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THE PERFORMANCE OF COUPLED MILD STEEL-ZINC SACRIFICIAL ANODE IN SIMULATING MARINE FOULING ENVIRONMENT

BY

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled **“The Performance of Coupled Mild Steel-Zinc Sacrificial Anode in Simulating Marine Fouling Environment”.** I also declared that it has not been previously submitted for the award for any degree or diploma or other similar title of this for any other examining body or University.

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LIST OF SYMBOLS

%	Percentage
µ	Micro
Ag	Silver
AgCl	Silver Chloride
Al	Aluminium
Au	Aurum
C	Carbon
Ca	Calcium
$CaCO_3$	Calcium Carbonate
Cl	Chloride
Cr	Chromium
Cu	Copper
E	Potential
Ecorr	Corrosion potential
e-	Electron
Fe	Iron
G	Grams
H	Hydrogen
I	Current
K	potassium
Li	Lithium
Mg	Magnesium
Mo	Molybdenum
Na	Sodium

NaCl	Sodium Chloride
Ni	Nickel
O	Oxygen
OH	Hydroxide
°C	Degree Celsius
SiC	Silicon Carbide
wt%	Weight Percent
Z	Impedance
Zn	Zinc

LIST OF ABBREVIATIONS

CE	Counter Electrode
DC	Direct Current
DOE	Design of experiment
EIS	Electrochemical Impedance Spectroscopy
Emf	Electromagnetic Field
FTIR	Fourier Transform Infrared Spectroscopy
ICCP	Impressed Current Cathodic Protection
mm	Millimeter
mm/y	Millimeter per year
OCP	Open Circuit Potential
ppm	Parts per million
Rp	Polarization Resistance
Rs	Solution Resistance
RE	Reference Electrode
SACP	Sacrificial Anode Cathodic Protection
SEM	Scanning Electron Microscope
SHE	Standard Hydrogen Electrode
SCE	Standard Colomel Electrode
WE	Working Electrode
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

THE PERFORMANCE OF COUPLED MILD STEEL-ZINC SACRIFICIAL ANODE IN SIMULATING MARINE FOULING ENVIRONMENT

ABSTRACT

Corrosion is no longer common in daily live, it is a natural process that cause severe failure problems which been receiving focus from worldwide including Malaysia Navy and marine fouling is one the biggest contributor to this concern matters. Hence sacrificial anode cathodic protection is selected to overcome the problems. This research studies the performance of coupled mild steel-zinc sacrificial anode in simulating marine fouling environment. The parameters are three type seawater (Pasir Gudang, India and Artificial seawater), marine fouling (cockles, clams and seaweed) and pH (6.5, 7.5 and 8.5). Immersion testing, linear polarization and electrochemical impedance spectroscopy (EIS) were conducted in this research and for characterization SEM and EDX analysis was used. Coupled mild steel and zinc with seaweed showed the highest weight gain due to calcareous deposit, which is 1.66 g for immersion testing. DOE was used to design the experiment for both linear polarization and electrochemical impedance spectroscopy. For linear polarization, the 3 parameters chosen are immersion days, type of seawater and type of fouling. The highest corrosion rate is 2.715 mm/year for 9 days of immersion, using India seawater and cockle which was expected to give significant effect on corrosion rate. Whereas the lowest corrosion rate is 0.48041 mm/years after 3 days immersed in Pasir Gudang seawater and seaweed. From EIS, cockles was chose as the marine fouling and the two parameter that being considered are pH and immersion days. It can be observed that the lowest bulk capacitance is 0.9971µF which is for 6.5 pH and 9 days. Whereas the highest bulk capacitance is 0.98969 µF for 7.5 pH and 6 days of immersion.

KEBERKESANAN GABUNGAN KARBON KELULI SEDERHANA DAN ANOD ZINK TERHADAP SIMULASI PERSEKITARAN MARIN FOULING

ABSTRAK

Kakisan adalah sesuatu yang tidak lagi asing kehidupan harian, ia merupakan kejadian semula jadi yang menyebabkan masalah kegagalan di mana mendapat perhatian seluruh dunia termasuk Tentera Laut Malaysia dan marin fouling merupakan salah satu daripada penyumbang terbesar kepada masalah ini. Penyelidikan ini mengkaji keberkesanan gabungan karbon keluli sederhana dan zink anod terhadap simulasi persekitara marin fouling. Parameter yang digunakan ialah 3 jenis air laut (Pasir Gudang, India dan Air laut buatan) marin fouling (kerang, lala dan rumpai laut) dan pH (6.5, 7.5, dan 8.5). Ujian rendaman, polarisasi selari dan ujian elektokimia impedan spektroskopi (EIS) adalah ujian yang dilaksanakan bagi eksperimen ini dan bagi ujian pencirian SEM dan EDX digunakan. Gabungan karbon keluli sederhana dan zink dengan rumpai laut menujukkan penambahan berat yang paling tinggi kerana mendakan kalsanus iaitu 1.66g bagi ujian rendaman. Menggunakan reka bentuk statistic eksperimen (DOE) sebagai garis panduan eksperimen bagi kedua-dua polarisasi selari dan elektokimia impedan spektroskopi (EIS). Bagi polarisasi selari, kadar hakisan tertinggi ialah 2.715 mm/tahun hasil dari rendaman selama 9 hari, air laut India dan kerang di mana sudah dijangkakan akan memberi kesan paling ketara terhadap kadar hakisan. Dimana pula kadar hakisan terendah ialah 0.48041 mm/tahun didapati dari 3 hari rendaman, air laut Pasir Gudang dan rumpai laut. Daripada EIS kerang telah dipilih sebagai marin fouling dan dua parameter yang dititik beratkan ialah pH dan hari rendaman. Ia dapat diperhatikan dimana kapasitan pukal terendah ialah

0.9971 µF didapati dari 6.5 pH dan 9 hari rendaman. Dimana pula kapasitan pukal tertinggi ialah 0.98969 µF for 7.5 pH dan 6 hari rendaman.

CHAPTER 1

INTRODUCTION

1.1 Background

Corrosion is the problem that face by any metal base structure in the surrounding and it can be presented due to many reason. It’s chemical or electrochemical reaction occur between metal and environment which lead to decaying of material and it properties. Electrolyte is needed to conduct electricity for the corrosion to occur. In this case, the electrolyte is from the seawater. The destructive process between electrolyte and metal occur electrochemically. There are four factors need to be present for corrosion to occur. The anode, cathode, electrolyte and an electrical connection are the four factors. Due to corrosion, the binding energy of metal is reduced and resulting the metal atom to oxidized. At anode the losses electrons are conducted to another site which is the cathode (AbdulKarim, 2009)

Structural degradation is one of the most harmful consequence facing by ships or any steel structure which causes by corrosion related problem. This is due to the corrosive environments by continuous presence of moisture and water the ships encounter in life cycle which lead to continuous process of corrosion reaction. These problems may lead to risk of environment pollution and risk of human lives due failures of the component to function (Soares et al., 2009). In addition, it also reducing the original durability and strength of the metal. To prevent and reduce the corrosion problem on metal base structures in seawater, cathodic protection is introduced. This can be done by changing the electrical potential of the component into the protection range, which can be done by galvanic coupling with a sacrificial anode (Rousseau et al., 2009a).

To help in preventing and reducing the corrosion problem, sacrificial anode cathodic protection (SACP) is introduced. It is one of the most efficient anti-corrosion method used to protect metal base structure for offshore. The galvanic current flow between the protected metal base structure and the anode are electrically connected in a conducting environment (Kim, 2017). The potential values of the anodes should be more negative than the protected metal for the method to work. Usually zinc or aluminium are used as an anode to provide cathodic protection to metal base marine structure. Usually the classic application of the SACP is by weld the anodes on the surfaces of the protected structure (Narozny et al., 2014)

1.2 Problem Statement

Royal Malaysian Navy (TLDM) have been facing the same problem for several years which is to find ways to solve or to slow down the metal hulls corrosion from occurring. They have spent more than million ringgit to solve this problem. To solve the problem, sacrificial anode cathodic protection method was used to prevent the ship hulls or metal base underwater structure from corroding.

The problem with cathodic protection are the design of the SACP must follows the international cathodic protection criteria. The selection, location and number of anode required must be determined prior to installation. This shows that, it is necessary to have the correct design of SACP for it to function accordingly (Kim, 2017). The problem become more significant when the ship part still undergoes corrosion although cathodic protection is applied. This may occur due to zinc anode is not functioning efficiently. Hence, it’s important to know the safe operating life and the optimal time frames of the asset availability.

Marine fouling is one of the natural phenomenon that need to be considered which may be harmful towards the safety operation of the offshore facilities. This is because the marine fouling does affect the performance of the protection. Research show that decomposition of organic matter in dead shell could cause corrosion becoming severe. Due to acidification and crevice corrosion from the fouling, zinc anode is not functioning efficiently. It is difficult to simulate dense fouling layer in the laboratory. Hence, barnacle and oyster powder was used due to its similarity (Jie Zhang, 2014).

1.3 Objectives

The main objectives for this research are:

a) To investigate how different type of marine fouling will affect the anode reliability.

b) To study the efficiency of zinc anode in different seawater as electrolyte with and without present of marine fouling.

c) To find out the electrochemical formation and transformation of corrosion on couple mild steel-zinc sacrificial anode with and without present of marine fouling in seawater.

1.4 Research Scope

In this experiment, three types of seawater used was from Pasir Gudang (Johor), Visakhapatnam (India) and artificial seawater. To investigate the effect of different seawater and marine parameter on the efficiency of zinc sacrificial anode in protecting the ship components.

Immersion testing is one of the most common corrosion measurement testing conducted to calculate the corrosion rate of the base metal. Linear polarization and electrochemical impedance spectroscopy (EIS) was used to measure the electrochemical properties of the SACP. After the testing was done, the coupled zinc anode and mild steel cathode morphology and microstructure was assessed using scanning electron microscope (SEM).

1.5 Outline of Chapter

In total, there are five chapter consists in the thesis. Introduction, objectives and scope of work regarding the project was discussed in chapter one. Whereas chapter two is on concept, theory and literature review related to the marine parameter affecting the efficiency of zinc anode. Meanwhile chapter three was explaining on experimental details and characterization approaches for the project. Then, the results and discussion of the project was focuses on chapter four. Finally, chapter five are for conclusion and recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Corrosion could be classified as degradation of materials properties due to interactions with environments. It's a natural phenomenon that occur on metal and wanted to be avoided. Research show that the annual costs which related to corrosion are high due to its important to ensure the safety use of the structure or component. There are several type of corrosion classification, the morphology of the attack, type of environment its exposed to, general corrosion, galvanic corrosion, pitting, and stress corrosion cracking (Shaw, 2006). Corrosion also lead to reduce of lifetime for component, due to surface roughness, reduction of strength and lead to component failure. It is important to record accurate data of past corrosion to improve and to avoid the failure from reoccurring. Different function of component have different concern need to be considered during selection of materials and design (Garbatov et al., 2016).

Galvanic corrosion occurred when different type of materials is electrically coupled in the same environment and can be controlled by material selection, coatings, inhibitors, and cathodic protection (Khadom and Abod, 2017). When coupled of dissimilar material are formed, there will be anode and cathode present. Anode will corrode faster and accelerate the corrosion stage compared to the metal cathode it will corrode slower or even stop the corrosion from occurring. Less noble metal will become anode whereas the more noble metal will become anode. Previous show that, in a highly conducting electrolyte severe corrosion can reduce and improve by having smaller anodic areas compare to cathode. Due to larger cathode lead to more oxygen reduction hence greater galvanic current (Hasan, 2014).

From Figure 2.1, electrolyte is conductivity solution use to transfer ions and electrical connection is compulsory for current to flow. Corrosion take place at anode due to metal loses its electron and change to ion in the solution.

$$M \rightarrow M^{Z+} + Ze^- \qquad (2.1)$$

Whereas at cathode, its attracts electron from anode and consumed for reaction at cathode. This reaction could form metal film, oxygen reduction and hydrogen evolution (Tavakkolizadeh, 2001)

$$N^{Z+} + Ze^- \rightarrow N \qquad (2.2)$$

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \quad pH > 7 \qquad (2.3)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad pH < 7 \qquad (2.4)$$

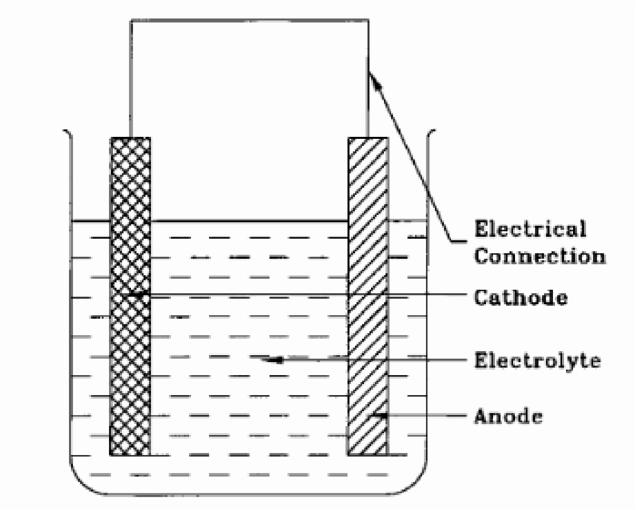


Figure 2.1: Galvanic cell

2.2 The EMF and Galvanic Series

Electromotive force series (EMF) is standard half-cell potential, which ranked metals based on its reactivity. From the series arrangement, metals located at the top is most noble with positive electrochemical potential whereas metals at the bottom is most active with negative electrochemical potential. When the two types of metals are connected, electron flow will occur result from potential difference. Resistivity to corrosion is based on the nobility. The more noble a metal is, the tendency to corrode is slower. In addition, EMF also can be used to predict the possible occurrence of galvanic corrosion (Revie and Uhlig, 2008).

In the EMF series, the half- cell reactions are written as reduction. The series goes from positive to negative, passing through the 0.00 which is the hydrogen reaction.

$$2H^+ + 2e^- \rightarrow H_2 \qquad E^o = 0.00\ V \tag{2.5}$$

From Table 2.1, the top positive potential values listed on the series is Au with potential values +1.498 V.

$$Au^{3+} + 3e^- \rightarrow Au \qquad E^o = +1.498\ V \tag{2.6}$$

Whereas the most negative values listed on the series from Table 2.1 is Li with potential values -3.040 V (McCafferty, 2010).

$$Li^+ + e^- \rightarrow Li \qquad E^o = -3.040\ V \tag{2.7}$$

The ranking of the EMF series is usually not the same in different media such as seawater, sulfuric acid and artificial perspiration. The series can be obtained by connecting the metal or alloy to the negative terminal and reference electrode at positive terminal of voltmeter (Ahmad, 2006).

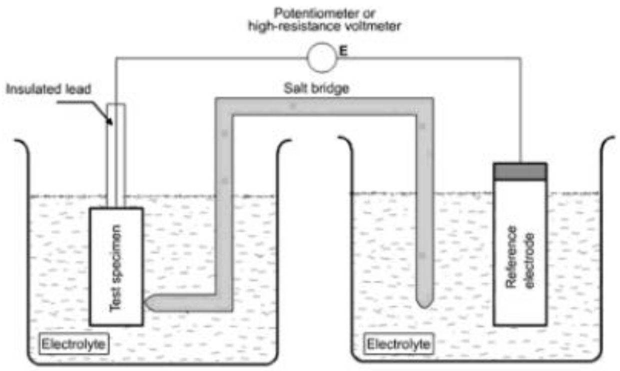
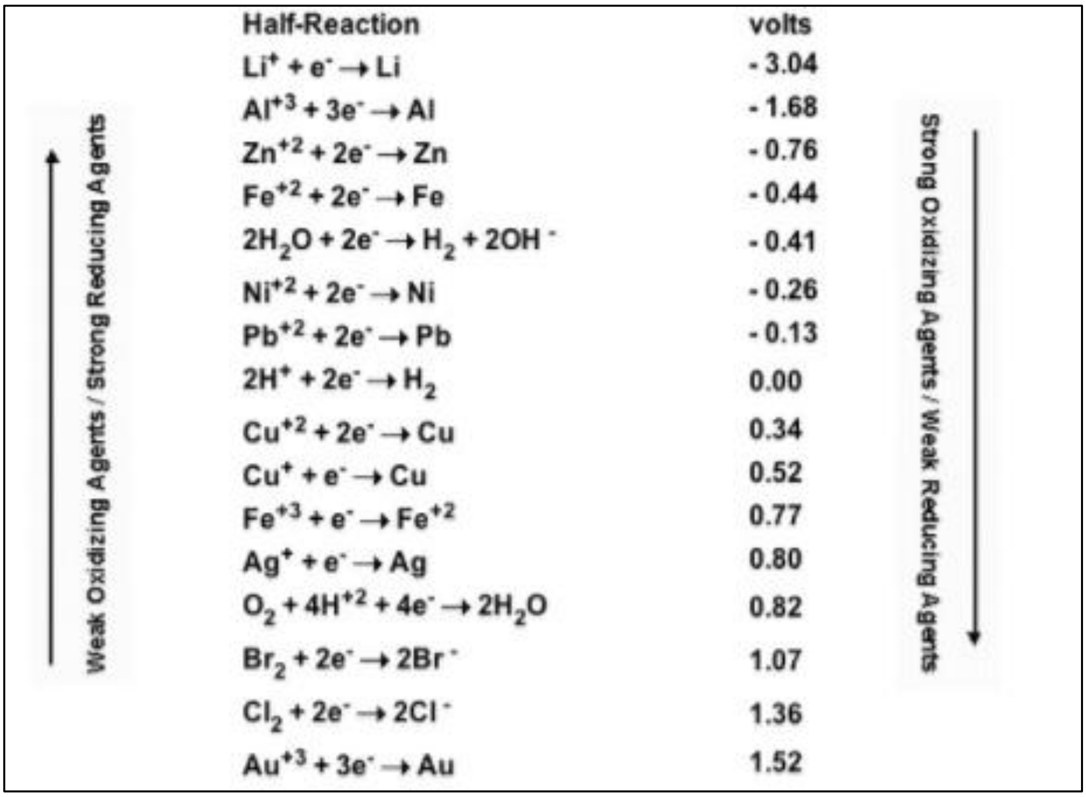


Figure 2.2: Laboratory technique for measuring the single electrode (corrosion) potential, Ecorr of metals and alloys in aqueous environments. Use of salt bridge (Ahmad, 2006)

Table 2.1: Standard electrode potentials at 25⁰C



Half-Reaction	volts
$Li^+ + e^- \rightarrow Li$	- 3.04
$Al^{+3} + 3e^- \rightarrow Al$	- 1.68
$Zn^{+2} + 2e^- \rightarrow Zn$	- 0.76
$Fe^{+2} + 2e^- \rightarrow Fe$	- 0.44
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	- 0.41
$Ni^{+2} + 2e^- \rightarrow Ni$	- 0.26
$Pb^{+2} + 2e^- \rightarrow Pb$	- 0.13
$2H^+ + 2e^- \rightarrow H_2$	0.00
$Cu^{+2} + 2e^- \rightarrow Cu$	0.34
$Cu^+ + e^- \rightarrow Cu$	0.52
$Fe^{+3} + e^- \rightarrow Fe^{+2}$	0.77
$Ag^+ + e^- \rightarrow Ag$	0.80
$O_2 + 4H^{+2} + 4e^- \rightarrow 2H_2O$	0.82
$Br_2 + 2e^- \rightarrow 2Br^-$	1.07
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36
$Au^{+3} + 3e^- \rightarrow Au$	1.52

2.3 Pourbaix Diagram

Pourbaix diagram is a potential-pH diagrams of compact summary thermodynamic data. The data obtain can be related to any metal in water for electrochemical and corrosion behaviour. From the potential and pH values in the diagram, the reaction of the metal can be estimated. Either it is in the stable region where the corrosion does not take place, immunity region where it does not react, or in the reaction region which can form specific oxides or complex ions. Therefor the pH or potential can be adjusted to meet the requirement values for stable region to avoid corrosion (Revie and Uhlig, 2008).

Nernst equations and solubility data for metal and its species was used to construct the pourbaix diagram. From the pourbaix diagram, the pH value is on the horizontal axis whereas the redox potential is on the vertical axis. Based on pourbaix diagram for water at 25⁰C as shown in Figure 2.6, there are 3 regions present in the diagram upper, middle and lower. Upper region is where water electrolysed anodically to O_2. Water electrolysed cathodically to H_2 at the lower region. Whereas at the middle region, water is stable and will not decompose (Wulfsberg, 1991).

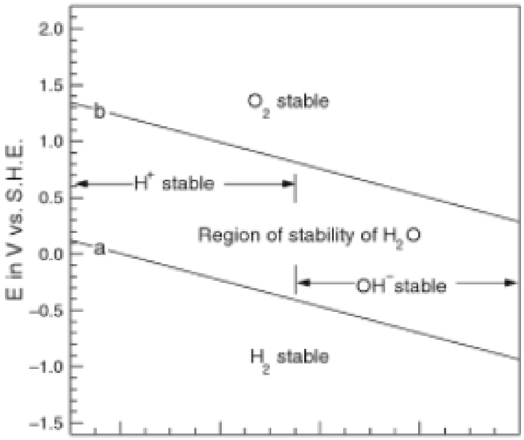


Figure 2.3: Pourbaix diagram for water at 25⁰C (Wulfsberg, 1991)

2.3.1 Pourbaix Diagram for Iron

From the diagram below in Figure 2.4, it shows that there is a horizontal and vertical line presented in the diagram. The horizontal line indicates that pH which related to neither H^+ and OH^- does not involve in the reaction. Whereas the vertical line indicates reaction involving H^+ and OH^- but not electron. In different oxidation state, corrosion of Fe can happen in acid and neutral solutions.

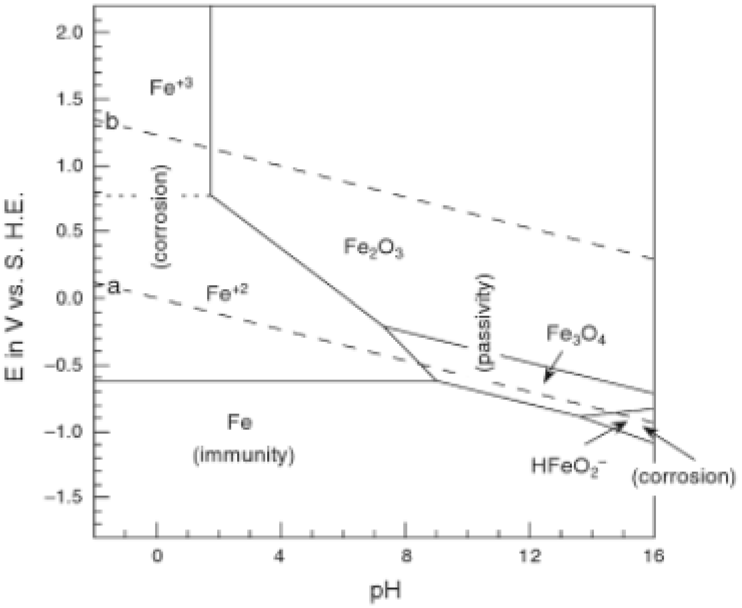


Figure 2.4: Pourbaix diagram for Fe at 25ºC (Wulfsberg, 2000)

At pH 1.76 represent equation $2Fe + 3H_2O \rightarrow Fe_2O_3 + 6H^+$ is equilibrium. Which mean that when the pH is more then 1.76, Fe_2O_3 is stable because formation of oxide film will act as protective film which will show some protection against corrosion. The iron oxide is in a passivation region which means Fe reacts in these will be forming protective oxide films but this only acceptable when it accounted by diffusion-barrier oxide layer. When the pH starts to drop, which is lower than 1.76 corrosion will occur without any protection this is because the ferric ions in solution are stable. Equation, $Fe_2O_3 + 6H^+ + 2e^- + 3H_2O$ is the equilibrium reaction represent by the sloping line between Fe^{2+} and Fe_2O_3. Same like before to the right side of the sloping line protection oxide layer will be form, whereas on if it move to the left side of the slopping line corrosion will occurred (Wulfsberg, 2000).

2.3.2 Pourbaix Diagram for Zinc

From diagram below it shows that pourbaix diagram of Zinc is like Aluminium. This is because dissolution of Zn occurs in acid solution and basic solution. Same as other pourbaix diagram, the diagram of Zn is obtained from Nernst equation and it is a diagram of an equilibrium potential as a function of pH from acidic to basic.

Figure 2.5 shows that at lower and higher pH values, Zn have higher corrosion rate whereas at intermediate pH it forms a passivation which is lower corrosion rate. The thermodynamic information agrees with kinetic data. At the upper side of horizontal anodic lines, the oxidised product is stable. Whereas on the lower side horizontal anodic equilibrium line, solid zinc is stable hence it immune to corrosion and cannot be dissolved (Rieger, 1994).

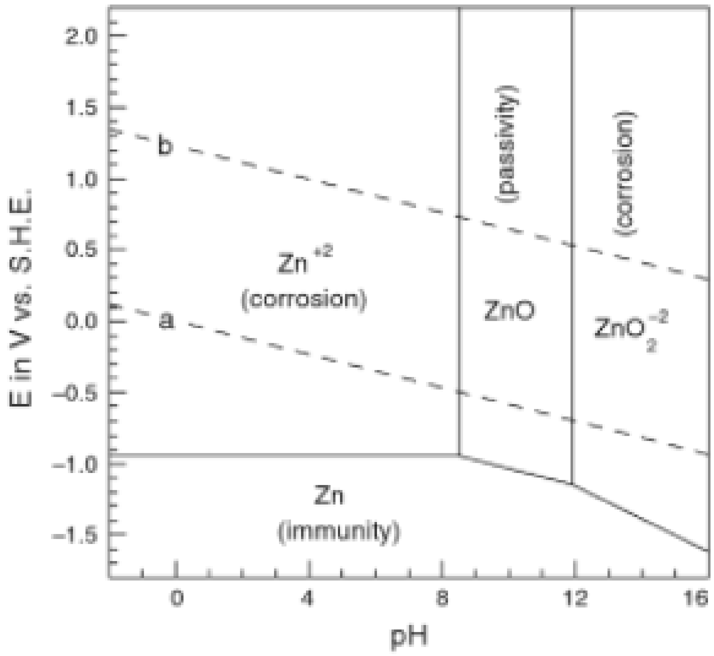


Figure 2.5: Pourbaix diagram for Zinc at 25ºC (Rieger, 1994)

2.4 Cathodic Protection

Cathodic protection is one the efficient method to lower down possibilities of corrosion to occur by using direct current (DC). The connection takes place from anode through electrolyte and followed by cathode which is the part that needs protections. The current that flow from the connection through the electrolyte is ionic current not electrical current. It can be done by reducing the potential different between anode and cathode. Hence to protect the structure from other source, current is applied so that the potential for the whole structure is the same (Revie, 2011).

The objective of cathodic protection is reducing or prevent corrosion from occur. These goals can be achieved by supply more electron which obtain from dc to the metallic part that need protections. From this action, the cathodic reaction rate is increase hence the anodic reaction is decrease. Due to shifting of cathode potential to anode hence the potential different is eliminated and corrosion is hardly to occur. As the transferring of electron take place, the cathodic reaction polarizes in the direction of local action anode potential. Cathodic protection is completed when the metallic structure become more negative. Corrosion can be prevented by minimizing the potential different between anode and cathode. Hence the lower the potential different, the cathodic protection is more efficient (Ahmad, 2006).

Usually, the hull of the ship which the bottom part that is in contact with the seawater will be painted and the paint is one of the method to prevent corrosion. Therefore, cathodic protection is one of the way to protect the ship hull when the paint protection breakdown and unable to give full protection performance. In actual practice, cathodic protection has been use to protect water storage tanks, buried pipelines, steel reinforcing bars in concrete structures located in marine environment and many other structure (McCafferty, 2010).

2.4.1 Types of Cathodic Protection

Cathodic protection is divided into two types: Impressed current cathodic protection (ICCP) and sacrificial anode cathodic protection (SACP). Sacrificial anode cathodic protection also known galvanic anodes, the sacrificial words come from the action of anodes to sacrifice itself to protect cathode which is the structure. For this type of protection, galvanic cell is done and its consist of anode by the more active metal and the less active metal as cathode. The most common metal chosen as anode for underground is magnesium and zinc, in seawater is zinc and aluminium alloy, whereas for fresh water magnesium become the primary choice. There is no external power use for SACP but the protective current comes from the electrochemical cell created when connected to cathode which is the structure that need protection (Baeckmann, 1997).

SACP is chosen to be used when requirement for current is low, which is around several hundred milliamperes to 4 or 5 A. Usually offshores structure only required low current usage hence SACP can be used to protected the structure. Well-coated, electrically isolated structures, offshore structures, ship hulls, hot-spot pipeline protection, heat exchanger water boxes are several examples that use SACP. For every invention, there are advantages and disadvantages. The advantages for SACP are its does not required external power, small maintenance, easy installation, not significance change of cathodic interference and less inspection required. Whereas the limitations are required good coating, high replacement cost, limited current output and lack of adjustment without resistors in anode circuits (Hack, 1999).

Whereas for Impressed current cathodic protection, its provide dc from a power source. The current is delivered to anodes made of a material having a very low or essentially inert dissolution rate. The anodes serve simply to introduce the protective current into the electrolyte. Usually transformer rectifier is use as the power source for ICCP, its function by lower down the incoming alternating current (AC) and convert it to dc. The anodes commonly use are high silicon, chromium-bearing cast iron, graphite, and junk steel. Magnetite and lead–silver anodes are also used, with lead–silver being confined to use in seawater (Adey, 2005).

Typically, ICCP is uses when high current is required, which is around 500 A and more. Apart from that, it also can be used for low current requirement to replace the SACP system. Long transmission pipelines, complex underground structures, pilings, marine structures and ship hulls are the common example for ICCP applications. Same as SACP, ICCP also have its advantages and disadvantages. The advantages are adjustable output, high current available, can be used for poorly coated or non-coated structures, and lower cost for replacement. The limitations are constant power required, frequent maintenance and inspections required, experienced workers is required prior to installation and cathodic interferences might occurs (Cicek, 2017).

2.4.2 Anode Material (Zinc)

To protect ships or any harbour structures, zinc is introduced as the sacrificial anode. The number of ships use zinc sacrificial anode increase year by year, hence it shows zinc is use commercially. (Rousseau et al., 2009b). Zinc is chosen due to its redox potentials is lower or in other words more negative than steel in the same conditions hence its will provide SACP to the steel structure in (Mouanga et al., 2013). For the protection action to take place, the anode and cathode which is the structure that need protections must be electrically connected and in conducting environment. For the anode to function effectively, location and number of anodes required must be accurate (Kim, 2017).

Although magnesium (Mg) the most negative potential values compare to aluminium (Al) and Zinc (Zn) but its more compatible for on shore structure, this is because the electrolyte which the soil or water have higher resistivity. Due to its more negative potential, the large difference in electropotential between anode and cathode will leads to disbanding of coating at cathode if its use in salt water. Hence Zn and Al is chosen for saltwater due to its lower resistivity (Zhang, 2013).

2.4.3 Cathode Material (Mild Steel)

One of the most common construction materials used for marine structure is mild steel due to its top mechanical properties. It is one of the abundant material on earths, other than that mild steel is cheaper compare to other metal. In addition, it can be welded hence it is suitable to form many type structure. Usually mild steel is use for ships, drilling platforms, offshore structure, underwater pipelines or cable as the examples. However, mild steel doesn’t have high corrosion resistance making it not suitable corrosive medium such as seawater which contains 3 – 3.5% sodium chloride. Hence, protection is required to prevent the metal structure from corroding (Yang, 2010).

2.4.4 Electrolyte (Seawater)

The compound that might exist in seawater are Na^+, Mg^{2+}, Ca^{2+}, K^+, Sr^{2+} as the major cation. Whereas the major anion is Cl-, SO_4^{2-} , HCO_3^-, Br^-, CO_3^{2-} , $B(OH)_4^-$,

F^-. Almost all this element can be found in most seawater which will lead to the properties of the ocean. Salt particle in seawater or marine environment contribute to pitting corrosion by deposited on the metal structure or surface of the metal structure (Ahmad, 2006).

2.5 Effect of seawater pH on the corrosion rate

Corrosion has leave severe impact on world-wide activity; the impact includes from structure deterioration to economic. Even in natural environment degradation of structure occur and its cannot be control but can be prevented. The corrosion occurred when the actual atomic, molecular, or ironic transport process take place at the interface of the structure. Metal type and environment media does play important roles for corrosion rate. Commonly, the corrosion rate increase as the acidity of the environment media increase (Muslim, 2014).

Generally, higher and lower pH does leaves remarkable effects on the corrosion rate. By having higher pH, it will leave significant effect on film formation by causing thickening of the passive film due to it iron oxide is more stable in alkaline solutions for a stainless steel. It is different in acid solutions, this is because its will be forming a chromium rich oxide film. This film form due to dissolution of chromium oxide is slower compared to iron oxide (Fattah-alhosseini and Vafaeian, 2015).

By exposing iron in aerated water at room temperature the corrosion rate shows significant change at different pH but from pH 4 to 7 the corrosion rate remains the same. This is because at this range, the corrosion rate is governed mostly by oxygen that react with absorbed atomic hydrogen and due to this surface depolarizing and reduction can continue. Figure 2.8 shows the effect of pH on the corrosion rate of iron in water. At lower pH value, oxide dissolve in water rather than deposited on top of the metal structure and form the film. Hence at pH lower than 4, ferrous oxide (FeO) is soluble. Due to this the metal structure is in direct solution with the acid solution causing the corrosion rate to become faster. In addition, at lower pH which is the acidic solution phase hydrogen is produced hence the corrosion rate is depend on two factors depolarization by oxygen and hydrogen evolution. This is different at higher pH because oxide layer is form hence the corrosion rate become slower. However, the effect of pH may not be the same for other type of water. This because in hard water, the protective film form on the surface of the structure is $CaCO_3$. To adjust the pH of water sodium hydroxide (NaOH) and hydrochloric acid (HCl) is use. To increase the acidity HCl is added, whereas to increase the alkalinity NaOH is added to the water (Revie and Uhlig, 2008).

2.6 Effect of marine fouling on submerged surface.

One of the most problematic aspect for oceans engineering system is the present of marine fouling. Marine fouling problems always causing technical problems and economic loss to the marine industry. This is because as the object surfaces continuously submerged in the seawater, the community of this organism which is the animals and plants will start to attack and growth on the structure. By present of marine fouling on the object surface, it will reduce the flowing of the fluids through the pipelines, reduce the heat transfer in the heat exchanger systems, reduce the ship’s speed and encrusting of the support legs of oil rigs (Al-Muhanna, 2016).

Other than that, marine fouling also may cause destruction of the protective coating which apply to reduce corrosion and this will lead to severe corrosion due to unprotected surface. In some cases, the build-up of slime and fouling on the metal structure may provide them protection from the erosive effects of sea water at high velocity. The type of fouling to occur is depend on the type of water in which the metal structure or ships to operate. Fouling starts to attach on the ship depending on type of service the ship employed and time spent at the port. This is because as the velocity of water pass through the surface exceed one knot, the fouling will have the difficulties to the surface of submerged ships. As the speed increase, previously attached fouling might be washed away if they have not been long established (Institution and Ships, 1952)

2.7 Corrosion Measurement

2.7.1 Immersion Testing

Immersion test is one of the easiest method to obtained the corrosion characteristics of the submerged metal part. The problem with this simple test is it does not provide information on the reaction mechanism and apart from that, it required long exposure time of sample to the corrosive environment. This test was done by submerging the metal surface in the corrosive environment and after several time intervals the weight was calculated hence the metallic corrosion is determined. In order to be more accurate, the corrode part need to be eliminate from the testing sample before the immersion test take place (Li, 2001).

The test can be divided into two categories, the first category is alternate immersion testing whereas the second category is the simple immersion testing. For alternate immersion testing, the testing sample is being submerged for several time intervals than the testing sample is removed from the medium and leaves to dried. Than the cycle take place for 100 times for the test to completed. Different from simple immersion test, where only small piece of sample is submerged to corrosive medium for certain period. The weight before and after of sample were recorded to determine the weight loss (Li, 2001).

From immersion testing corrosion rate in mm per years (mm/y) can be calculated by using this equation. The initial weight and volume of the testing sample must be recorded upon testing.

$$CR = \frac{w}{D\,x\,A\,x\,t}\,x\,k \tag{2.8}$$

Where:

w = weight loss in milligrams (g)

k = constant (87.6)

D = metal density in grams per centimetre cube (g/cm^3)

A = area of testing sample in centimetre square (cm^2)

t = time in hours

2.7.2 Open Circuit Potential (OCP)

In open circuit potential, the potential between working electrode which the testing sample and references electrode is measured using a multimeter. There should be no current supply the system upon measurement. The information can be gathered from this test is the thermodynamic tendency of testing sample to involve in the electrochemical corrosion reactions upon the medium provided. The thermodynamic stability of the will results on the tendency of metal to corrode. The nobler OCP are more thermodynamically stable hence the tendency to corrode is lower compared to less noble metal (Sahrani, 2008)

Apart from that the corrosion potentials might be different as the immersion time in the corrosive medium increase. An increase in potential reading shows that depolarization of cathode hence the corrosion reaction is occurring on the testing sample surface. Whereas if the potential reading between working electrode and reference electrode become lower, the tendency of corrosion reaction also low. A rapid changes in the corrosion potential could be due to depolarization, enhancement of anodic reaction or protective film is form on the testing sample (Sahrani, 2008)

2.7.3 Linear polarization resistance (LPR)

One of the most efficient electrochemical method to measure corrosion is by using linear polarization resistance. The corrosion rate was calculated by keep track the relationship between electrochemical potential and current generated between electrically charged electrodes in a process stream. In aqueous solution, LPR able to show the most efficient and fast feedback method. The corrosion rate of the testing sample can be obtained almost instantly (Klassen, 2004).

There are few advantages using of LPR, which it can monitor and measure corrosion in shortest time. Even any changes in corrosion rate can be detected as soon as possible. Due to the effectiveness, effectiveness of the prevention programme and process change can be determined. Hence this action can be used to determine the suitable inhibitor in shorter time. Apart from that, LPR also can determine and measure the pitting tendency on testing sample. In addition it also can give information on metal behaviour (Klassen, 2004).

There is some problem with Tafel plot extrapolation which obtain from LPR is the sample of surface is often show large changes after extensive polarization. Due to non-destructive of cathode, the cathodic branch of polarization curve is measure first. However, if significant amount of hydrogen atom by the working electrode during hydrogen evolution, the steady-state corrosion potential may not be regained after the polarizing potential has been turned off. After extensive anodic polarization, the working electrode will become rough (McCafferty, 2010).

a Working Electrode

For corrosion testing, working electrode is the testing sample which come from the actual part of the metal structure but in smaller size for testing. In the electrochemical, working electrode is the part where the reaction occurred. The shape and size of the sample can be various, depending on the applications (Bard, 2001).

b Reference Electrode

In the electrochemical cell reference electrode is a stable electrode with an established potential value which use as a reference for potential controls and measurement. With a very high input impedance on the electrometer, the current flow is keep to zero or near to zero which obtained from counter electrode to close the current circuit. Basically, reference electrode use to measure potential (Bard, 2001).

c Counter Electrode

In the electrochemical cell, counter electrode which also known as auxiliary electrode is the electrode used to closed the current circuit. Inert material such as graphite, Pt, Au and glassy carbon are the example of the counter electrode. Although the counter electrode does not involve in the reaction, the current flowing between working electrode and counter electrode causing limiting factor in the kinetics of process during testing if the size of working electrode is bigger than counter electrode. Hence for efficiency of testing, the total surface area of counter electrode need to be bigger than working electrode (Bard, 2001).

2.8 Electrochemical Impedance Spectroscopy (EIS)

Instead of the common DC-based current-vs-voltage study, electrochemical impedance spectroscopy was done using AC signal. By applying AC signal to the testing sample, the response is obtained hence impedance is calculated. From the gained result, its then being analysed using fit and simulation to yield film resistance, reaction kinetics, polarization resistance, and other parameters which govern the corrosion processes and reaction mechanisms. Using this method, corrosion inhibitors and anti-corrosive film can be study or develop (Mouanga et al., 2013)

Ohm's law is used to defines in terms of the ratio between voltage, E and current, I giving resistance, R:

$$R = \frac{E}{I} \tag{2.9}$$

Resistance (R) means the ability of the circuit to resist electrical current flow. Whereas impedance (Z) means measuring the ability of circuit to resist electrical current flow. To measure the response, little amount of potential of fixed frequency is applied hence impedance at each frequency is obtained using:

$$Z = \frac{E}{I} \tag{2.10}$$

EIS using a modern three electrode potentiostat required working electrode, counter electrode, reference electrode and electrolyte for corrosion testing. The arrangement of the electrode plays important roles, as the reference electrodes need to be place next to the working electrode as close as possible. This was done to ensure it place at the electrode-electrolyte interface. These processes include the fast mass transfer reaction, slow-paced charge transfer reaction, and diffusion processes at the interface. A double layer capacitance is observed at the interface due to the presence of Outer Helmholtz Plane (OHP) and Inner Helmholtz Plane (IHP) at the electrode surface as shown in Figure 2.6 (Zia, 2016)

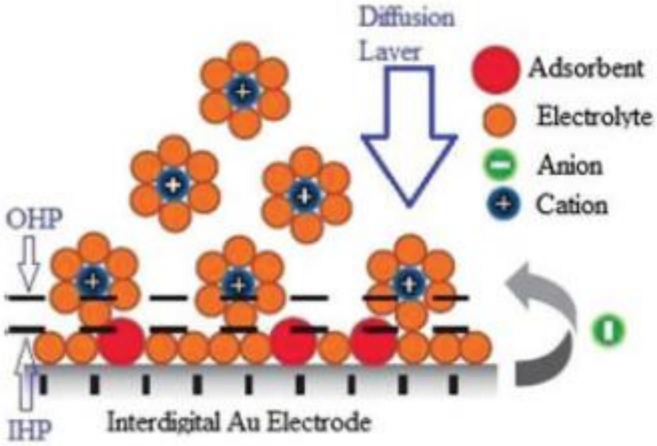


Figure 2.6: Kinetic processes taking place at electrode electrolyte interface (Randle's cell model) (Zia, 2016)

CHAPTER 3

MATERIALS AND METHOD

3.1 Introduction

This chapter described the used of raw materials, preparations of samples, types of testing and procedures of the experiment. In general, this work consists of four major sections which are; preparation and characterization of zinc (Zn) anode and mild steel, preparation and characterization of seawater, preparation of marine fouling and the corrosion activities of zinc (Zn) anode coupled mild steel in seawater as electrolyte.

Generally, this project is divided into four parts: casting of zinc anode and preparation of the base metal, immersion testing, electrochemical corrosion testing and characterization. Figure 3.1 shows the summary of this research from sample preparation to characterization.