn controls the corrosion behavior of such alloy. The major phase as it was clear from the x-ray diffraction analysis is shown in figure (4.4).

It is clear from the polarization curves of this alloy that, the corrosion current density is shifted to higher corrosion current ranging from (1.51 μA/cm^2)in A-alloy to (8.9μA/cm^2) in the case of B-alloy.

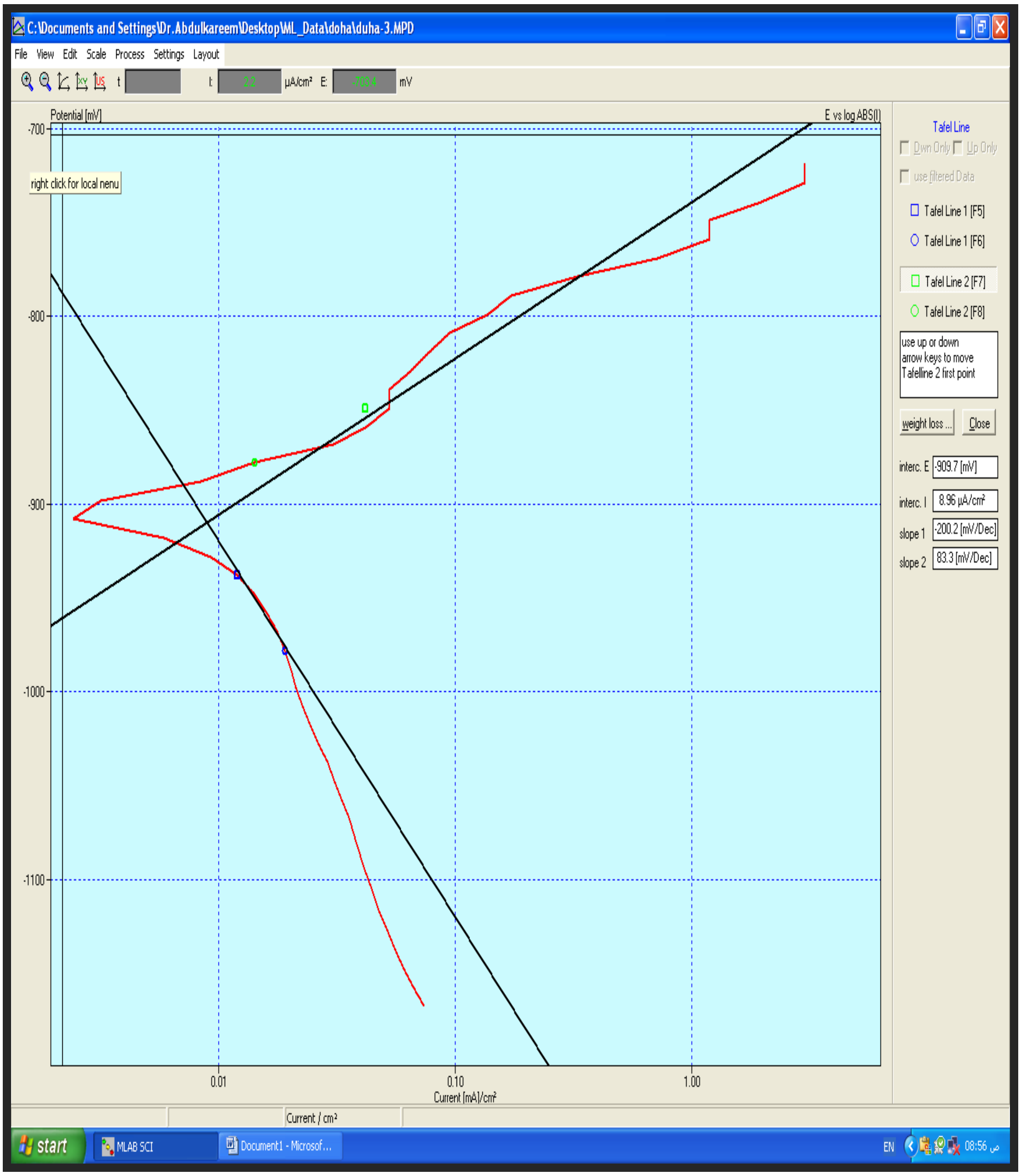


Fig (4.15)

Polarization curve for (B-alloy) sample immerse in AL-FAO soil solution.

4.3.4 ***Tafel Extrapolation Test of C-Alloy***

Polarization curves of C-alloy as shown in figure (4.16) shows that ($E_{corrosion}$) = (-1031.0 mV), i_{corr} for this alloy is equal to (12.36 µA/cm²), which is the highest current corrosion among the tested alloys.

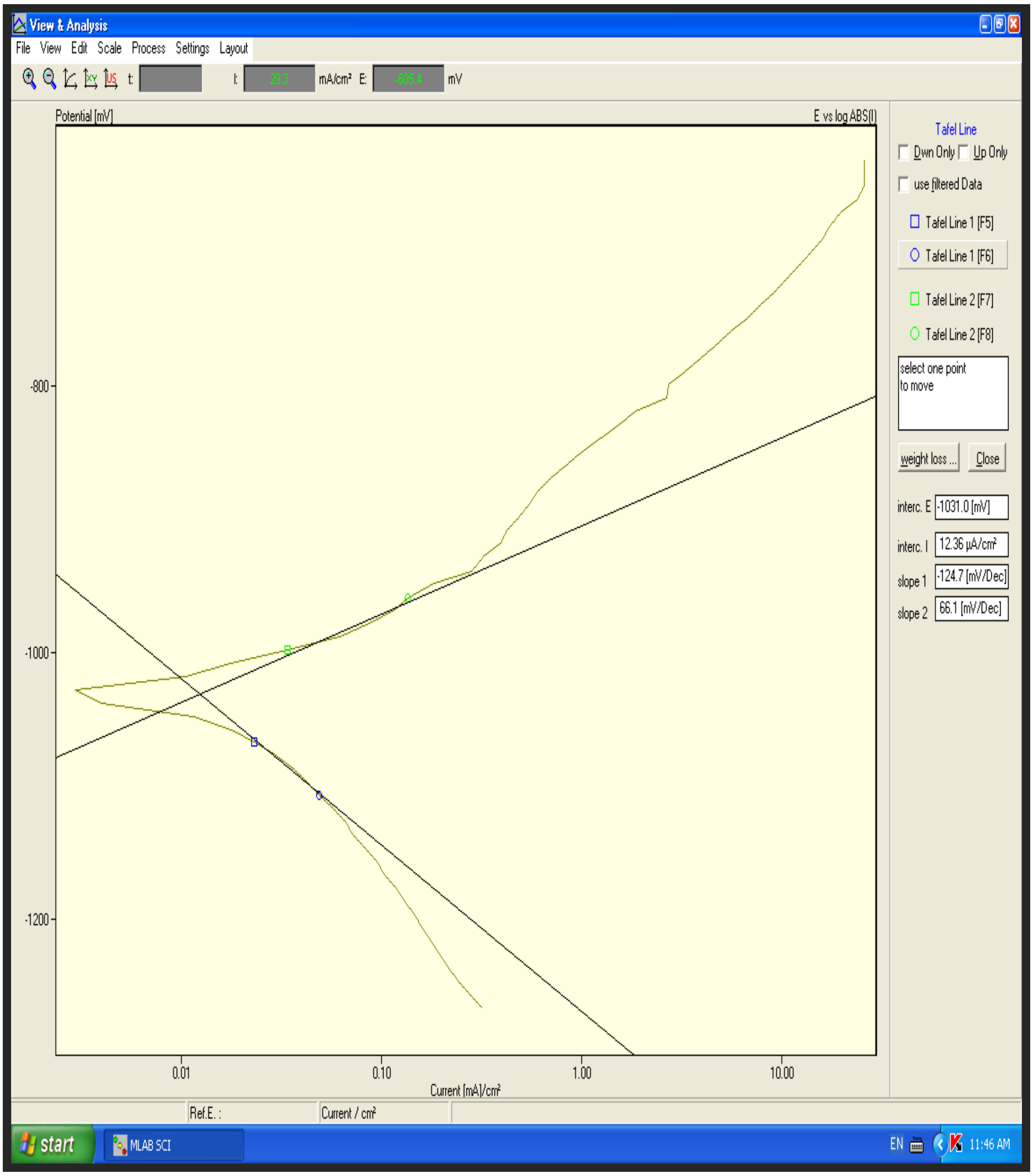


Fig (4.16)
Polarization curve for (C-alloy) sample immerse in AL-FAO soil solution.

4.3.5 ***Tafel extrapolation test of D-alloy***

The polarization curves of D- alloy as shown in figure (4.17) below shows that i_{corr} for this alloy is high (6.63 µA/cm²), ($E_{corrosion}$) = (-960.4mV). This alloy shows good surface activation (i.e. high i_{corr})

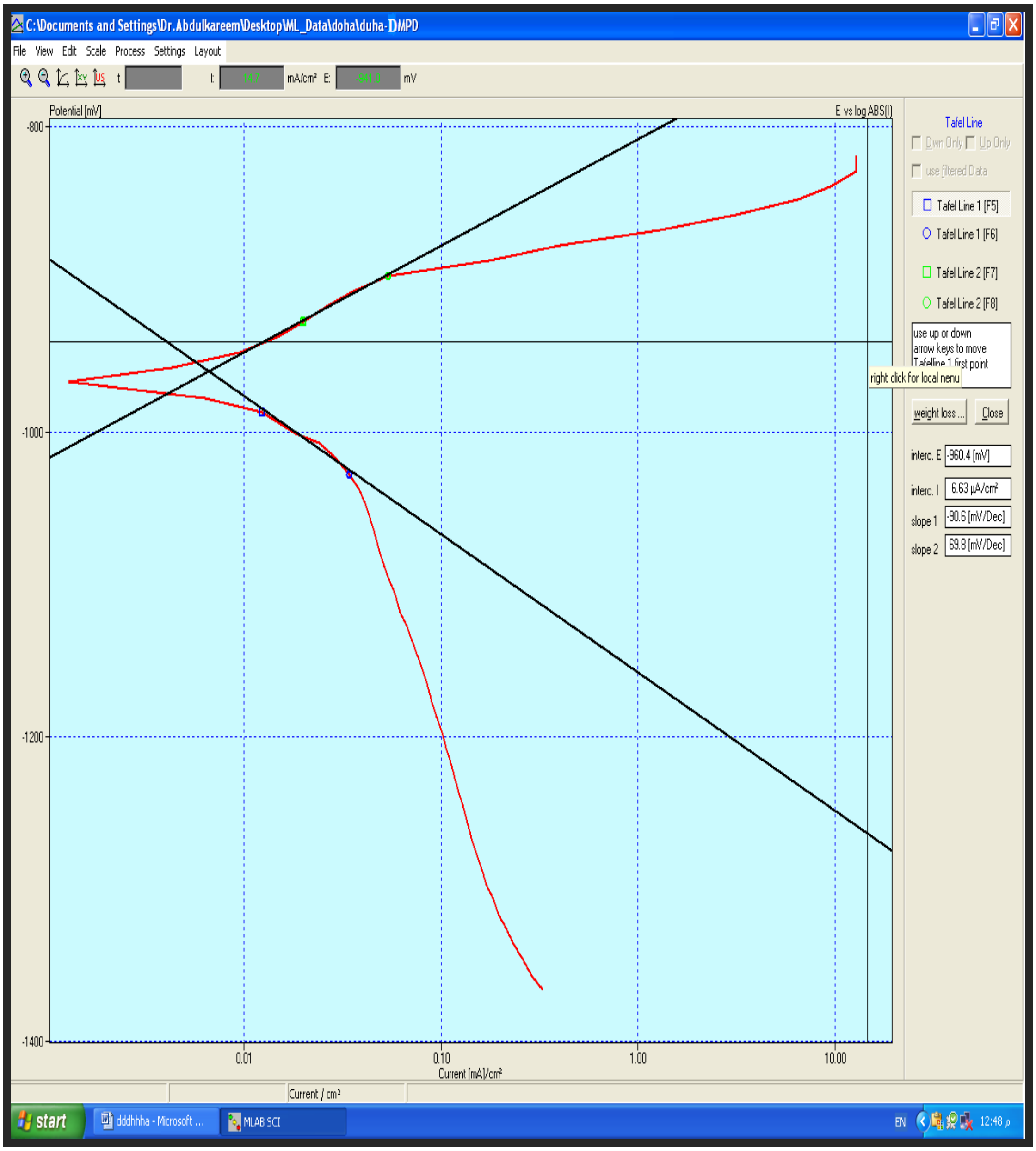


Fig (4.17)
Polarization curve for (D-alloy) sample immerse in AL-FAO soil solution.

4.3.6 ***Tafel Extrapolation Test of E-Alloy***

Figure (4.18) shows, the polarization data of the sacrificial anode (E-alloy).The polarization curve shows that the i_{corr} of alloy is equal to *(*8.16

μA/cm²) which is higher than that of D and A alloy and also lower than that of C and B alloy. ($E_{corrosion}$) = (-1080.1mV).

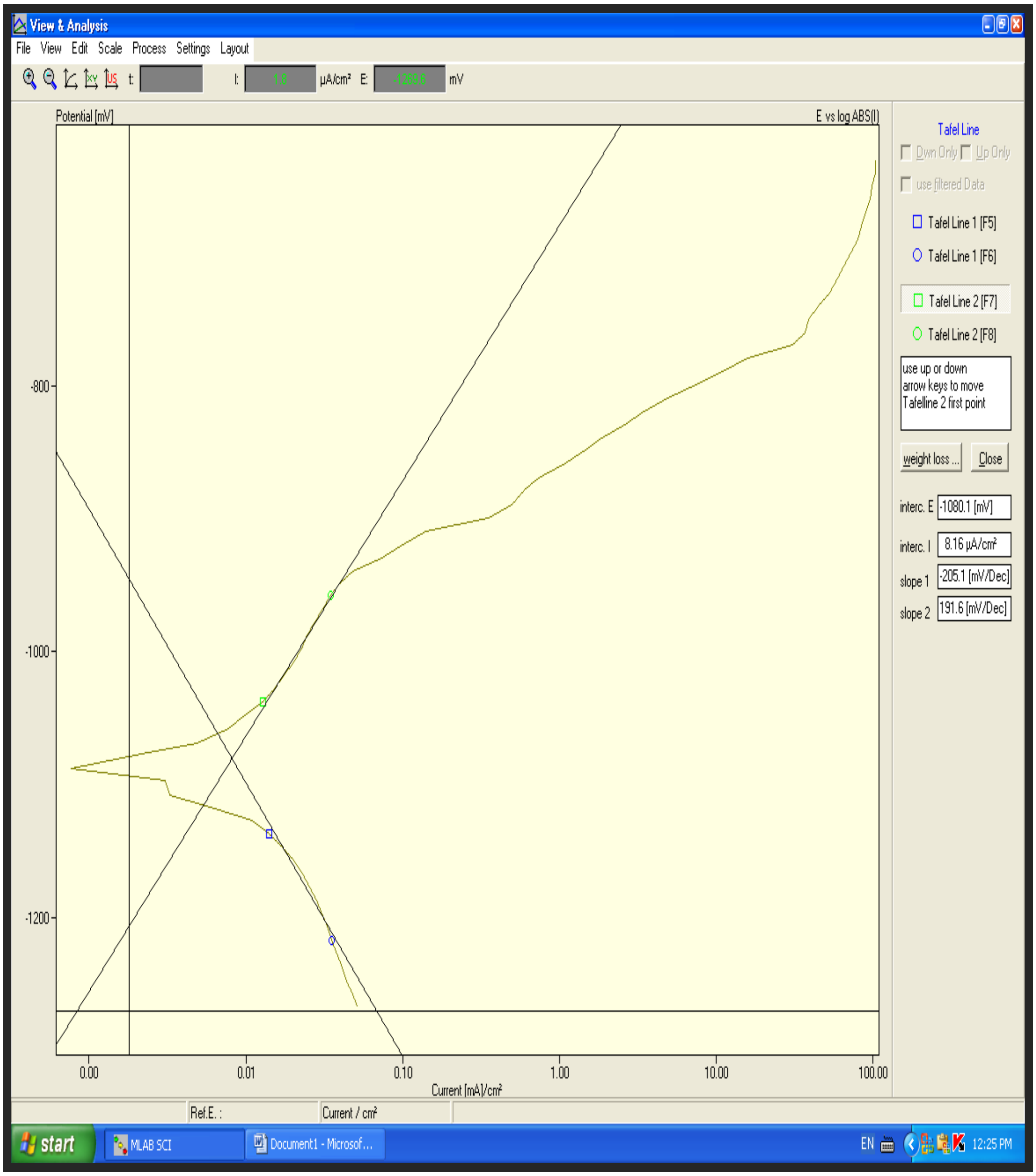


Fig (4.18)

Polarization curve for (E-alloy) sample immerse in AL-FAO soil solution

4.3.7 ***Tafel Extrapolation Test of Mg-Alloy***

Figure (4.19) shows, the polarization data of the sacrificial anode (Mg -alloy) .The polarization curve shows that the i_{corr} is equal to (67.08μA/cm²), which is the highest i_{corr} among all the tested Al-alloys that are produced in this work. This value proves the higher activity and lower efficiency* of Mg-alloy.

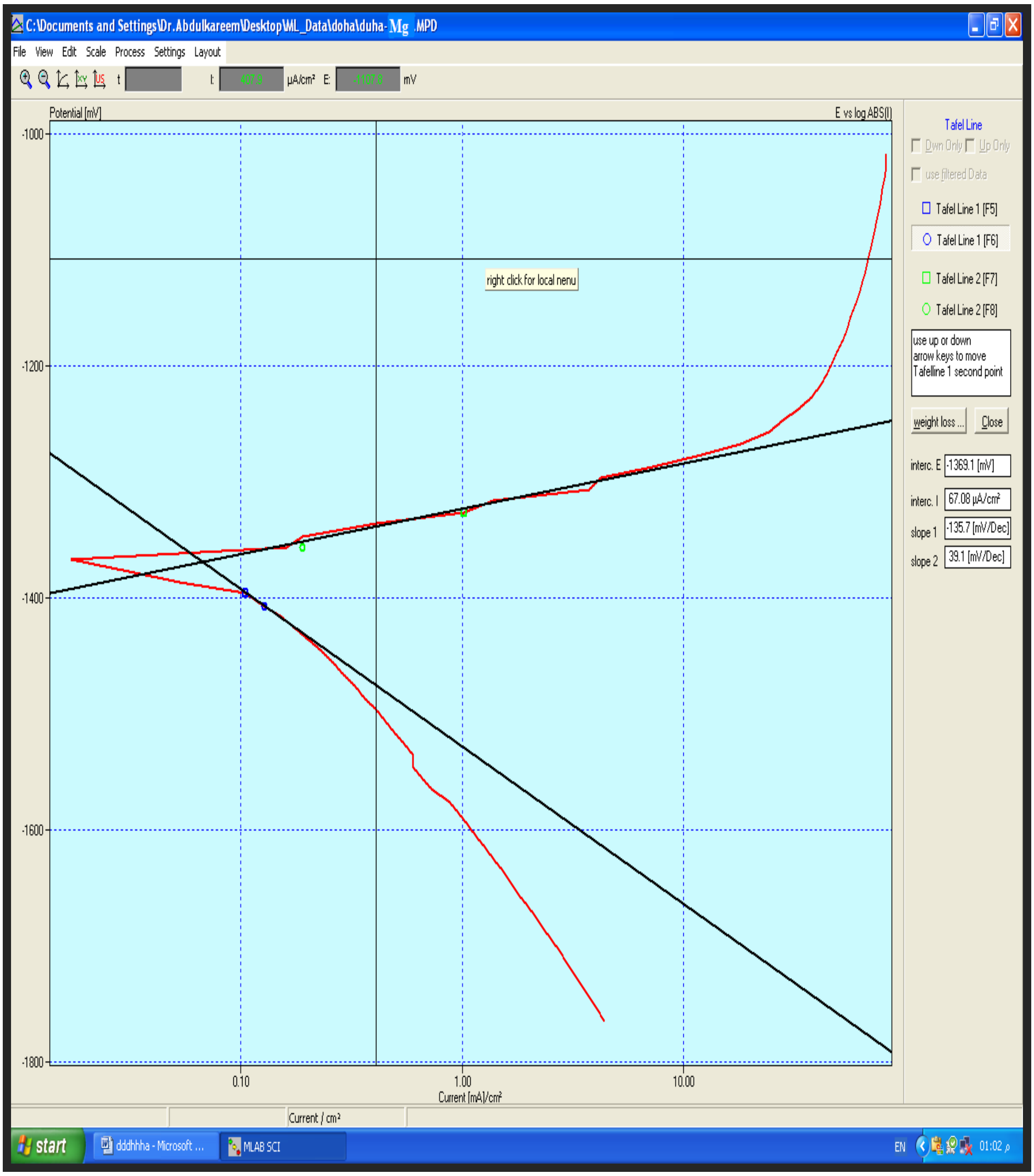


Fig (4.19)
Polarization curve for (Mg-alloy) sample immerse in AL- FAO soil solution

* Efficiency%=practical current capacity (CC)/Theoretical current capacity (CCth)
CC=i.t/Δw (A.hr/kg) , CCth is given for each alloy

4.4. Discussion of Wight Loss Results & Microstructural Observation:-

Weight loss measurement of each the consumable or sacrificial anode that connect to steel or protected structure gives a reliable indications about how much material to be required for the protection the specific structure (i.e. pipeline) and also what exactly the materials behaves electrochemically during the exposed time to the corrosive medium.

4.4.1 *Steel Pipe Sample*

Firstly the steel pipe sample was tested separately in AL-FAO soil in order to study the behavior of steel in this medium (i.e.AL-FAO soil). The soil has been prepared in soil laboratory under high attention after the analysis of AL-FAO soil and determining its characteristics such as pH, chlorides content...etc. Room temperature was selected to be a tested temperature.

Figure (4.20) shows the rate of steel pipe specimen consumption (dissolution) that represents the corrosion rate with the time at constant temperature in AL-FAO soil.

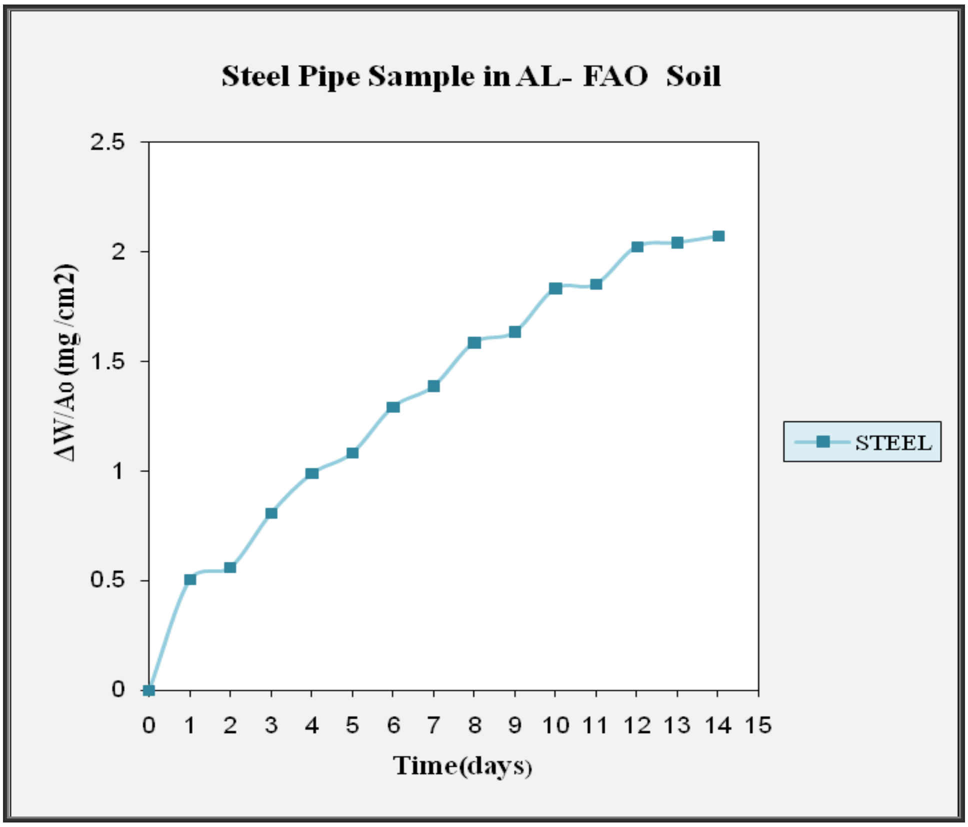
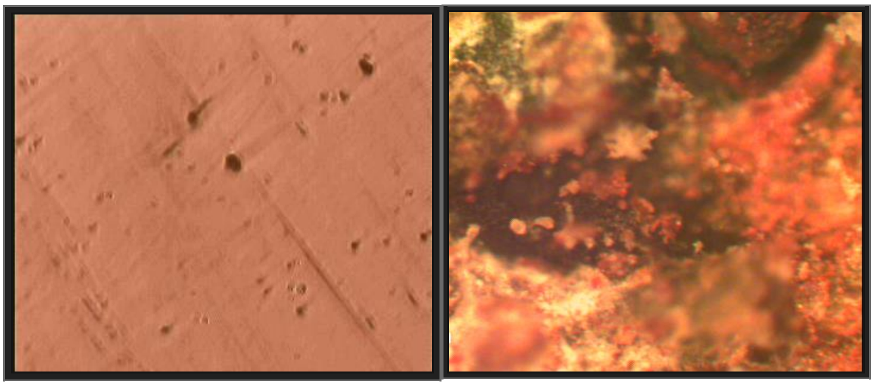


Figure (4.20)
Specific weight loss of steel with time at constant temperature in the media of AL-FAO soil

It is noted from the above figure that a relatively uniform specific weight loss with time (i.e. the specific weight has been decreased).This decreasing is due to the oxidation of steel surface as a result of rusting the pipe surface with $(Fe_2O_3).H_2O$ [61].

The oxidation film seems to be a porous look like, poorly adherent, coarse and non protective film and this fits the results obtained by other researchers [61] [62] [63].Pitting corrosion is so clear on the steel pipe specimen surface due to the aggressive effect of Cl^- ions that is presented in large amounts in the soil of AL-FAO region in a large amounts and that will make the corrosion continuous on the surface of steel pipe specimen [62] [64] [65].

Figure (4.21) represents the micrograph of steel sample prior to and after 14 day exposure to the AL-FAO soil media .Figure (4.21) (a) shows that steel surface is clean with the presence of small defect on the steel surface, while figure (4.21) (b), shows the existence of dark surface and obscure surface appearance. The uniform attack is the dominants attack as well as pitting corrosion and that can be noted clearly by visual observation. The uniform corrosion is characterized by the scales layer that present clearly on the surface of specimens.



(a) (b)

Figure (4.21)

Micrograph of steel pipe sample prior and after exposure to AL-FAO soil.100x

(a) Before exposure. (b) After exposure

4.4.2. *Examination of Sacrificial Anode System*

After the determination of corrosion behavior of steel pipe samples in the medium of AL-FAO soil, where a uniform and pitting corrosion are clear occurring on the surface of steel pipe which in turn causing a continuous corrosion. The next step is the examination and evaluation of the behavior of produced aluminum alloys and Mg-alloy in the protection of steel pipe samples.

The tests are carried out by connection of the dissimilar materials (i.e. the sacrificial and protected material) and immersion the couple of materials in the AL-FAO soil .The couple now represent a galvanic cell, where the Al-alloy represents the anode and the steel pipe sample represent a cathode. Knowing that, the test is carried out at room temperature.

The surface area of steel specimens used in this work $A_{surface}$ is (10. 3372cm^2) and for alloys $A_{surface}$ is (8.1012 cm^2).These surface areas were chosen and settled constant during all the weight loss practices.

Generally, the cathodic reaction is so expected as that given in the equations (2.2) (2.10) (2.11).The anodic reactions are the consumption of Al, Zn, Mg metals are as follows:-

$$Al \rightarrow Al^{+3} + 3e^- \quad \ldots\ldots\ldots \quad (4.1)$$

$$Mg \rightarrow Mg^{+2} + 2e^- \quad \ldots\ldots\ldots \quad (4.2)$$

$$Zn \rightarrow Zn^{+2} + 2e^- \quad \ldots\ldots\ldots \quad (4.3)$$

The following is a detailed exploring and discussions of the corrosion behavior of Al prepared alloys and Mg-alloy as a system with the steel pipe samples:-

1. **Discussion of weight loss test of the sacrificial anode A- alloy that connected to the steel sample:**

A-alloy is the first alloy that is prepared with a given chemical composition as shown in table (3.1).This alloy was chosen firstly for the weight loss evaluation during the protection process of steel pipe samples. Figure (4.22) shows the results of ($\Delta W/A_0$) for the alloy (i.e. A-alloy) and steel pipe sample with the increasing exposure time at the conditions adopted in this work.

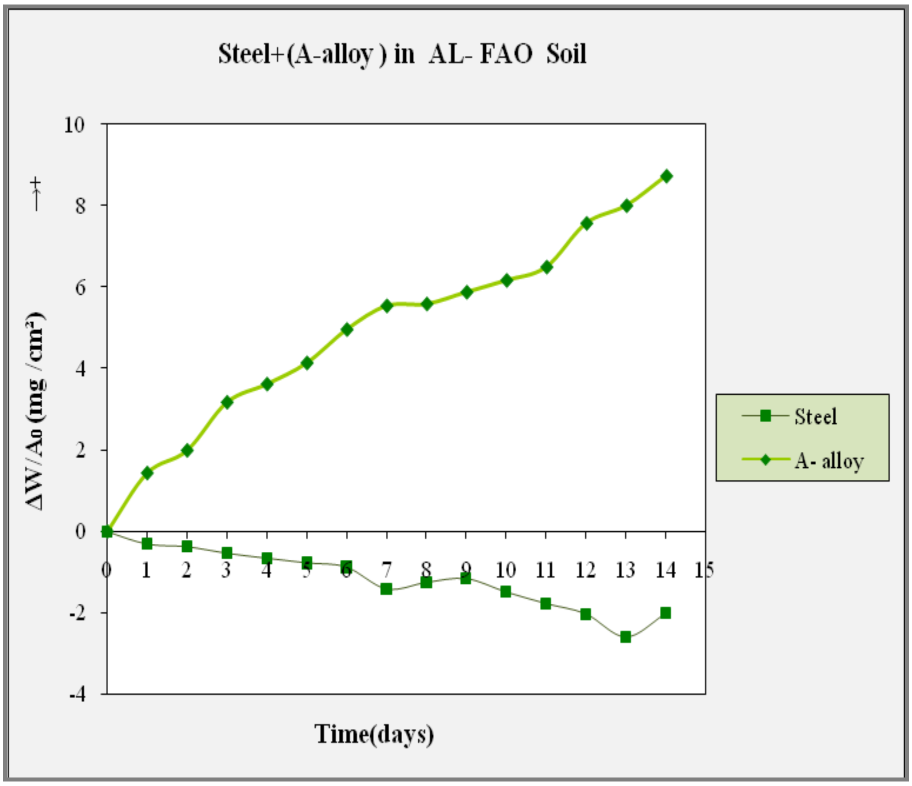


Fig (4.22)
Relation between ($\Delta W/A_0$-Time) for (Steel + A-alloy) cell in AL-FAO soil

It is clear from the above figure that the weight loss of the selected alloy (i.e. A-alloy) is increasing almost uniformly with increasing exposure time. The weight loss is still increasing at the first 14 day of exposure time to reach the value of (8.721 mg/cm^2).The steel pipe sample in the other hand shows some increasing in weight (i.e.no weight loss)with the increasing of exposure time.

Many reasons could be expected standing behind such behavior of A-alloy during this preliminary testing. These reasons can be summarized as follows:-

a. Electrical connecting of A-alloy to the steel pipe sample in the medium of AL-FAO soil creates a potential generated between the anode that is represented by A-alloy and cathode that is represented by steel pipe sample. As a result, a driving voltage will be developed and it will lead to the corrosion of more active metal of the two metals that were connected (i.e. A-alloy).Consequently, a discharge current will be developed according to equations (4.1), and (4.3) above passing between the anode (A-alloy) and cathode (steel sample).As a result, the less active metal (steel pipe sample) will be protected cathodically against corrosion. Ions will be liberated to the electrolyte (AL-FAO soil) while, the electrons moved towards the cathode via the electric conductor (i.e. copper wire).

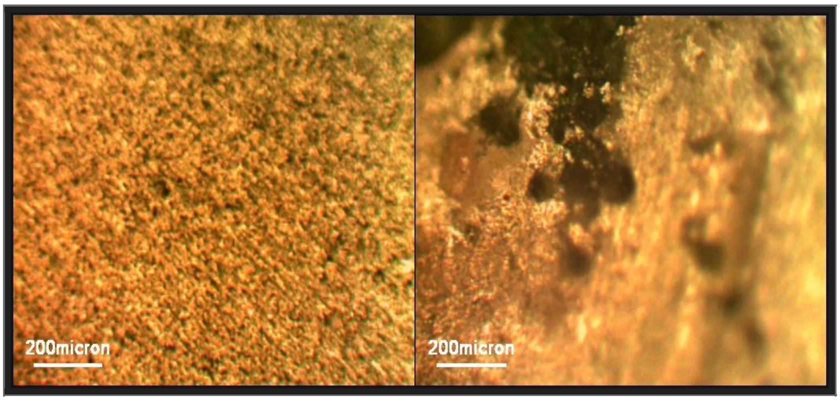
b. The chlorides ions (Cl-) that are available in high percentage in AL-FAO soil play an important role in the acceleration of the protective oxide film removing. This film (Al_2O_3) form naturally on the surface of A-alloy. The chlorides ions do a penetration of oxide film and then corrosion will proceed continuously, and this agrees to the results of the previous work [66]. The effect of alkalis soil also plays an effecting role in the continuous corrosion of Al-alloys [54].

c. On the other hand and as it was explained above, the steel pipe sample seems to be stable electrochemically where the corrosion by rusting is almost stopped. That can support the idea behind the use of A-alloy as a sacrificial to protect the steel pipe sample cathodically.

d. The reason behind the weight gain in steel pipe sample is the formation of film on the steel surface. The film forms as a result of the chemical reaction of the products at the cathode electrode (i.e. the existence of hydrogen atoms on the steel surface)[67] .However, there is weight gain in steel pipe sample as shown in figure (4.22),consequently weight loss has comeback again at the days of

(8,9and 14),where a significant weight loss is observed. The weight loss can be regarded due to the absence of protection in these days.

Figure (4.23) represents the micrograph of A-alloy prior to and after 14 day exposure to the AL-FAO media. Figure (4.23) a, represents the A-alloy before exposure to AL-FAO media. It shows the existence of small dark points randomly distributed through the alloy surface. Figure (4.23) b, shows the surface of A-alloy after 14 day of exposure time in AL-FAO soil. It is characterized by the spread of localized attack (pitting corrosion) in the alloy surface.



a) (b)

Figure (4.23)
Micrograph of (A-alloy) prior and after exposure to AL-FAO soil.100x
(a) Before exposure. (b) After exposure

(Al-Zn) alloys are known of its lower resistance to corrosion [68] ,as a result A-alloy will corrode when it connect to steel in media contains a high amount of chlorides & pH=8.4 (i.e. alkali media)as mentioned above .Also the lower amount of Zn in this alloy will make the alloy subjected to localized corrosion and that was shown in figure (4.23)where pitting corrosion appeared clearly in this alloy, but the results of Tafel extrapolation test show that A-alloy is the less alloy in the amount of output current. This behavior is due to the lower zinc content in this alloy which cause self corrosion and it is the principal cause of efficiency loss(i.e. the lower output current) [69].

2. Discussion of weight loss test of the sacrificial anode B- alloy that connected to the steel sample:-

Figure (4.24) shows the results of ($\Delta W/A_0$ -Time)for the system of (steel pipe sample + B-alloy).A clear increasing in weight loss of B-alloy as the exposure time has increased until it reaches a value of (3.956mg/cm^2)at the end of 14 day of exposing time. The steady or uniform increasing in weight loss at the first 9 days is interrupted at the 10 and 11 day of exposing time. The non uniform behavior can be attributed to the formation of a passivation layer on the B-alloy surface.

The continuous dissolving of B-alloy is continues, while the steel pipe sample gains weight in uniform manner at the first four days of exposing time ,in the fifth day weight loss occur in steel sample .The weight loss can be regarded due to the absence of protection in this day. After five days a uniform stable behavior is due to the retuning of cathodic protection by B-alloy, which is in turn due to the development of current between the electrodes.

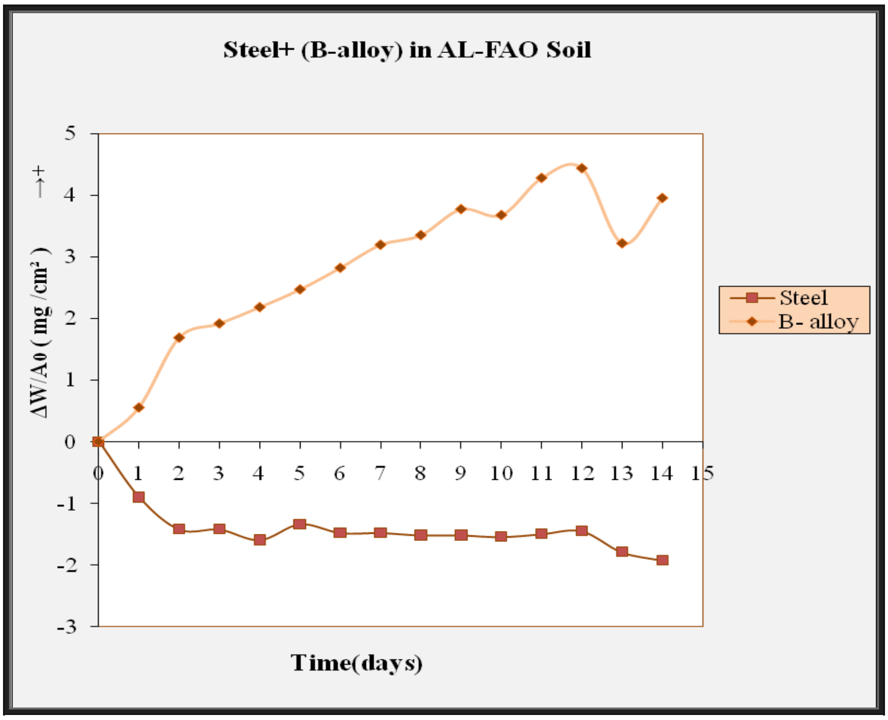
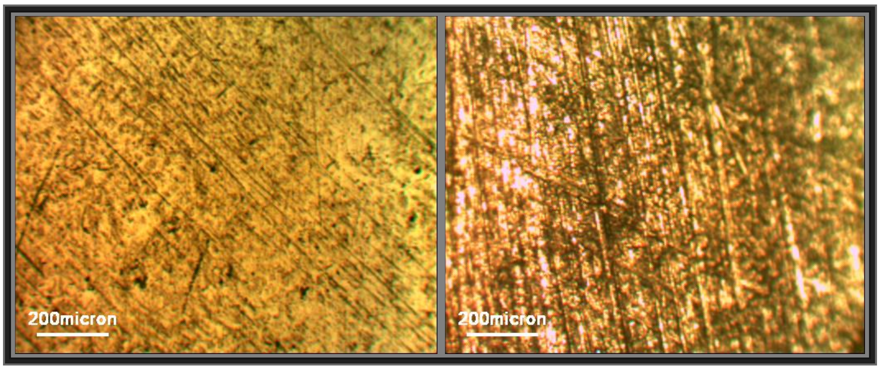


Fig (4.24)

Relation between ($\Delta W/A_0$ -Time) for (Steel + B-alloy) cell in AL- FAO soil

Figure (4.25) represents the micrograph of B-alloy prior to and after 14 day exposure to the AL-FAO soil media. Figure (4.25) a, represents the B-alloy prior to immersion in AL-FAO soil, it is reveals irregular small dark regions evenly distributed through the alloy surface. Figure (4.25) b represents the B-alloy after immersion in AL-FAO soil. This figure shows a general and local corrosion attack.



(a) (b)

Figure (4.25)

Micrograph of (B-alloy) prior and after exposure to AL-FAO soil.100x

(a) Before exposure. (b) After exposure

3. Discussion of weight loss test of the sacrificial anode C- alloy that connected to the steel sample:-

Figure (4.26) shows the results of ($\Delta W/A_0$ -Time) for the system of (steel pipe sample + C -alloy). It shows a clear uniform increasing in weight loss of C -alloy as the exposure time has increased until it reaches a value of (4.885 mg/cm^2) at the end of 14 day of exposing time. The figure (5.26) shows continuous dissolution of C-alloy with increasing exposure time.

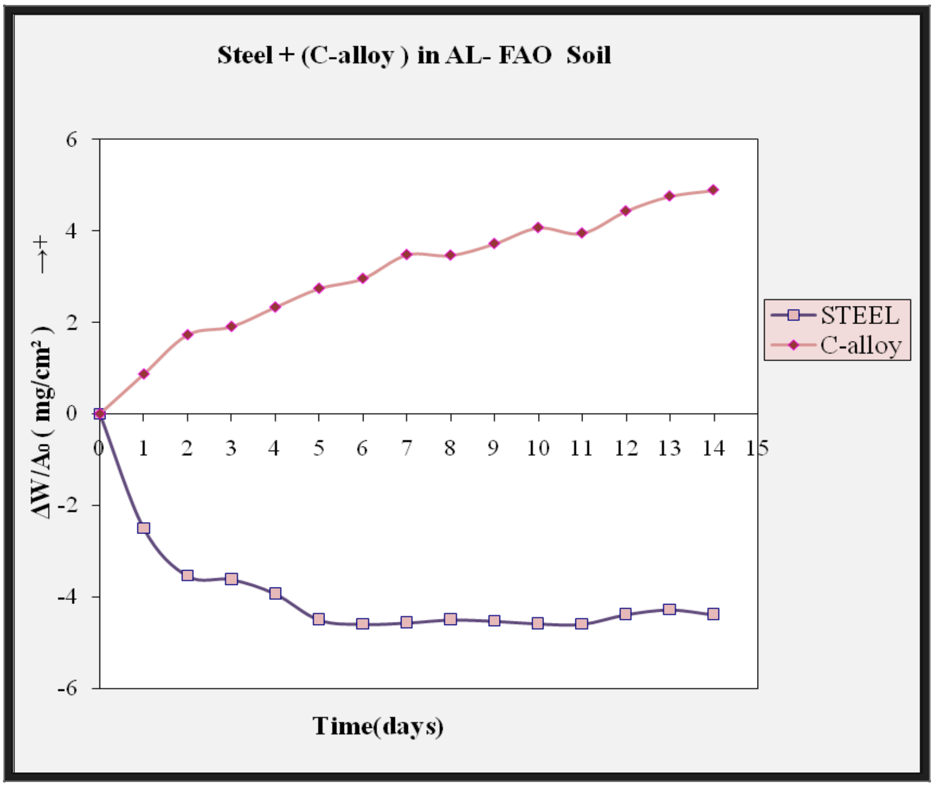
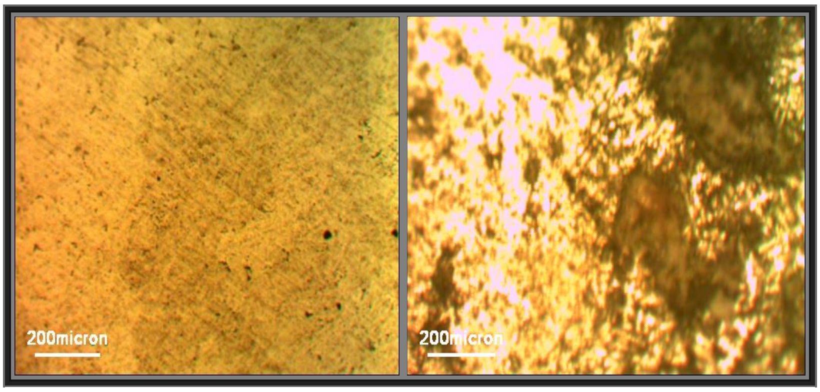


Fig (4.26)
Relation between ($\Delta W/A_0$ -Time) for (Steel + C-alloy) cell in AL- FAO soil

So that this alloy is preferred more than other alloys by which it gives a higher corrosion current density with a uniform dissolution and early passivated steel pipe sample. This alloy contains the same Zn content as that of B-alloy with noticeable increasing in Mg content. This increasing in Mg content (i.e.10%wtMg) will reveal τ (Mg_{32} (Al, Zn) $_{49}$) phase in this alloy as well as there is a small amount of β phase. These phases are useful in obtaining the depolarization features of this alloy. On the other hand steel pipe sample gains weight uniformly with increasing the exposure time till reaching steady state at the first 5 days as it was stated above.



(a) (b)

Figure (4.27)
Micrograph of (C-alloy) prior and after exposure to AL-FAO soil.100x
(a) Before exposure. (b) After exposure.

Figure (4.27) represents the micrograph of C-alloy prior to and after 14 day exposure to the AL-FAO soil. Figure (4.27) a, represents the C-alloy before exposure to AL-FAO soil. It's shows the existence of small dark spot as well as large dark regions which can be observed clearly as compared with B. Figure (4.27) b, represents the C-alloy after immersion in AL-FAO soil. The morphology of this alloy shows the attack seems to be general as well as the existence of localized corrosion and whitish corrosion products on the alloy surface.

4. Discussion of weight loss test of the sacrificial anode D- alloy that is connected to the steel sample:-

Figure (4.28) shows the results of ($\Delta W/A_0$ -Time) for the system of (steel pipe sample + D -alloy).D-alloy shows decreasing in weight with increasing exposure time until it reaches a value of (8.062 mg/cm^2) at the end of 14 day of exposing time.

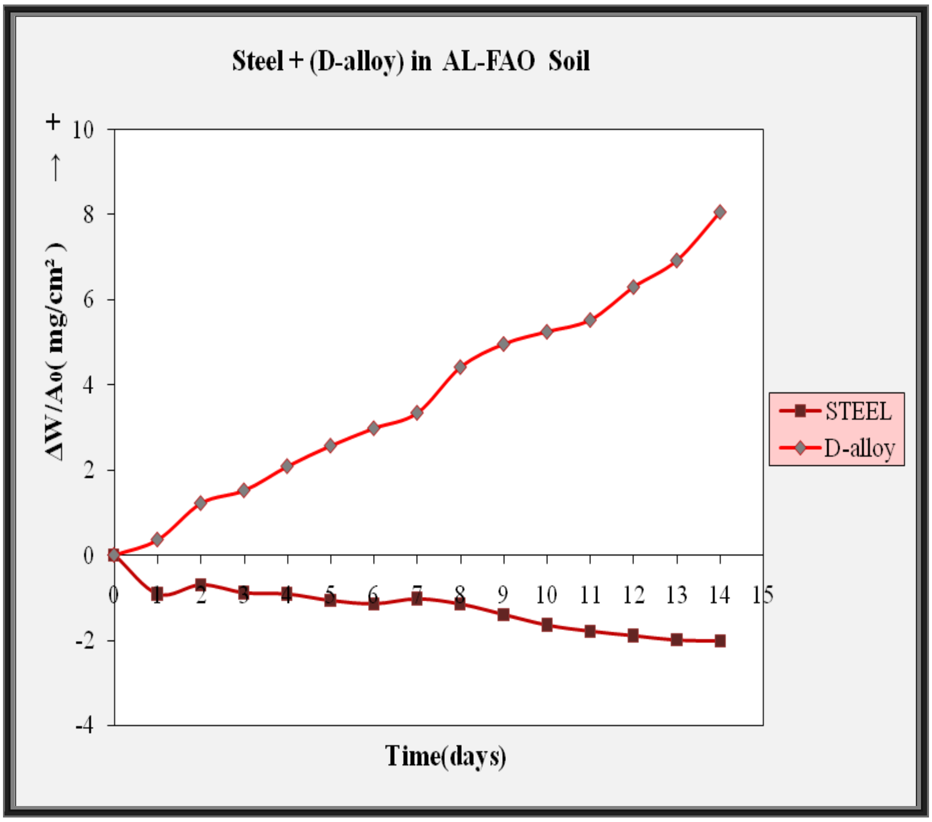
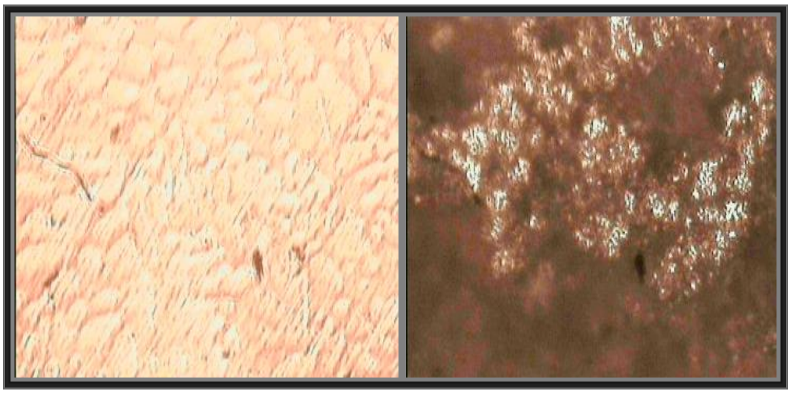


Fig (4.28)
Relation between ($\Delta W/A0$ -Time) for (Steel + D-alloy) cell in AL-FAO soil

An almost uniform dissolving of D-alloy is continues with the exposing time that is accompanied with a little weight gain of the steel pipe sample. Figure (4.28) shows that weight loss in D-alloy is larger than the other alloys (A, B and C). This can be attributed to the higher Zn and Mg content in this alloy among the prepared Al-alloys in this work that in turns will lead to the existence of a large amount of τ phase as shown in table (4.4) that works as a key factor to promote a good surface activation of the anode avoiding the formation of the continuous, adherent and protective oxide film on the alloy surface. This agrees with the results of previous research [27]. The increment in weight gains of steel sample is almost constant with the exposure time until it reaches the steady state in the days 12, 13, 14. This means that the protective film (i.e. formed on the steel surface and causes passivation of steel) is stable. As a result, the steel pipe sample will be cathodically protected from corrosion by the D-alloy that serves as a sacrificial anode.

Figure (4.29) represents the micrograph of D-alloy prior to and after 14 day immersion in AL-FAO soil. Figure (4.29) a, represents the D-alloy before exposure to AL-FAO soil. In this figure a network of dark interdenderitic phases as well as grain boundaries occur in this alloy. Figure (4.29) b, represents the D-alloy after exposure to AL-FAO soil, D-alloy surface exhibited a rough, pitting, dark gray surface differs from the alloy surface (before immersion in soil) as well as the spread of general attack that can be examined clearly. Also figure (4.29) b shows the presence of whitish corrosion products on the alloy surface.



(a) (b)

Figure (4.29)
Micrograph of (D-alloy) prior and after exposure to AL-FAO soil. 100x
(a) Before exposure. (b) After exposure

5. Discussion of weight loss test of the sacrificial anode E- alloy that connected to the steel sample:-

Figure (4.30) shows the results of ($\Delta W/A_0$) for the alloy (i.e. E-alloy) and steel pipe samples with the increasing exposure time at the condition adopted in this work.

A clear increasing in weight loss of E-alloy as the exposure time has increased until it reaches a value of ($5.633 mg/cm^2$) at the end of 14 day of exposing time. Improvement in the behavior of this alloy (i.e. increasing of specific weight loss) in comparison with the (A, B, C) alloys can be regarded to the existence of τ phase as a dominant phase, but D-alloy appears to be more effective than E-alloy (i.e. weight loss of D-alloy is higher than weight loss for E-alloy) and as a result more effective than E-alloy.

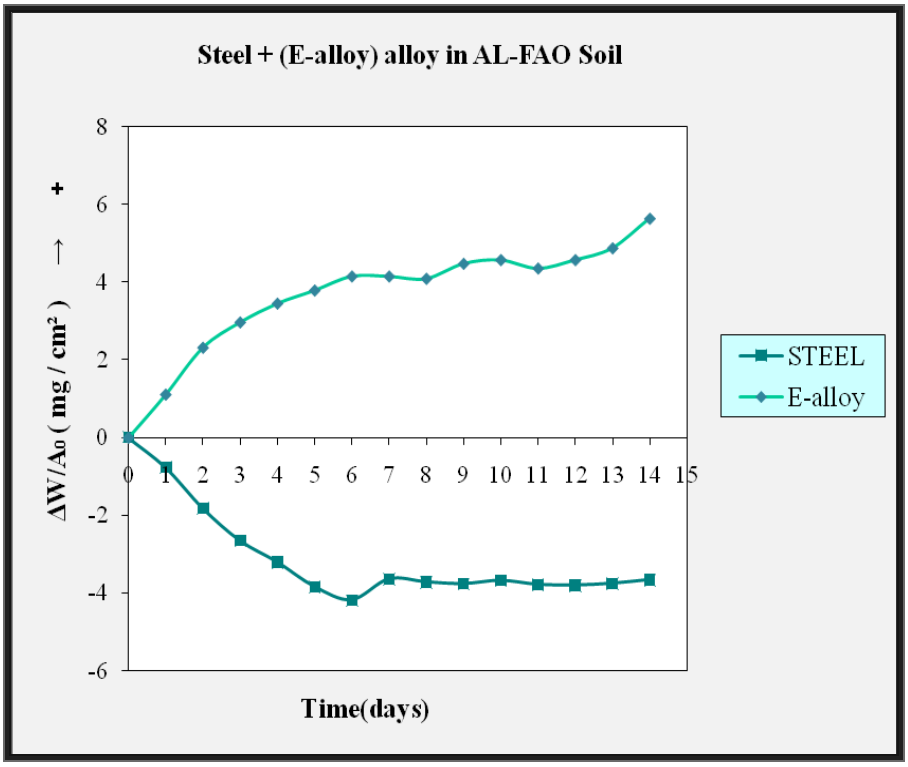
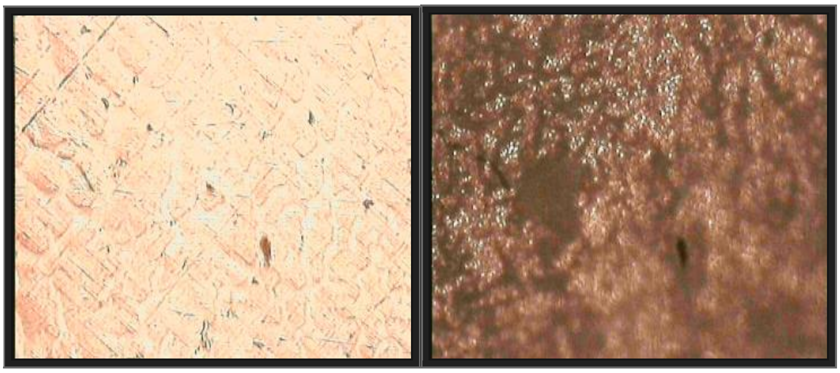


Fig (4.30)
Relation between ($\Delta W/A_0$-Time) for (Steel + E-alloy) cell in AL-FAO soil

Also figure (4.30) shows an increasing in weight gain of steel with increasing exposure time, the steel pipe sample gains weight in uniform manner at the first six days of exposing time. The steel sample shows losing in weight in the 7th day of exposing time, then weight gain is come back in the days (8, 9, 10,…,14) and reaches the steady state. This means that E-alloy achieved the cathodic protection of steel pipe sample.

Figure (4.31) represents the micrograph of E-alloy prior to and after 14 day immersion in the AL-FAO soil. Figure (4.31) a, represents the E-alloy before exposure to AL-FAO soil. It shows well developed grains, figure (4.31) a, represents the E-alloy after immersion in A L-FAO soil. It shows a dark gray surface, general attack as well as pitting corrosion and intergranular corrosion).



(a) (b)

Figure (4.31)
Micrograph of (E-alloy) prior and after exposure to AL-FAO soil. 100x
(a) Before exposure. (b) After exposure

6. Discussion of weight loss test of the sacrificial anode Mg- alloy that connected to the steel sample:-

Mg alloys are using in AL-FAO region to protect the steel pipes cathodically as mentioned previously. Figure (4.32) shows the results of ($\Delta W/A_0$) for the alloy (i.e. Mg-alloy) and steel pipe sample with the increasing exposure time at the condition adopted in this work. It is clear from the figure that the weight loss in this alloy (i.e. Mg -alloy) is increasing largely with increasing exposure time until it reaches a value of (240.63 mg/cm^2) at the end of 11 day of exposing time. This value is greater than the weight loss value of Al-alloys produced in this work, which means that Mg alloy is so effective in the protection of the steel pipes in AL-FAO soil, but it needs to be, replaced consequently in short time (low efficiency) and as a result higher cost. This replacement is very important in order to ovoid the steel pipes exposure to aggressive effect of Cl^- ions that exist in high amount in AL-FAO soil, and as a result the steel pipes damage.

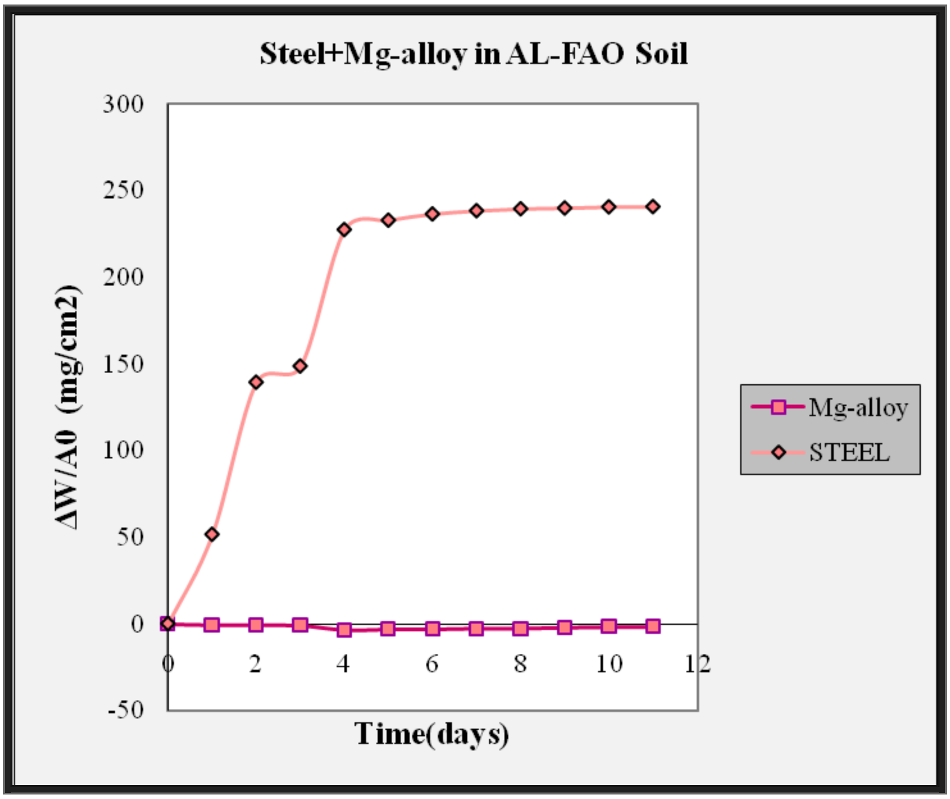


Fig (4.32)
Relation between ($\Delta W/A_0$ -Time) for (Steel + Mg-alloy) cell in AL-FAO soil

Steel pipe sample shows continues increasing in weight with increasing exposure time during the days1, 2, 3, 4. After 4th day an increasing in weight gain occurs. This behavior can be regarded to the consumption of almost the whole alloy mass (i.e. Mg-alloy) during the first days (1, 2, 3, 4) as shown in figure (4.32).After that the steel is poorly protected by the remaining Mg alloy and finally steel will be corroded (no sacrificed anode exist to protect it).This behavior can be noted in figure (4.33).

Figure (4.33) shows the micrograph of Mg- alloy before immersion in AL-FAO soil for 14 days. This figure represents the micrograph of alloy before exposure to AL-FAO soil media, while a white layer forming on the alloy surface after only 1 day of immersion in soil. This layer is continuous forming after 2, 3, 4,5,6,7 days. The layer can be removed by scrubbing under running tap water using soft brush. This layer can be considered as the corrosion products on the alloy's surface.

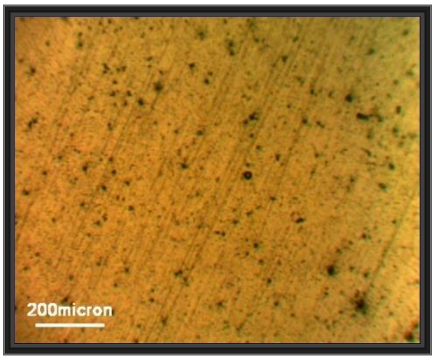


Figure (4.33)
Micrograph of (Mg-alloy) prior exposure to AL-FAO soil. 100x

4.5 Current Measurement Discussion:-

Measurement of current carried out by connection the poles of micro-ampere apparatus to the anode &cathode electrode wire and reading the passage current. Principally, the connection of steel sample to another steel sample result in no current passing between the electrodes (steel samples) because they have the same potential (i.e. no driving voltage between them). Results of current measurements are shown below:-

Table (4.6)

Passage Current in Different Immersion Time in (Steel+ Alloys).

	Passage current (μA)					
Time (days)	**A-Alloy**	**B-Alloy**	**C-Alloy**	**D-Alloy**	**E-Alloy**	**Mg-Alloy**
1	620	820	1040	1200	1200	2000
2	800	800	1000	1000	1000	2000
3	600	780	900	1100	1000	1700
4	470	780	920	1100	800	1700
5	580	700	900	1100	800	400
6	580	700	1000	1000	850	400
7	600	650	1000	1200	950	200
14	600	670	1000	1200	1000	---

Results of current measurement in (Steel+ A-alloy) show that the maximum value of A-alloy current reaches (800 μA) at the second day of exposure time. The results, also shows a swinging in current values until it becomes approximately constant in the last seven days (i.e. from7 to 14). This behavior can be explained as following:

A-alloy began to dissolve (works as anode for steel) causing the passing of current. The swinging in current values can be explained as a result of the existence of passive film on alloy surface which cause the lowering of the dissolved (Al, Zn) ions and as a result the decreasing of current .The final current values represent the stable passing current.

For (Steel+ B-alloy) current reaches (820 μA). Also results show swing in current values at the last day the current value reaches (670 μA).Explanation of this behavior is: B-alloy began to dissolve (works as anode for steel) causing passing of the first value of current, swing in current values result from the existence of phases in alloy that differs in that it is activity and as a result the passage current will be changed by time.

For C-alloy the passing current reaches (1040 μA). This value is higher than B-alloy current value improvement in current value which can be regarded due to the existence of β,τ-phases in alloy which cause breaking down of passive film exists on C-alloy surface. Then, it is became approximately constant in the days (from 6 to 14) and reached (1000 μA).

In (Steel+ D-alloy) the current value reaches (1200 μA) then it becomes approximately constant in the days (from 7 to 14) and reaches (1200 μA). The existence of τ-phase in a highest amount among the produced alloys in this work can be the reason of these current values of this alloy.

(Steel+ E-alloy) the measured current reaches (1200 μA) .Then it reaches to (1000 μA) at the 14th day. This alloy shows high current value. This is due to the effect of τ-phase & other phases that exist in this alloy which affect the corrosion behavior of alloy.

Resulting data of (Steel + Mg-alloy) shows that the value of passing current in Mg-alloy is greater than the value of passing current in the products Al-alloys and this is the result of higher driving voltage in (steel +Mg-alloy) as compared with (steel +Al-alloys) which results in the passing of higher current, but this behavior of Mg-alloy causes dissolution of it in short time and lowering Mg-alloy efficiency as a result.

It can be shown that the passed current in this test is greater than the current in Tafel extrapolation test this difference in the current value are due to the overvoltage of hydrogen on platinum surface is smaller than overvoltage of hydrogen on steel surface which is high; as a result the output current density will be higher in the last case (current measurement of sacrificial anode system) than the current density in Tafel extrapolation test [70].

CHAPTER FIVE

CONCLUSIONS & RECOMMENDATIONS FOR FUTURE WORKS

5.1 Conclusions:-

According to the results and findings above the following can be concluded:

1. It is possible to produce Al-alloys works as a candidate sacrificial anodes for the protection of the Oil pipes in Southern of Iraq (Al-FAO region), where the chlorides available in high percentage.

2. The prepared Al-alloys used in this work differ in its activation as a sacrificial anode according to its chemical composition.

3. Generally all the prepared Al-alloys provide the protection for steel pipes with different efficiency at lower current density (1.51 – 12.36 $\mu A/cm^2$) in comparisons with the used Mg-alloy.

4. The criteria for choosing sacrificial anode material are" The material must be dissolved uniformly with maximum current density".

5. The prepared C-alloy was clearly satisfied with the above criteria where a uniform weight loss ratio accompanied with a noticeable current density (i.e. 12.36 $\mu A/cm^2$).

6. The sequence of the prepared Al-alloys that are candidate to work as a sacrificial anodes is as follows:

   a. As it was stated above, C-alloy has a maximum current density with a uniform time depending on weight loss. The reason behind this behavior is attributed to the chemical composition of this alloy (5.5 Zn + 8 Mg) that developed a set of phases such as ß(Al_2Mg)-phase in addition to the τ($Mg_{32}(Al,Zn)_{49}$)-phase that exist in a larger amount this time as compared with τ($Mg_{32}(Al,Zn)_{49}$)-phase that is developed in B-alloy.

   b. The higher content of phase above plays an important role in breaking down the protective oxide film that can be formed on the Al-alloys surface, and as a result increasing its effectiveness as a sacrificial anode by a uniform increasing of dissolution (i.e. corrosion).

   c. B-alloy was the second prepared alloy that is a candidate to work as sacrificial anodes at the conditions adopted in this work. It gives (9.78μA/cm²) with almost uniform weight loss. The reason behind such behavior was attributed to the chemical composition (5.5 Zn + 8 Mg) that developed ß (Al2Mg)-phase that found the dominant phase and τ (Mg_{32} (Al, Zn) $_{49}$) that present in less amount of C-alloy.

d. E-alloy was the third prepared alloy that was originally reprepared for comparisons gives (8.16 $\mu A/cm^2$) with a less uniformity in weight loss.

e. D-alloy was the forth candidate alloy to work as a sacrificial anode. It gives a noticeable low current density (6.63 $\mu A/cm^2$) with a less uniformity in weight loss.

f. A-alloy was fifth candidate alloy to work as a sacrificial anode with lower current density, because it gives the most lower current density among the produced Al-alloys (1.51 $\mu A/cm^2$) with a less uniformity in time depending on weight loss.

7. The prepared C-alloy was found superior than the Mg-alloy that is originally used in cathodic protection of oil pipe lines in Southern of Iraq. This superiority comes as a result of uniform dissolution or weight loss rate of C-alloy in front of non uniform dissolution of Mg alloy that make the calculations of working life is too difficult.

8. The ability of using AL –FAO soil solution as etching solution for (Al-Mg-Zn) alloys.

5.2 Recommendations for Future Work:-

1. Using more Zn & Mg weight percentages that are uncovered during this study.
2. Studying the effect of Indium addition on the behavior of the prepared Al-alloys that are adopted in this work.
3. Studying the behavior of the prepared Al-alloys in this work in multi mediums other than AL-FAO region such as seawater...etc.
4. Studying the effect of heat treatment on the electrochemical behavior of prepared Al-alloys in this work.
5. Designing of sacrificial anode cathodic protection system using the new prepared Al-alloys that produced in this work.