

CERTIFICATION OF APPROVAL

Design Of A Cathodic Protection Against Corrosion For Marine And Offshore Structure

by

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MUHAMAD FARIZUDDIN ANWAR BIN MANSOR

ABSTRACT

Large marine structures and machineries such as oil platforms and ships use numerous ways to propagate or prevent corrosion, and one of the technique is Cathodic Protection (CP). For more than 50 years, CP has been employed to prevent corrosion on pipelines, storage tanks as well as buried and submerged metallic structures. It is the most effective and least expensive method for controlling corrosion. Large marine structures have probably the greatest application of cathodic protection, followed by marine machineries and equipments such as vessels and pipelines. As the technology progresses gradually, the application of CP increases as more structures being constructed or built around or even submerged in aggressive corrosion environment. Designs of CP were often based upon guesswork than the application of science. This condition serves as the basic of the project, with the aim of improving the performance of CP system by introducing new design of sacrificial anode CP block. This improvement is mainly achieved by increasing the protection area of the sacrificial CP anode block. The characteristic that will be improved is determined first, which acts as initial step of the project's methodology. After the design has been completed, fabrication session commenced, followed by an experimental work and analysis of the corrosion protection effect on the new design. The experiments have been done using basic immersion technique, and the final results were obtained using FerroVer® method of the Powder Pillow Test. The result obtained from the analysis proved that the design modification upon the CP sacrificial block has a significant effect of improvement onto the corrosion protection performance.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Corrosion is deterioration of essential properties in material due to reactions with its surroundings, by the means of a loss of electron of metals reacting with water or oxygen [1]. Most structural alloy corrodes merely from exposure to moisture in the air, but the process can be strongly affected by exposure to certain substances; and for marine and offshore structure, exposure to salt water. Cathodic Protection is the practice of using electrochemical reactions to prevent the corrosion of steel structures. Cathodic Protection is a technique to control the corrosion of a metal surface by making that surface the cathode of an electrochemical cell, or in other words it is a process that minimizes the anodic dissolution of a metallic structure by reducing the electrical potential energy difference between the anodic and cathodic site on the surface of a metal when placed into a conductive electrolyte.

1.2 PROBLEM STATEMENT

Large marine structures have probably been the subject that has the greatest application of cathodic protection. From the application used in natural waters of Lake Maracaibo, Venezuela, to the more aggressive environments of the Gulf of Mexico, the technology progressed gradually, especially during the period of instability in the Middle East that urges human to find alternative fuel supplies. Urgent exploitation of the North Sea resources has forced the industry to develop new technology for them to take place in the competition. Corrosion protection of the vastly expensive structures had to be based upon cathodic protection systems, for which the available scientific data were sparse. Designs were often based more upon inspired guesswork than the application of science.

But as the industry evolved, the technology of corrosion protection had advanced till the optimum corrosion protection has been discovered, but only for certain applications.

1.3 OBJECTIVE

The main goal of the project is to design and fabricate a CP sacrificial anode block for marine and offshore structure, with the aim of achieving the following:

1. Increase the protection area of the CP sacrificial anode block by having a larger volume of surface area.
2. Adaptable design for marine structures and vessels.

1.4 SCOPE OF STUDY

The study to identify the characteristics of CP that can be improved will be based on an experiment that investigates the effect of surface area to the performance of CP against corrosion, as well as investigating the application suitability of the proposed CP specifically for offshore structures, rudders and propellers of ships or boats. The characteristic of the CP that can be modified to improve the performance of the corrosion protection is the surface area of the sacrificial anode block. The normal design being used by the industry is a solid block. By implementing this new design characteristic, it is believed that the performance of CP can be improved and at the same time, several problematic characteristics such as weighty block can be reduced.

CHAPTER 2

LITERATURE REVIEW

2.1 CORROSION OF METALS

Corrosion of metals is significantly understood to be the process of degradation of materials caused by various means of process, often by chemical surface reactions with aggressive components of the environment. Metals are synonym to corrosion problems, and various structures built using this kind of materials are subjected to have higher risk of corrosion related failures. A common example of corrosion is rusting of iron, by the formation of rust. Rust which is a mixture of hydroxides of iron and oxides is a product of reaction between surface atom, oxygen and water [2]. Both factor of corrosion reaction, oxygen and water, present in the surrounding moist atmosphere or aqueous solution. Because of this condition of reaction, corrosion consequently differs from wear, a form of material failure and degradation caused by mechanical friction, such as abrasion. Corrosion and wear is further differentiated by the primary product produced; non-metallic solid or dissolved chemical species by corrosion and metallic particles produces by wear. Several metals, mainly very noble ones such as gold or platinum, are impervious against corrosion under normal environmental condition. But other metals such as aluminium and its alloys, titanium and its alloys, iron and steels, the chemical reaction with atmospheric oxygen surrounding is spontaneous. Corrosion reaction in aqueous solution is significantly increased because of the presence of dissolved salts, acids, or bases, which creates and electrically conducting with the alliance of these electrolytes [2]. Marine water environment is an exact example of electrolytic solution which has been significantly related to various kind of corrosion failure experienced by numerous marine structures such as offshore platform and ships.

2.2 CORROSION IN CORROSIVE ENVIRONMENT: MARINE OR SEA WATER

Corrosion rate is significantly increased in corrosive solution, such as sea water. The corrosion rate increase as the concentration of corrosive solution increase [1]. Marine water solution or sea water is a form of corrosive solution that contains various kinds of salts, mainly sodium chloride, NaCl [3]. A 3.5% solution of NaCl is often used to stimulate seawater in the laboratory, but such solutions are often more insistent than natural seawater, especially toward carbon steel. Figure 1 below shows the effect of NaCl concentrations on corrosion of iron in aerated solution.

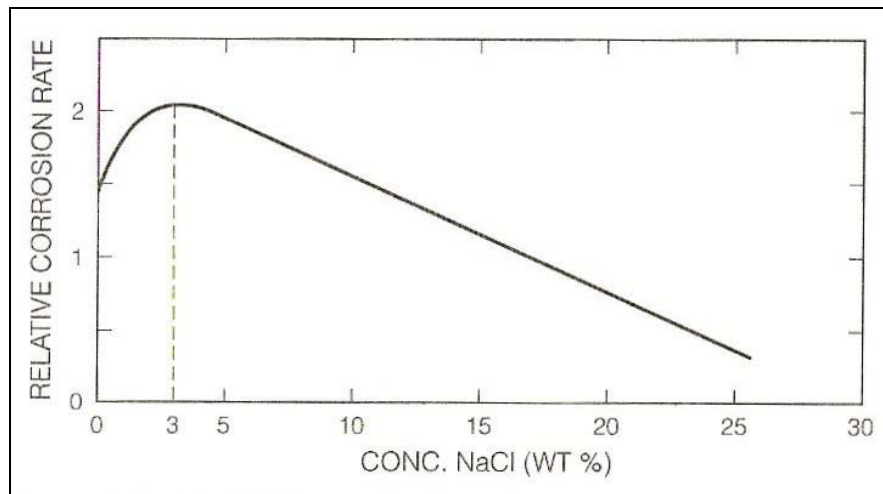


Figure 2.1: Effect of NaCl concentration on corrosion of iron in aerated solutions [3]

Sea water is a very complex system affected by various level of concentration, access of dissolved oxygen, salinity, minor ion concentrations, biological organisms as well as pollutants. These characteristics can increase corrosion rate in coastal and seawaters, but also can limit the corrosion activity such as built of biofouling surface layer in seawater upon the component or equipment. A much more standard sea water solution can be made up in the laboratory, which can create a much more conducive environment for experiment thus producing more accurate result of experiments.

2.3 CATHODIC PROTECTION

Cathodic Protection can be applied as a corrosion protection method to protect various types of steel, namely steel, copper, lead, and brass in numerous conditions of soil and almost all kinds of aqueous media [5]. As one of the most popular means of corrosion prevention methods, Cathodic Protection (CP), was being used long before the science of electrochemistry has been used [1]. British Naval ships had used this protection method since 1824 by Sir Humphrey Davy. The principles of CP can be explained by referring to the corrosion of a typical metal, M, in an acidic environment. By means of electrochemical reactions, the process of metal dissolution and hydrogen gas evolution occurred, for example:



CP is achieved when the metal structure to be protected is supplied with electrons, or in the other hand, it is accomplished by supplying an external current to the protected material, or to the corroding metal [5]. With regards to reactions described from Equations (1) and (2), it indicates that the addition of electron to the metal, or in this case, the protected structure, will be liable to smother metal dissolution as well increasing the rate of hydrogen evolution. In the other words, the structure will be protected if currents enter it from the electrolyte, on the surface of which local-action cells operate as illustrated in Figure 2.2.

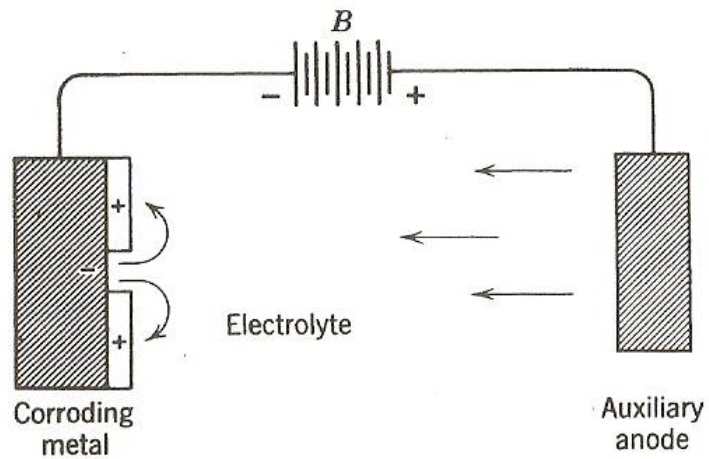


Figure 2.2: Cathodic Protection by superposition of impressed current on local-action current [5].

There are two means to protect a structure cathodically, by an external power supply or by appropriate galvanic coupling. Appropriate galvanic coupling which is also known as sacrificial anode method typically use sacrificial metal consist of magnesium-base and aluminium-base alloy [5].

2.4 SACRIFICIAL ANODES CATHODIC PROTECTION

A structure can be protected cathodically by the appropriate galvanic coupling, or by connection to a second metal called sacrificial anode. Galvanic or sacrificial anodes are made in various types using various kinds of anodes, mainly alloys of magnesium and aluminium which has more active corrosion potential. In this galvanic couple, the structure is being positive or noble and is cathodically polarized. On the other hand, the active metal is anodically dissolved. Sacrificial anodes serve essentially as sources of portable electric energy [5]. For example, a buried steel is protected with a sacrificial anode of magnesium (refer Figure 2.3).

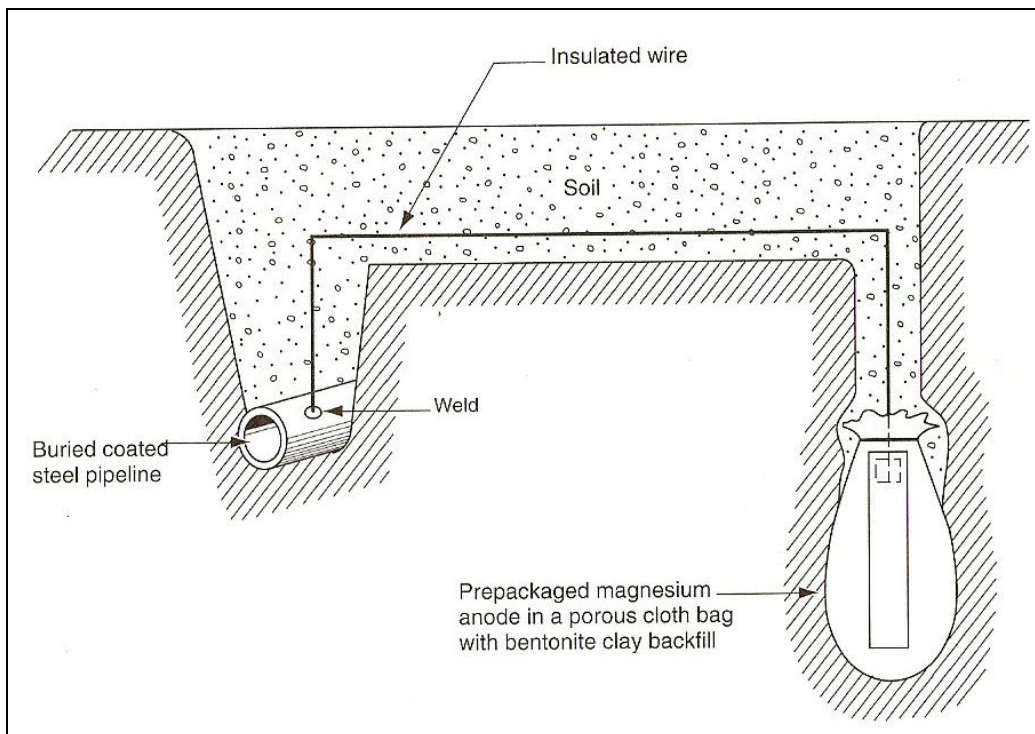


Figure 2.3: Cathodic Protection with a sacrificial anode [3]

Figure 2.4 shows another example of sacrificial anode CP used to protect a domestic water tank, and also being used to protect offshore drilling platform (Figure 2.5)

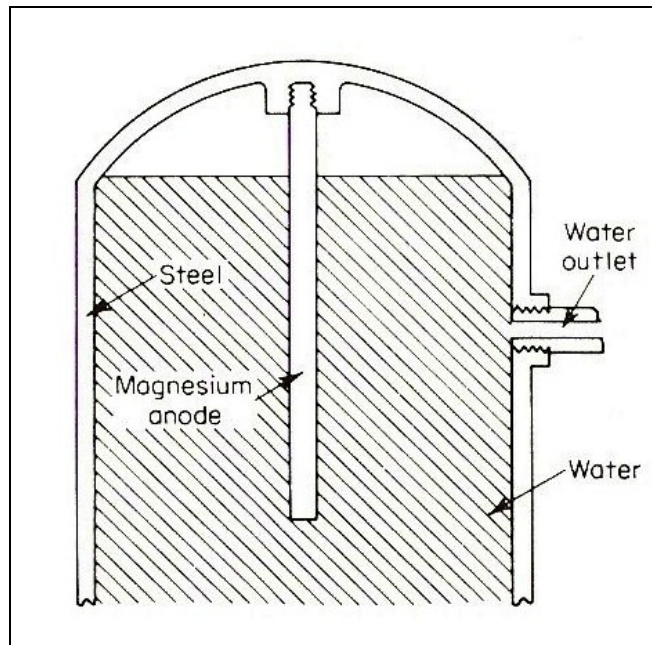


Figure 2.4: CP of a Domestic hot-water tank using a sacrificial anode [3]

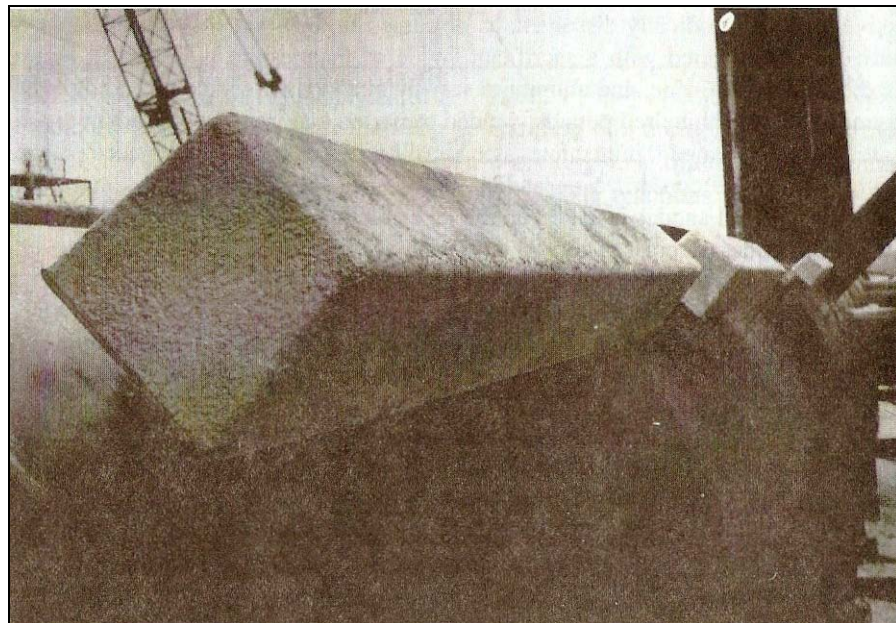


Figure 2.5: Aluminium sacrificial anodes installed on an offshore drilling platform [3]

2.5 GALVANIC EFFECT

The general definition of galvanic effect is the basis of modern battery technology, or can be inter-connected to the mechanism of cathodic protection. However the microscale definition of Galvanic Effect described by Henry Petroski (1988) as:

“a non-homogeneous distributions of charge across the electrified solid or liquid interface that give rise to variations in the electrochemical potential over tiny areas within the whole.”

The galvanic effect is also related to the principles of dissimilar metal corrosion, which can be further defined as corrosion that occurs when two different metals are coupled to form a basic wet corrosion cell. This corrosion principle is also called as bimetallic corrosion, or multimetallic corrosion.

2.6 THE GALVANIC SERIES

The galvanic series is an establishment of an order of corrosion tendency. Such series is of very practical value because it enables a rapid prediction of the corrosion resistance of a dissimilar metal couple. The galvanic series has several advantages compared to electrochemical series [4], which are:

- The galvanic series is measured under arbitrary conditions of temperature, pressure and electrolyte, while electrochemical series is considered under standard conditions and is independent of other species in the environment.
- The galvanic series contains pure metals and alloys, a significant practical advantage as compared to electrochemical series that list data only for metals.
- The galvanic series is a relative qualitative series listing an experimental order of nobleness of metals, while the electrochemical series is an absolute quantitative series listing electrochemical data for use in precise calculations.

Figure 2.6 shows the galvanic series of selected metals at 25°C in sea-water. In general, it can be inferred that the greater the separation of any two metals, the greater will be the corrosion of the more active metal.

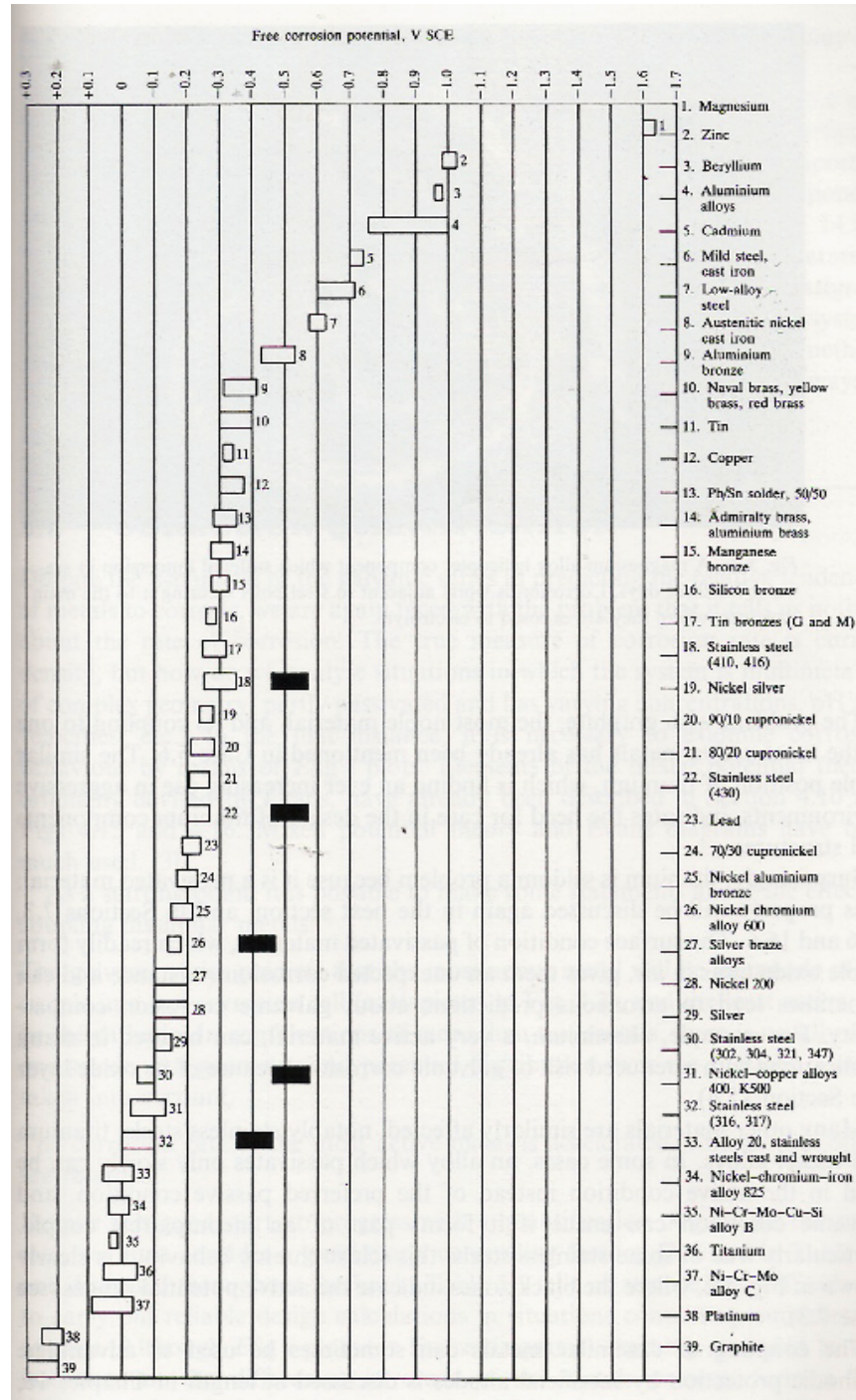


Figure 2.6: Galvanic Series in Sea-water [4].

2.7 FRESH WATER AQUARIUM BACTERIAL TRAP BLOCK

The design of a fresh water aquarium bacterial block has efficiently trapped bacteria that exist in the water. The unique celled-block that divides the block into segmented sections acts like a 'room' that urges the bacteria to gather without using any chemicals to attract it, and the application of this block is shown in Figure 2.7 and 2.8 below.



Figure 2.7: Application of Aquarium Bacterial Block in Water Filter



Figure 2.8: The block being put directly into the aquarium's water

This unique design (refer Figure 2.9) can be implemented on a cathodic block protection, giving several advantages than other blocks being used today. The advantages that can be achieved by implementing the basis of this design are:

- The cost of manufacturing might be reduced because less amount of material used to manufacture a single block.
- Increase the sectional area to material weight ratio. The segmented design increased the effective area that provides bigger coverage of corrosion protection

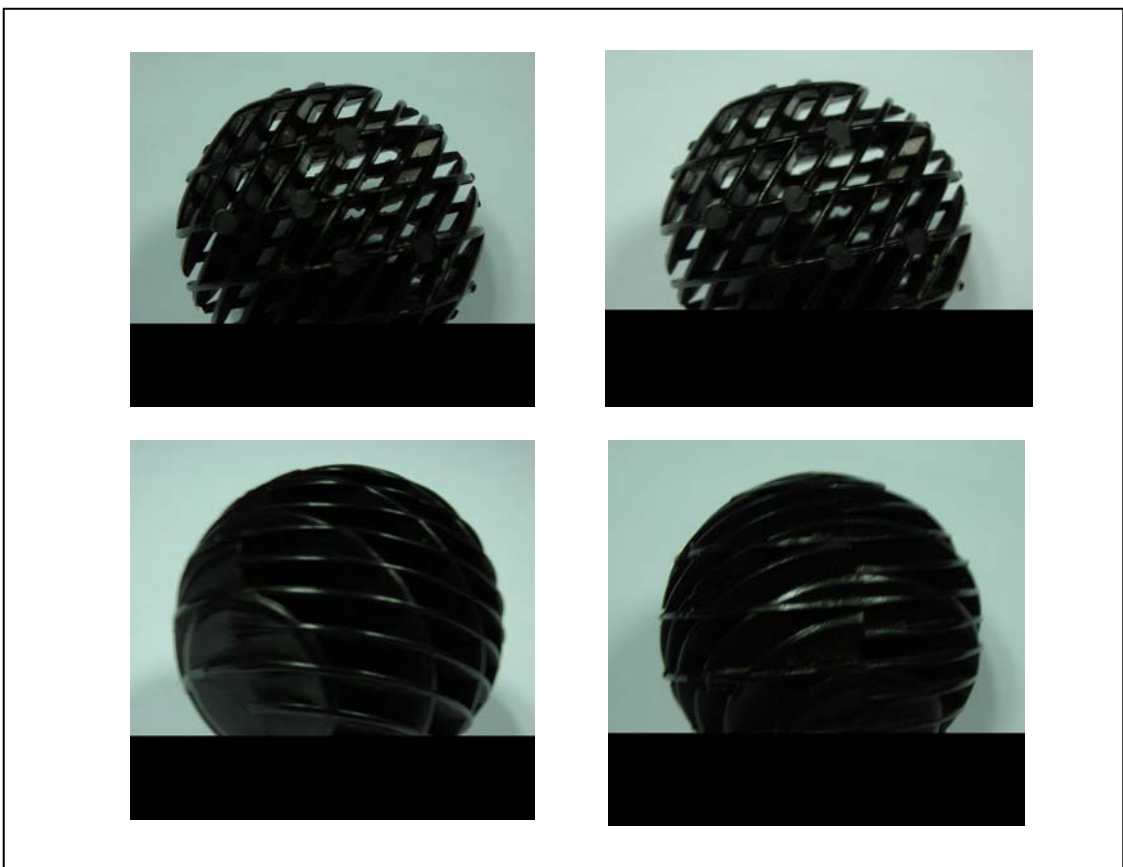


Figure 2.9: Shape of Aquarium Bacterial Trap Block

CHAPTER 3

PROJECT METHODOLOGY

3.1 OVERALL PROCEDURE AND METHODOLOGY

The initial step of this project is to study and identify the current design and performance of CP application. Areas that can be improved are then identified and being put into consideration as the base of hypothesis of each experiment that will be conducted. Several designs are then proposed according to the identified characteristic of CP sacrificial block that will be fabricated and tested, as well as choosing the material as the sacrificial block. Fabrication stage is then being implemented, as the block will be fabricated from the chosen sacrificial material, and based on the design being proposed. Experiment to improve the identified characteristics is being done, as well as proving the relations of the characteristics with the performance of CP. After conducting the experiment for the CP sacrificial block has been done, the results obtained will be analysed, and identified as new design characteristic that will be fabricated accordingly to each component of CP. Final design will be proposed based on the result analysis. Figure 3.1 shows the simplified flow of the project's methodology.

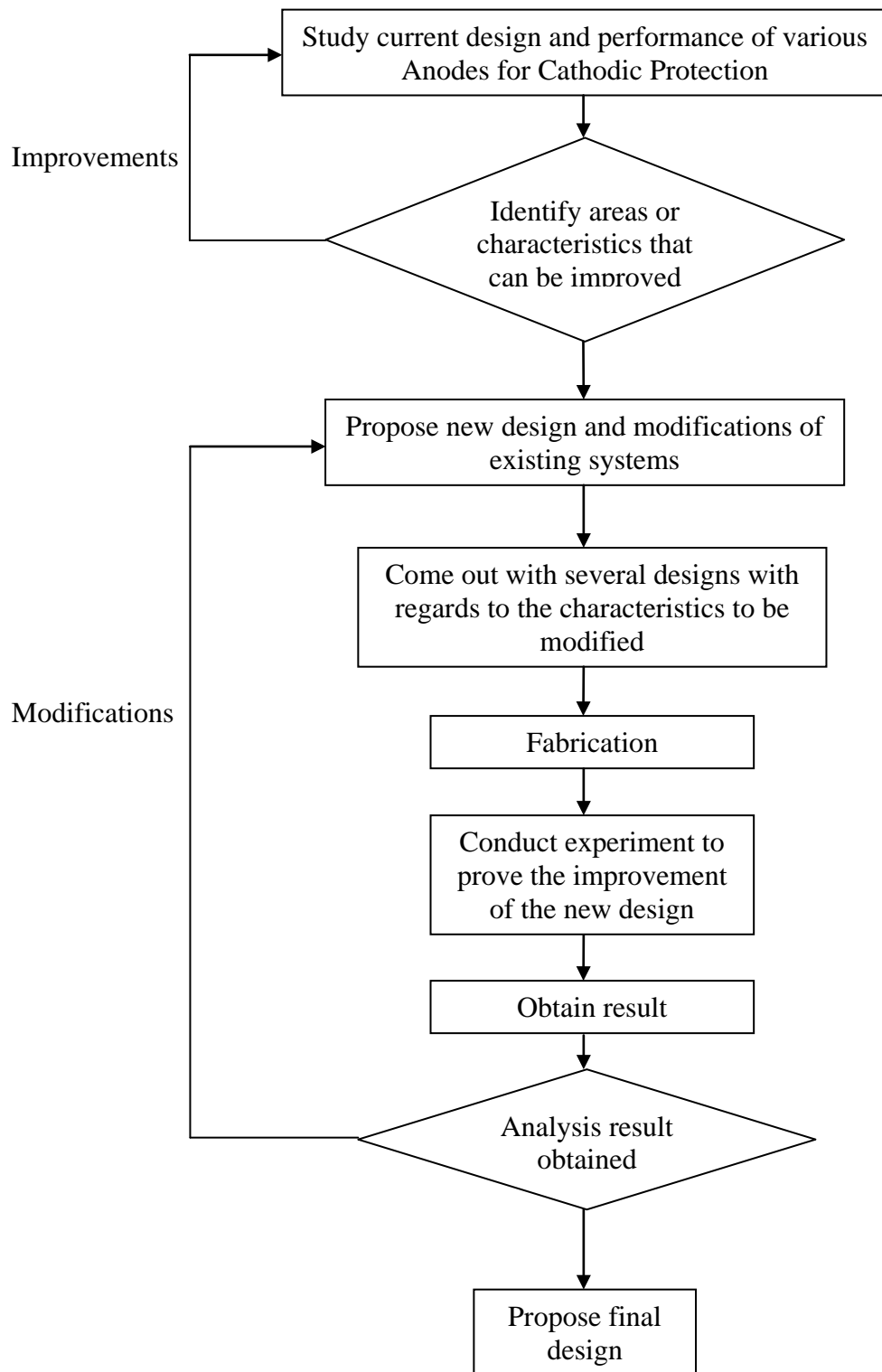


Figure 3.1: Methodology of project.

3.2 DESIGN OF SACRIFICIAL BLOCK

Several designs have been identified based on the scope of the project that has been mentioned earlier; increase the protection area of the CP block by having a larger volume of surface area. These designs are also being identified to suit the purpose of the experiment, which is to prove the improvement of the CP block fabricated based on the new design. The designs including dimensions are as follows:

Set 1

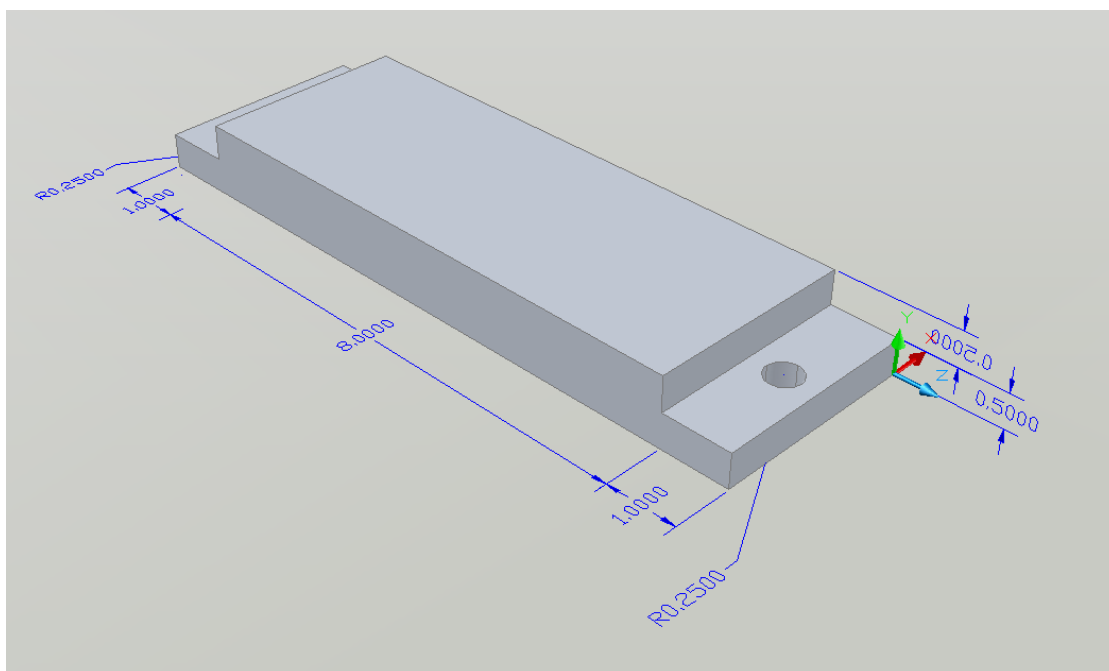


Figure 3.2: Design of Sacrificial Anode A

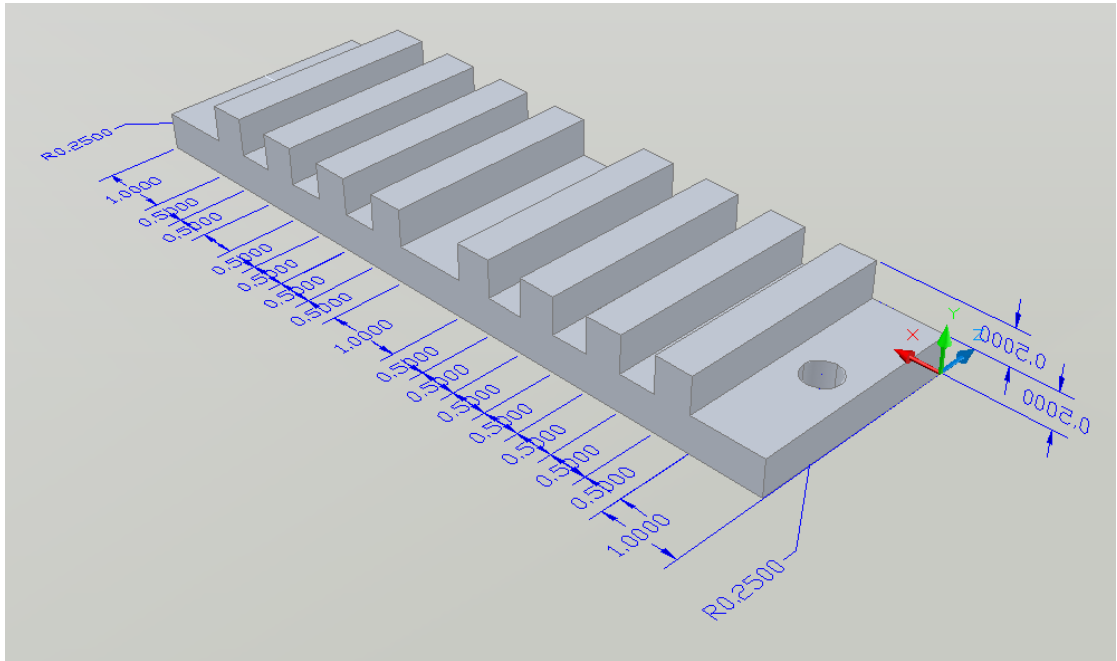


Figure 3.3: Design of Sacrificial Anode B

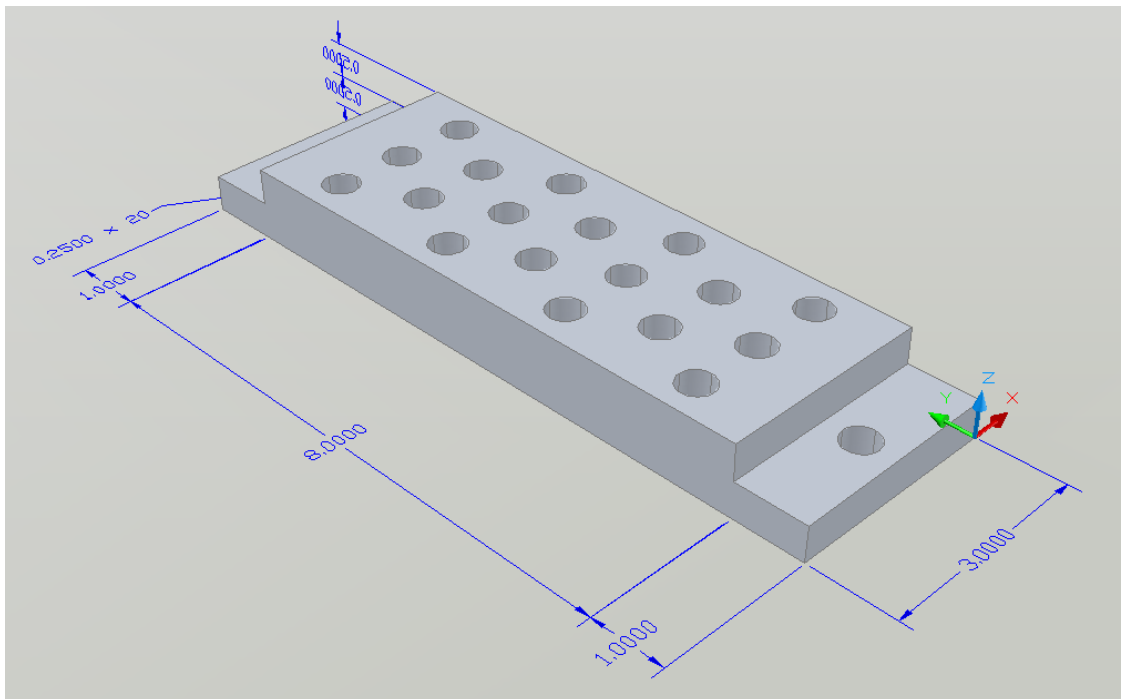


Figure 3.4: Design of Sacrificial Anode C

Set 2

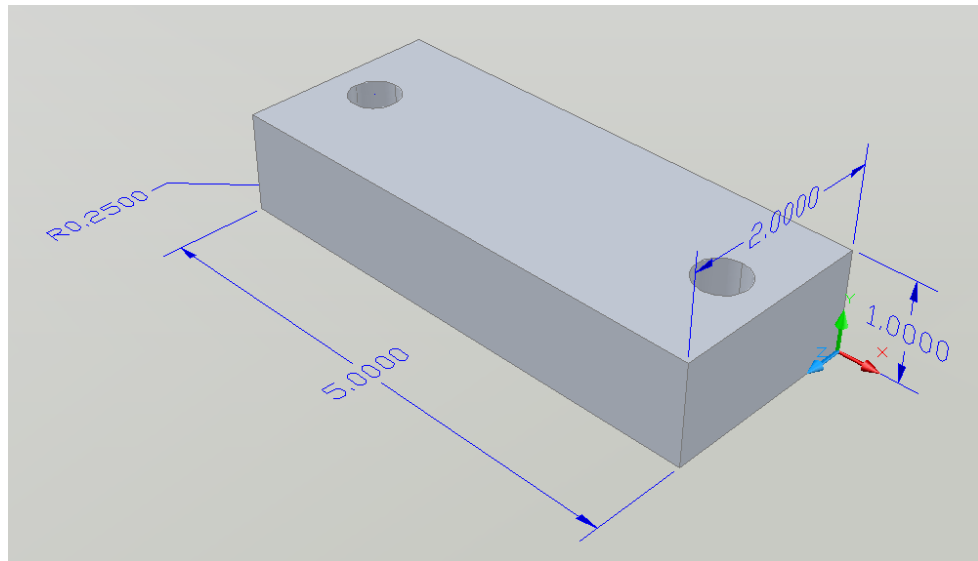


Figure 3.5: Design of Sacrificial Anode D

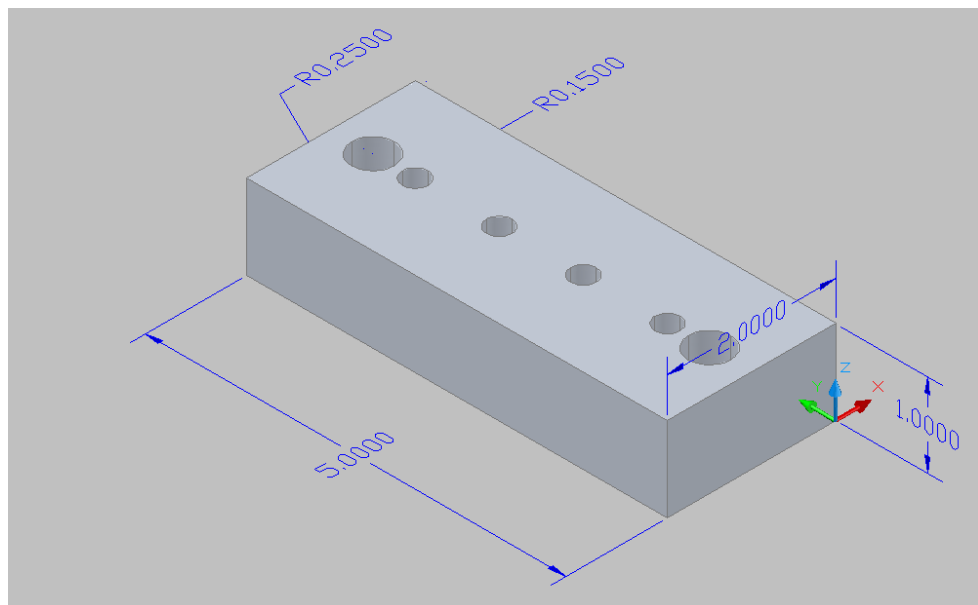


Figure 3.6: Design of Sacrificial Anode E

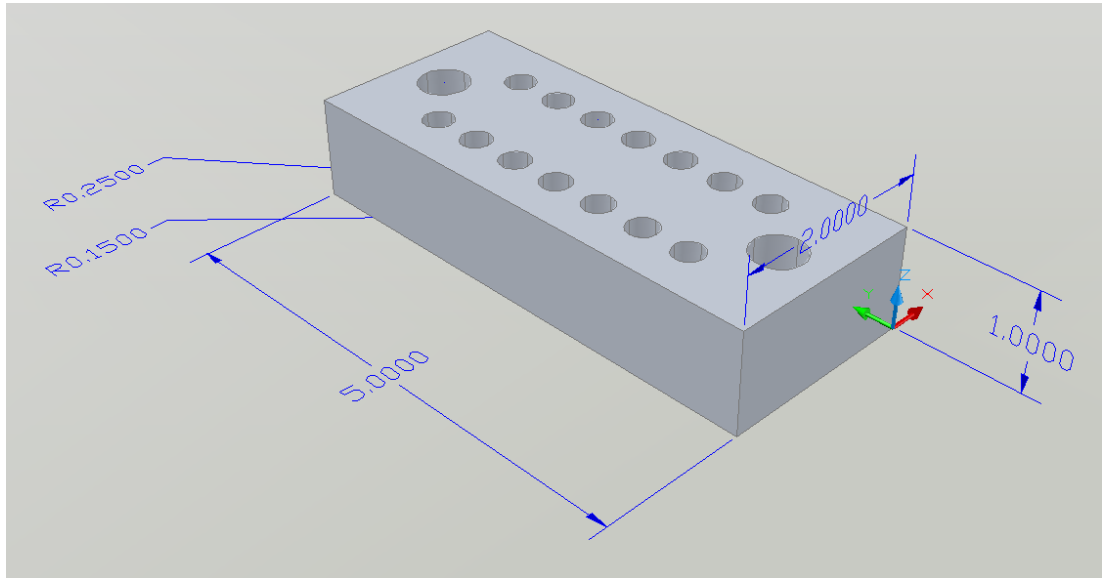


Figure 3.7: Design of Sacrificial Anode F

3.3 PROCEDURE OF EXPERIMENT

The methods of experiment of investigating the performance of the sacrificial anodes and proving the objective of the project are as below:

1. Preparation of protected material (mild steel) and sacrificial anodes.
2. Preparation of sea water solution, 4 containers of 1 litre of solution each.
3. Immersion of the samples in the plastic beaker containing the sea water solution for 14 days.
4. Record the condition of samples as well as the solution after 7 days (1 week) and 14 days (2 weeks) of immersion.
5. Observation of result.
6. Analysis of result using Powder Pillow Test.

3.4 RESULT ANALYSIS – FerroVer® METHOD

Adapted from the Standard Methods for the examination of wastewater [6], the FerroVer® method of the Powder Pillow Test specifically functions as iron or Fe ion detector in various type of water, and in this case, sea water.

Apparatus for the FerroVer® method are:

1. FerroVer (r) Iron Reagent powder pillow
2. Sample cells, 1-inch square, 10 mL
3. Beakers
4. DR 2800 Spectrophotometer device

Procedures

1. Turn on the DR 2800 device.
2. Choose “Stored Program”
3. Choose Test Method (265, Iron, FerroVer)
4. Prepare the samples. Fill a clean square sample cell with 10 mL of sample.



Figure 3.8: Sample cells, 1-inch square, 10 mL

5. Add the contents of FerroVer® iron reagent powder pillow to the square sample cell. Swirl the sample to mix. An orange colour will form, if iron is present.



Figure 3.9: FerroVer® iron reagent powder pillow

6. Press the 3-minute timer. A three-minute reaction occurred.
7. Prepare A blank sample by filling a second square sample cell with 10 mL of sample.
8. When the timer expires, insert the blank into the cell holder with the fill line facing right.
9. Press ZERO button, a reading of 0.00 mg/L Fe will display.
10. Place the prepared sample into the cell holder with the fill line facing right.
11. Press READ button, showing results in mg/L Fe
12. Repeat steps 4 to 11 for each solution sample.

3.5 TOOLS / EQUIPMENT REQUIRED

Several tools are required, mainly for the fabrication of the CP sacrificial anode block. For the fabrication process, basic machining tools are used such as vertical turret milling machine and pedestal drill. As for the analysis of experiment results, DR 2008 Spectrophotometer is being used to determine the concentration of iron or Fe ion in the solution.



Figure 3.10: EASTAR 5VM Vertical Turret Milling machine

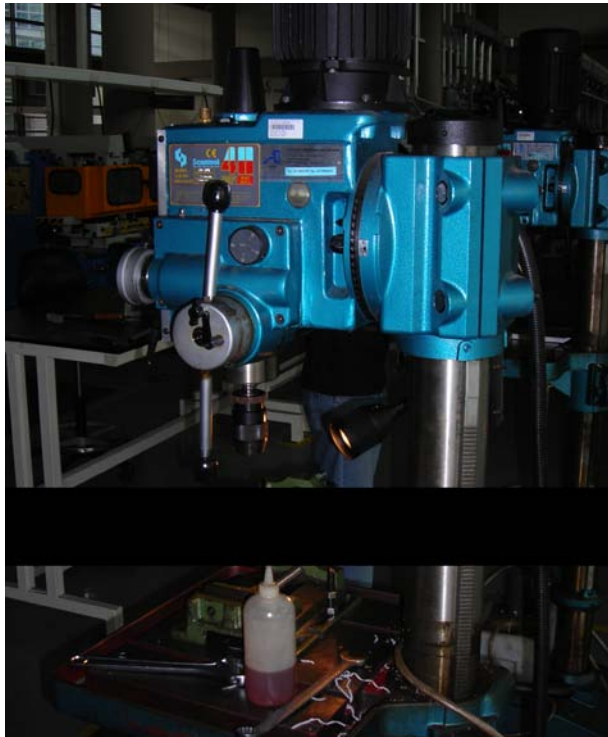


Figure 3.11: Pedestal Drill machine



Figure 3.12: DR 2800 Spectrophotometer

CHAPTER 4

FABRICATION OF SACRIFICIAL ANODE

The fabrication of proposed designs of the Sacrificial Anodes has been done, and followed by an experiment to investigate about the characteristics of the design being proposed based on the objectives of the project. An experiment to prove the objective of the experiment is also being done, with the aim of achieving the said objectives.

Sacrificial Anodes

Sacrificial Anode A

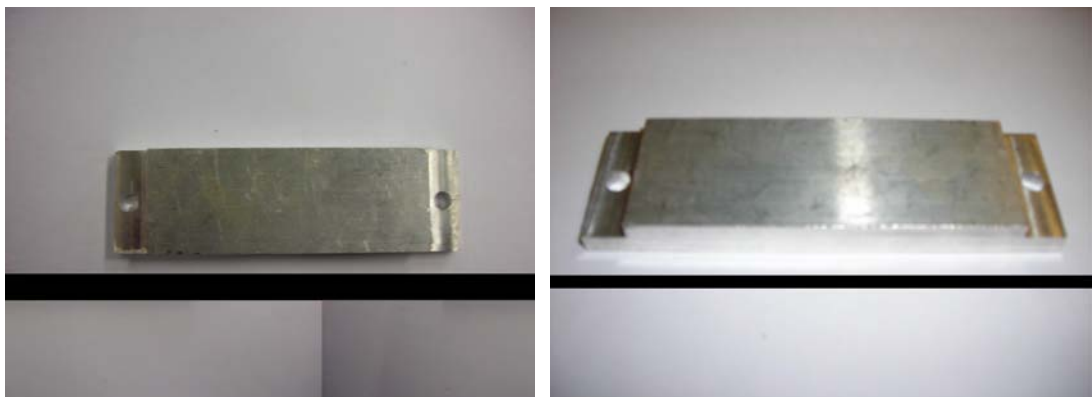


Figure 4.1 and 4.2: Sacrificial Anode A

Material	: Aluminium
Surface area	: 54 cm ² (area exposed to the electrolyte)
Weight	: 69 g

Sacrificial Anode B

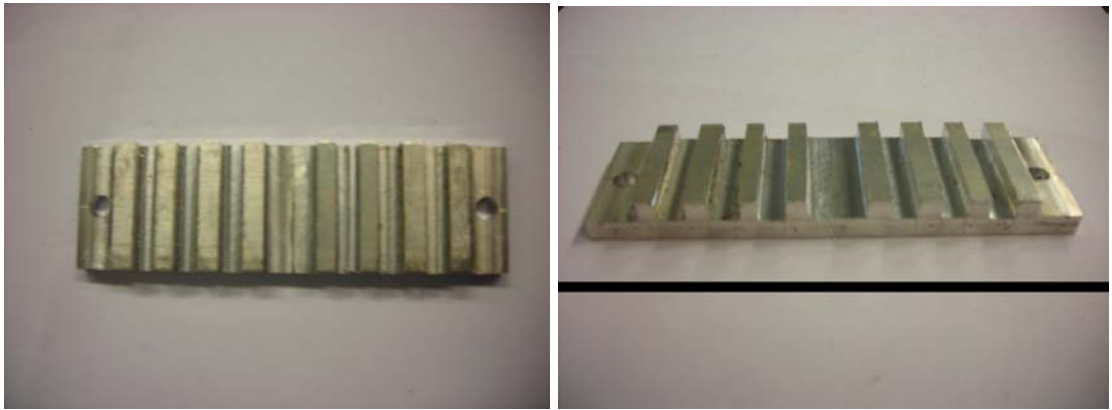


Figure 4.3 and 4.4: Sacrificial Anode B

Material : Aluminium
Surface area : 72 cm² (area exposed to the electrolyte)
Weight : 53 g

Sacrificial Anode C

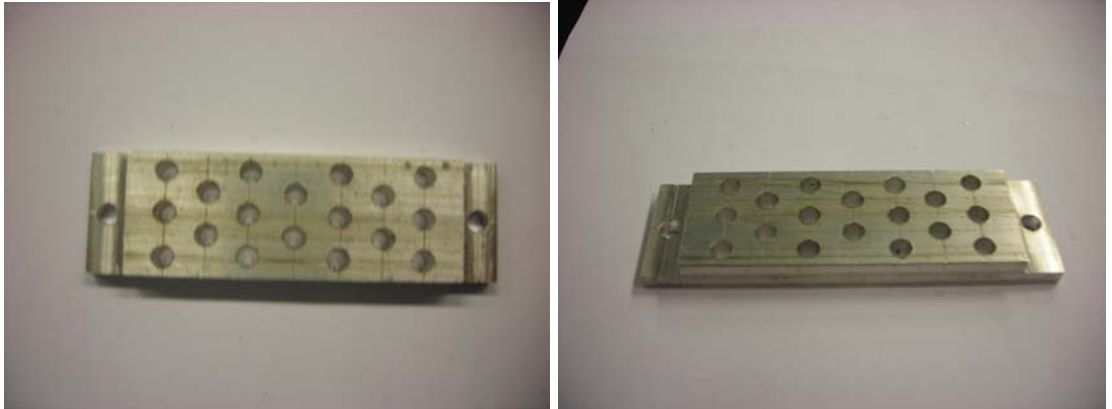


Figure 4.5 and 4.6: Sacrificial Anode C

Material : Aluminium
Surface area : 74 cm² (area exposed to the electrolyte)
Weight : 59 g

CHAPTER 5

EXPERIMENTAL WORK & ANALYSIS

An experiment has been set up to investigate the relationship of the surface area of sacrificial anode upon the protection against corrosion to the steel. The assumption of having larger surface area of CP sacrificial anode block which creates larger protected surface area against corrosion acts as the hypothesis for this experiment.

5.1 PREPARATION OF SAMPLES AND EXPERIMENT

Protected Material: Mild Steel

Sacrificial Anode Material: Aluminium



Figure 5.1: Steel Plate

Set 1

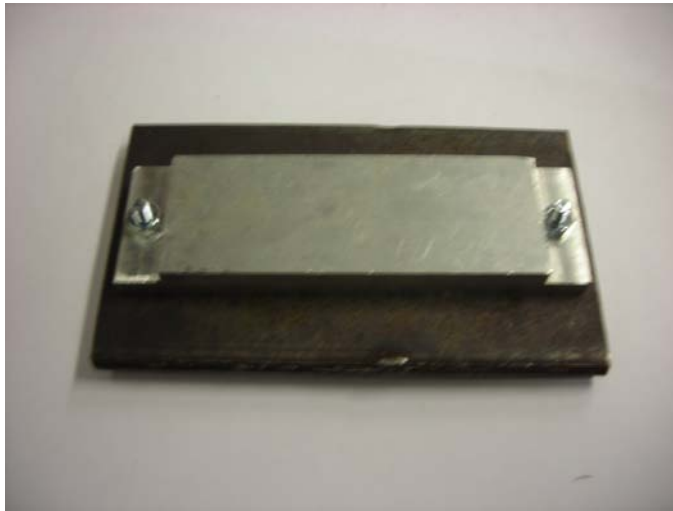


Figure 5.2: Sacrificial Anode A being stacked on Steel Plate



Figure 5.3: Sacrificial Anode B being stacked on Steel Plate



Figure 5.4: Sacrificial Anode C being stacked on Steel Plate

Set 2



Figure 5.5: Sacrificial Anode D being stacked on Steel Plate

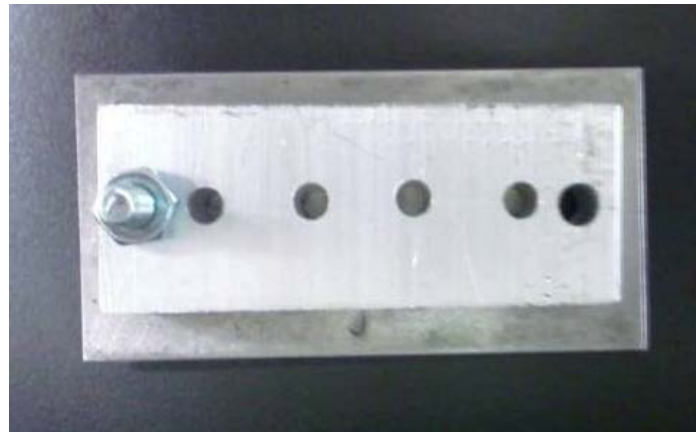


Figure 5.6: Sacrificial Anode E being stacked on Steel Plate



Figure 5.7: Sacrificial Anode F being stacked on Steel Plate



Figure 5.8: Marine water (electrolyte) preparation, using AquaMarine Salt

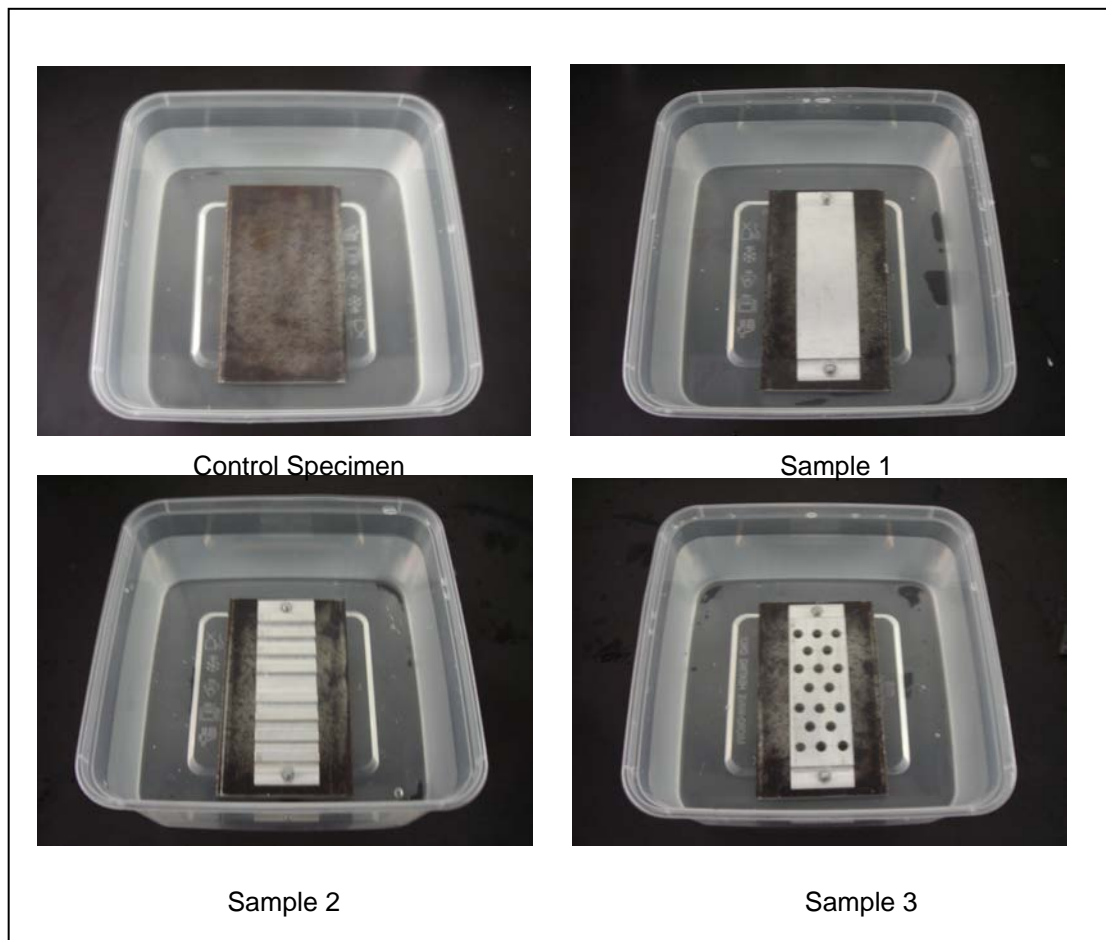


Figure 5.9: Control Specimen (Steel Plate without Sacrificial Anode) and Sacrificial Anodes A, B and C being submerged in Sea Water (Electrolyte)

5.2 RESULT FROM OBSERVATION

Set 1

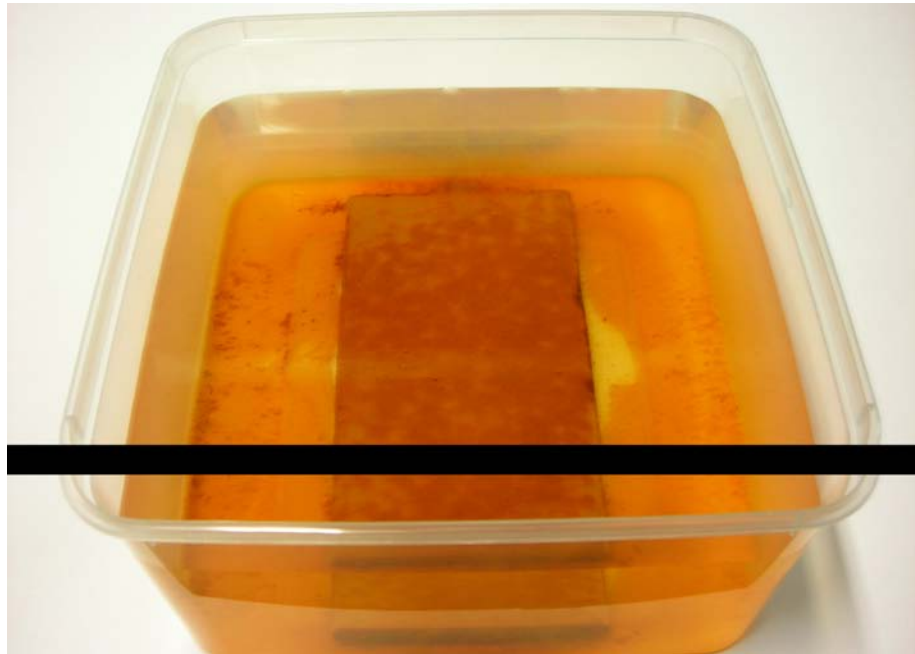


Figure 5.10: Control Specimen after 7 days

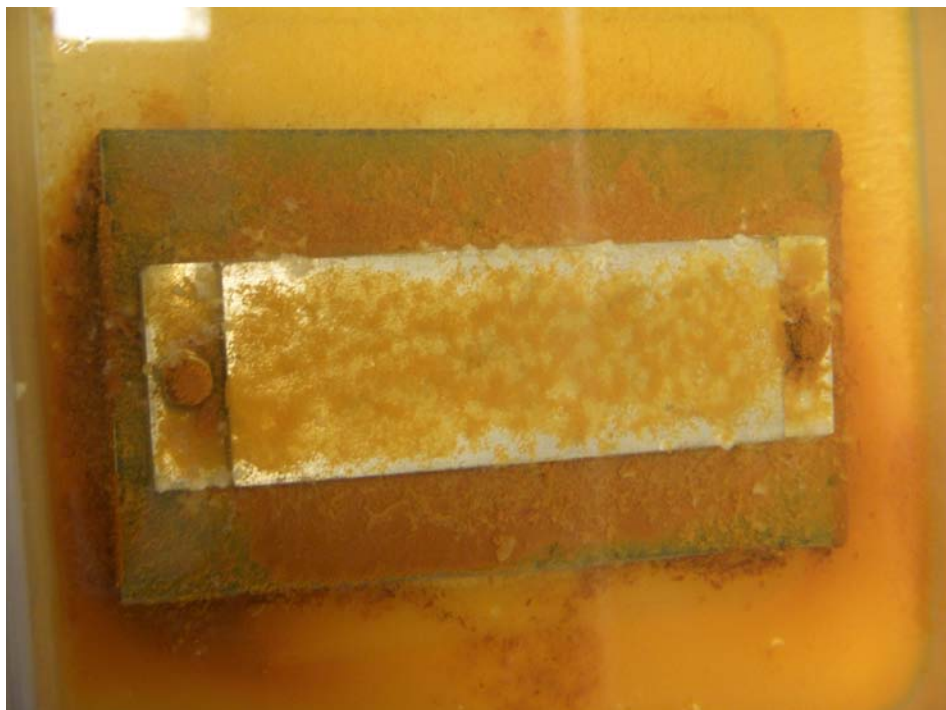


Figure 5.11: Sacrificial Anode A after 7 days (Sample 1)

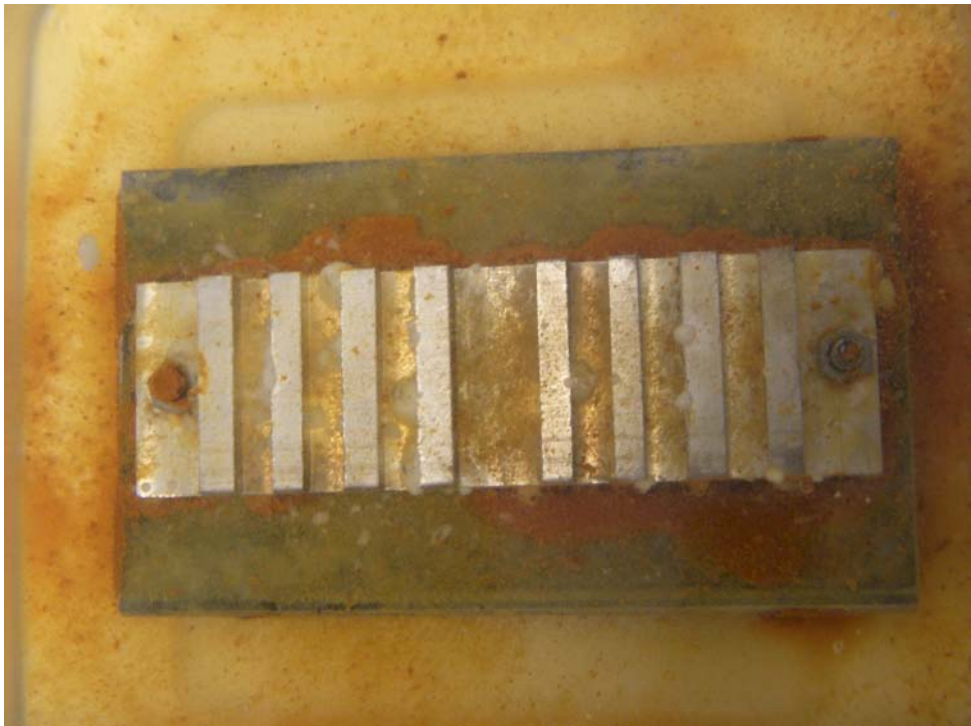


Figure 5.12: Sacrificial Anode B after 7 days (Sample 2)



Figure 5.13: Sacrificial Anode C after 7 days (Sample 3)

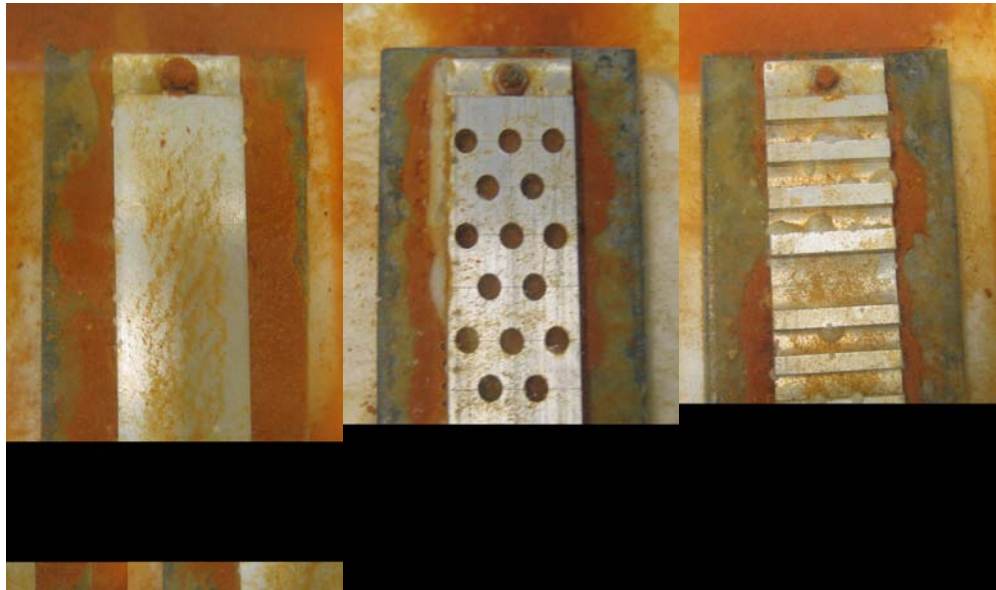


Figure 5.14: (From left) Sacrificial Anodes A, B and C after 14 days

Set 2



Figure 5.15: (From left) Sacrificial Anodes D, E and F after 14 days



Figure 5.16: (From left) Control Specimen, Sacrificial Anodes D, E and F after 14 days



Figure 5.17: Sacrificial Anode D after 14 days



Figure 5.18: Sacrificial Anode E after 14 days



Figure 5.19: Sacrificial Anode F after 14 days

From the condition of the samples after 14 days of immersion in sea water, several justification of initial result based mainly from visual observation upon the condition of the samples and the sacrificial anodes conditions are stated as below:

Set 1

1. Protected Steel of Sacrificial Anode A (Sample 1) experience highest corrosion rate, followed by Sample 2 and Sample 3.
2. Sacrificial Anode C gives best protection to the mild steel.

Set 2

1. Protected Steel of Sacrificial Anode D (Sample 4) experience highest corrosion rate, followed by Sample 5 and Sample 6.
2. Sacrificial Anode F gives best protection to the mild steel.

This initial justification is constructed based on visual inspection of the solution, assuming the protected material (mild steel) in solution that has the darkest brownish colour experience highest corrosion rate. (Refer figure 5.10 until 5.13)

5.3 FINAL RESULT

The initial result based on visual inspection somehow gives an early conclusion that the hypothesis of the experiment is proven. But to further support the assumption being made, an analysis upon the solution that acts as electrolytes for each sample has been conducted. Due to the limited range of reading for FerroVer® method Powder Pillow test (0.02 to 3.00 mg/L Fe), the solution is first being diluted using distilled water to 1/100 of the actual concentration for Set 1, and 1/20 for Set 2 specimens. The results are as follows:

Set 1

Solution	Fe ion Concentration (mg/L Fe)			
	1	2	3	Average
Control Specimen	1.45	1.48	1.40	1.44
Sample 1 (Sacrificial Anode A)	0.56	0.55	0.57	0.56
Sample 2 (Sacrificial Anode B)	0.38	0.36	0.37	0.37
Sample 3 (Sacrificial Anode C)	0.23	0.22	0.23	0.226

Table 1: Concentration of Fe ion in diluted sample solution (Set 1)

Actual Fe concentration in the solutions is as followed:

Solution	Fe ion Concentration (mg/L Fe)
Control Specimen	144
Sample 1 (Sacrificial Anode A)	56
Sample 2 (Sacrificial Anode B)	37
Sample 3 (Sacrificial Anode C)	22.6

Table 2: Actual Fe ion concentration in the sample solution (Set 1)

Set 2

Solution	Fe ion Concentration (mg/L Fe)			
	1	2	3	Average
Control Specimen	1.54	1.56	1.52	1.54
Sample 4 (Sacrificial Anode D)	0.31	0.31	0.32	0.313
Sample 5 (Sacrificial Anode E)	0.26	0.25	0.27	0.26
Sample 6 (Sacrificial Anode F)	0.14	0.16	0.15	0.15

Table 3: Concentration of Fe ion in diluted sample solution (Set 2)

Solution	Fe ion Concentration (mg/L Fe)
Control Specimen	30.8
Sample 4 (Sacrificial Anode D)	6.26
Sample 5 (Sacrificial Anode E)	5.2
Sample 6 (Sacrificial Anode F)	3

Table 4: Actual Fe ion concentration in the sample solution (Set 2)

CHAPTER 6

CONCLUSION AND RECOMMENDATION

Corrosion is deterioration of essential properties in material due to reaction with the surrounding environment. CP serves as the most popular choice of corrosion protection method, and the most employed method of corrosion protection for marine structures and machineries.

The scope of the project is to identify the characteristic of CP that can be improved. The surface area of the CP's sacrificial anode block is the chosen characteristic and initial hypothesis of increasing the protection area by increasing the surface area of the sacrificial anode block has been taken into consideration.

Several designs that have been introduced signify the increment of surface area of the block, as well as several pattern of fabrication method. The sacrificial anode block that has been fabricated from aluminium, which is the best candidate of CP, namely the Sacrificial Anode A, Sacrificial Anode B and Sacrificial Anode C for Set 1, and Sacrificial Anode D, Sacrificial Anode E and Sacrificial Anode F for Set 2. For Set 1, Sacrificial Anode A has the lowest surface area value, followed by Sacrificial Anode B and Sacrificial Anode C. While for Set 2, Sacrificial Anode D has the lowest surface area value, followed by Sacrificial Anode E and Sacrificial Anode F.

Experiments involving Set 2 specimens are being done due to a justification that the different fabrication methods implemented to fabricate Sacrificial Anode A, B and C might affect the results obtained. To achieve the desired surface area increment, Sacrificial Anode B is being fabricated using milling method while Sacrificial Anode C is being fabricated using drilling method. It is believed that drilling method induced higher residual stress which helps in dispersing electron from the surface of the sacrificial anode. So the higher corrosion protection induced from Sacrificial Anode C might be influenced by the level of residual stress within the block despite its highest

surface area value. Because of this justification, Set 2 Specimens were introduced, where the Sacrificial Anodes were fabricated using similar fabrication method.

Based on the observation of the results, it can be initially concluded that the mild steel being stacked with Sacrificial Anode C (Set 1) and Sacrificial Anode F (Set 2) experienced the lowest corrosion rate. This initial conclusion is then supported by the further analysis of the sample, using the FerroVer® method of the Powder Pillow Test. The analysis shows clearly that the sea water solution of sample 3 (Sacrificial Anode C of Set 1) and sample 6 (Sacrificial Anode F of Set 2) has the lowest concentration of Fe ion, or iron indicating that the mild steel of sample 3 and sample 6 corroded at the lowest rate.

Based on the result obtained from the analysis, it can be clearly concluded that increasing the surface area of sacrificial anode gives significant improvement of corrosion protection by the sacrificial anode. Thus, the objective of this project is achieved.

The design characteristics of having higher value of surface area can be implemented onto the existing design of CP, by introducing grooves or holes onto the sacrificial anode block during fabrication process.

As for the recommendation, further experiment should be conducted by having fabricated sacrificial anode block with similar pattern, but different value of surface area. As an example, the desired surface area difference is achieved using only one method fabrication; either introduces groove by milling or holes by drilling. Other surrounding or environmental effect such as subsea current should also being taken into consideration for future experimental work.

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