CHAPTER 1

INTRODUCTION

1.1 Project Background

Carbon steel is commonly used metal in daily life. There are various types of equipment and facilities made from carbon steel. The current condition of the ball valve made from untreated carbon steel on the offshore facilities was badly corroded on the external part of the valve within two years. Even with proper maintenance, due to the exposure of the valve to the extreme environment of sea weather, the valve gradually corroded. Basically, most of the corroded valves experiencing high torque and eventually jammed.

In order to minimized the cause of corrosion, analytical and laboratory studied need to be conducted to investigate the main factors that influence the corrosion rate of the untreated carbon steel when exposed to offshore environment and further can be used to predict the lifespan of the valves as well as the maintenance plan of the valves.

1.2 Problem Statement

The valves made from untreated carbon steel have been badly corroded even with proper maintenance. In order to understand the mechanism of the atmospheric corrosion, the influence of Sodium Chloride (NaCl) deposition on atmospheric corrosion of untreated carbon steel is needed to be studied.

1.3 Objectives of Study

As a main accelerator of atmospheric corrosion of metals in marine environment, NaCl can attract water vapor from humid air to form thin water film on the metal surface. The role of this water layer is to provide a medium for mobilization ions. NaCl dissolved in the layer also raises the conductivity of the electrolyte. This will greatly increase the electrochemical corrosion and affect the composition of the corrosion products. It is therefore a great interest to study the influence of NaCl on the atmospheric corrosion of metals.

The main aim of the present work is to study the effect of atmospheric corrosion of NaCl on untreated carbon steel and come up with the graph of relationship between the NaCl concentration and corrosion rate. The data gathered would help to further predict the lifespan of the valves. Meanwhile, a simple corrosion mechanism is presented to explain the experimental observations.

1.4 Scope of Study

The scope of study is to conduct experiment on the specimens. The study will consist of several laboratory simulation of atmospheric corrosion in order to investigate the influence of NaCl deposition of atmospheric corrosion of untreated carbon steel. The experimental setup and procedure will be explained in the chapter 3 of this report.

CHAPTER 2

LITERATURE REVIEW

2.1 Carbon Steel Valve: An Overview

A Valve is a mechanical device that controls the flow of fluid and pressure within a system or process. A working valve controls the system or process fluid flow and pressure by performing any of the following functions:

- Stopping and starting fluid flow Varying (throttling) the amount of fluid flow
- Controlling the direction of fluid flow
- Regulating downstream system or process pressure
- Relieving component or piping over pressure

The ball valve consists of a few basic parts which are the body, the bonnet, trim or internal elements, actuator, and packing. The basic parts of the valve are illustrated in appendices. The ball valve is a rotation motion valve that uses a ball shaped disk to stop or to start fluid flow. One of the basic parts of the ball valve is the valve body. The body or sometimes called the shell, is the primary pressure boundary of the valve. Io serves as the principal element of a valve assembly because it is the framework that holds everything together.

The body, is the first pressure boundary of a valve, resists fluid pressure loads from the connecting piping. It receives inlet and outlet piping through threaded, bolted or welded joints [1]. Valve bodies are cast or forged into a variety of shape using variety of material and in my case is untreated carbon steel. The failure of the valve body due to external corrosion will then eventually make the valve jammed.

This problem has been occurring in PETRONAS Platform, Duyong field firewater line and consumes a large amount of money for maintenance. So, this study will investigate the influence of NaCl deposition on atmospheric corrosion of untreated carbon steel and calculate the corrosion rate of the untreated carbon steel and further the life span of the valve could be predict

2.2 Corrosion Theory

Corrosion is defined as the deterioration of a material, usually a metal, because of a reaction with its environment and which requires the presence of an anode, a cathode, an electrolyte, and an electrical circuit [2]. Corrosion occurs by an electrochemical process. The process is similar to that which takes places when a carbon-zinc “dry” cell generates current. Basically, an anode (negative electrode), a cathode (positive electrode), an electrolyte (environment), and a circuit connecting the anode and cathode are required for corrosion to occur. Dissolution of metal occurs at the anode where the corrosion current enters the electrolyte and flows to the cathode. The general reactions (reactions, if an alloy is involved) that occurs at the anode is the dissolution of metals as ions. Equation 2.1. Shows the generals reaction at the anode:

$$M \rightarrow M^{n-} + 2^{e-} \ldots\ldots\ldots \; (2.1)$$

Where,

M = metal involved, n = valence of corroding metals species, e = electrons.

Examination of this basic reaction reveals that a loss of electrons, or oxidation, occurs at anode. Electrons lost at the anode flow through the metallic circuit to the cathode and permit a cathodic reaction (or reactions) to occur. In alkaline and neutral aerated solutions, the predominant cathode reaction is as in the equation 2.2:

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

The cathodic reaction that usually occurs in de-aerated acids is as in the equation 2.3 which produces hydrogen gas:

$$2H^- + 2e^- \rightarrow H_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (2.3)$$

The general electrochemical reaction in aerated acids is as in the equation 2.4.The cathodic reaction is:

$$O_2 + 4H^- + 4e^- \rightarrow 2H_20 \ldots\ldots\ldots\ldots \ (2.4)$$

All of these reactions involve a gain in electrons and a reduction process.

The number of electrons lost at the anode must equal to the number of electrons gains at the cathode. For example, if iron (Fe) was exposed to aerated, corrosive water, the anodic reaction would be

$$Fe \rightarrow Fe^{--} + 2e^- \quad \ldots\ldots\ldots\ldots\ldots \ (2.5)$$

At the cathode, reduction of oxygen could occur.

$$O_2 + 2H_2O + 4e^- \rightarrow 4\ (OH^-) \ldots\ldots\ldots\ldots \ (2.6)$$

Because there can be no net gain or loss of electrons, two atoms of iron must dissolve to provide four electrons required at the cathode. Thus, the anodic and cathodic reactions could be

$$2 \quad Fe + O_2 + 2H_2O \rightarrow 2\,Fe^{--} + 4\,(OH^-) \ldots\ldots.\ (2.7)$$

After dissolution, ferrous ions (Fe^{2+}) generally oxidize to ferric ions (Fe^{3+}); these will combine with the hydroxide ions (OH^-) formed at the cathode to give the corrosion product called rust (FeOOH or Fe_2O_3 x H_2O). Anodic reactions involved dissolution of metals electrochemically, and the secondary product (rust) is formed as a result of cathodic reaction.

2.3 Atmospheric Corrosion

Atmospheric corrosion is a corrosion of materials when exposed to the air and its pollutants rather that immersed in liquid [3]. Atmospheric corrosion can be further classified into dry, damp, and wet categories.

The Cathodic and Anodic Half-Cell Reactions in Atmosphere Corrosion are as below [4].

2.3.1 The cathodic process [4].

If it is assumed that the surface electrolyte in extremely thin layers is neutral or slightly acidic, then the reaction would be as in the equation 2.8 which shows the reaction of hydrogen ions to form hydrogen gas:

$$2\,H^+ + 2e^- \rightarrow H_2 \quad \ldots\ldots\ldots\ldots\ldots.\ (2.8)$$

can be ignored for atmospheric corrosion of most metals and alloys. Exceptions to this assumption would include corrosive attack under coatings (such as filiform corrosion) and other crevice corrosion conditions. The reduction of atmospheric oxygen is the most important reaction in which electrons are taken up. For atmospheric corrosion in near-neutral electrolyte solution, the equation 2.9 shows the oxygen reduction reaction that is most likely to occur:

$$O_2 + 2H_2O + 4e^- \rightarrow 4\,(OH^-) \;\ldots\ldots\ldots\; (2.9)$$

Two reactions steps may actually be involved, with hydrogen peroxide as an intermediate species, according to equation 2.10 and 2.11; the product of the reaction is hydroxide ions.

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2(OH^-) \;\ldots\ldots\ldots\; (2.10)$$

$$H_2O_2 + 2e^- \rightarrow 2\;OH^- \ldots\ldots\ldots\ldots(2.11)$$

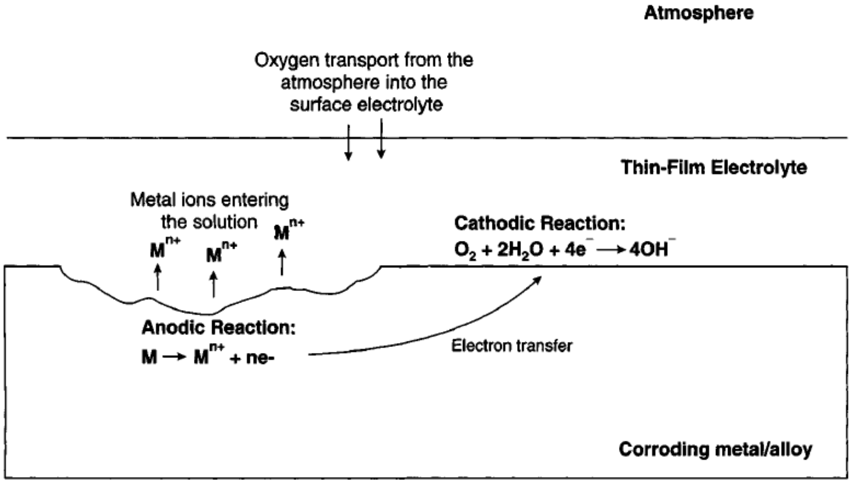


Figure 1: Mechanism of atmospheric corrosion

(Simplified for a “theoretical” clean surface).[16]

If oxygen diffuses from atmosphere through the electrolyte film to the metal surface, diffusion limited current density should be arguably apply. It has been shown that a diffusion transport mechanism for oxygen is only applicable to an electrolyte layer thickness approximately 30µm and under strictly isothermal conditions. In thicker layer and non-isothermal conditions convective effects are dominant, which increase the limiting current density to higher values than predicted by simplified diffusion equations. The predicted limiting current density of oxygen reduction in an electrolyte layer thickness of 30 um significantly exceeds practical observations of average atmospheric corrosion rates. On this basis, it can be argued that the overall rates of atmospheric corrosion are not likely to be controlled by the cathodic oxygen reduction process but rather by the anodic reaction(s).

The research of Stratmann and Streckel [5] on iron and iron-copper alloys showed that atmospheric corrosion kinetics are highly complex. These researchers measured fluctuations in atmospheric corrosion rates, rather than considering average rates. Remarkably high corrosion rates for iron (up to 1 mA/cm^2) were observed as transients during the drying period of the surfaces. Such high corrosion rates can be rationalized on the basis of accelerated oxygen reduction, as the electrolyte thickness is reduced in the drying phase. Interestingly, however, the high corrosion rate transients were only observed in the wet to dry transitions, not in the dry to wet cases. These fundamentally important results indicate that the oxygen reduction rate is not only a function of the electrolyte film but also the composition of surface oxide layers that varies from wet to dry conditions. It was shown that the corrosion rate during the important surface drying phase is determined by three competing reactions [13]:

(i) acceleration of oxygen reduction in the early drying stage,
(ii) surface passivation with drying, and
(iii)Deceleration of oxygen reduction in the last drying stage. Copper additions to iron were shown to reduce the rate of oxygen reduction (at low alloying levels) and enhance surface passivation (at high alloying levels).

2.3.2 The Anodic Process

The equation 2.11 is a simplified oxidation reaction represents the anodic half-cell for atmospheric corrosion:

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

The formation of corrosion products (metal oxides and hydroxides), the solubility of corrosion products in the surface electrolyte, and the formation of passive films affect the overall rate of the anodic metal dissolution process and cause deviations from simple rate equations assuming activation control. Passive films distinguish themselves from corrosion products, in the sense that the former tend to be more tightly adherent, are of lower thickness and provide a higher degree of protection from corrosive attack. Atmospheric corrosive attack on a surface protected by a passive film tends to be of a localized nature. Surface pitting in aluminum and stainless alloys is an example of such attack. Relatively complex reaction sequences have been proposed for the corrosion product formation and breakdown processes to explain observed atmospheric corrosion rates for different classes of metal.

2.4 Important Variables in Atmospheric Corrosion

2.4.1 Time of Wetness

From the above theory, it should be apparent that the time of wetness of the corroding surface is a key parameter, directly determining the duration of the electrochemical corrosion processes. This variable is a complex one, since all the means of formation and evaporation of an electrolytic solution on a metal surface must be considered.

The time of wetness is obviously strongly dependent on the critical relative humidity. Apart from the primary critical humidity, associated with clean surfaces, secondary and even tertiary critical humidity levels may be defined, where the corrosion rate increases abruptly. Hygroscopic corrosion products and capillary condensation of moisture in corrosion products are thought to account for these, respectively. A capillary condensation mechanism may also account for electrolyte formation in microscopic surface cracks and the metal surface/dust particle interface.

Other sources of surface electrolyte include chemical condensation (by chlorides, sulfates, and carbonates), adsorbed molecular water layers, and direct moisture precipitation (ocean spray, dew, and rain) [6]. The effects of rain on atmospheric corrosion damage are somewhat ambiguous. While providing electrolyte for corrosion reactions, rain can act in a beneficial manner by "washing away" or diluting harmful corrosive surface species

2.4.2 Sulfur Dioxide

Sulfur dioxide ($S0_2$), a product of the combustion of sulfur containing fossil fuels, plays an important role in atmospheric corrosion in urban and industrial type atmospheres. It is adsorbed on metal surfaces, has a high solubility in water and tends to form sulfuric acid in the presence of surface moisture films. Sulfate ions are formed in the surface moisture layer, by the oxidation of sulfur dioxide according to [4]. The equation 2.12 shows the reaction:

$$SO_2 + O_2 + 2\,e^- \rightarrow SO_4^- \quad \ldots\ldots\ldots\ldots\text{(Equation 2.12)}$$

The required electrons are thought to originate from the anodic dissolution reaction and, in the case of iron, from the oxidation of ferrous to ferric ions. For iron, it is the formation of sulfate ions that is considered to be the main corrosion accelerating effect from sulfur dioxide. The presence of these sulfate ions ultimately leads to the formation of iron sulfate ($FeSO_4$).Iron sulfate is known to be a corrosion product component in industrial atmospheres and is mainly found in layers at the metal surface. The iron sulfate is hydrolyzed by the reaction equation 2.13:

$$FeSO4 + H_2O \rightarrow FeOOH + SO_4^{2-} + 3H^+ + e^- \ldots\ldots\ldots\ldots\text{(Equation 2.13)}$$

The corrosion stimulating sulfate ions are reliberated by this reaction, leading to an autocatalytic type of attack on iron [4]. The acidification of the electrolyte could arguably also lead to accelerated corrosion rates but this effect is likely to be of secondary importance due to buffering effects of hydroxide and oxide corrosion products. In nonferrous materials such as zinc, sulfate ions also stimulate corrosion but the autocatalytic corrosion mechanism is not established.

2.4.3 Chlorides

Atmospheric salinity distinctly increases atmospheric corrosion rates. Apart from the enhanced surface electrolyte formation by hygroscopic salts such as NaCl and $MgCl_2$, direct participation of chloride ions in the electrochemical corrosion reactions is also likely [4]. In ferrous metals, chloride anions are known to compete with hydroxyl ions for combining with ferrous cations produced in the anodic reaction. In the case of hydroxyl ions, stable species tend to be produced. In contrast, iron chloride complexes tend to be unstable (soluble), resulting in further stimulation of corrosive attack. On this basis, metals such as zinc and copper, whose chloride salts tend to be less soluble than those of iron, should be less prone to chloride induced corrosion damage [4], consistent with practical experience

2.4.4 Other Atmospheric Contaminants

Hydrogen sulfide, hydrogen chloride, and chlorine present in the atmosphere can intensify atmospheric corrosion damage, but they represent special cases of atmospheric corrosion, invariably related to industrial emissions in specific microclimates [4]. Hydrogen sulfide is known to be extremely corrosive to most metals/alloys and the corrosive effects of gaseous chlorine and hydrogen chloride in the presence of moisture tend to be stronger than those of "chloride salt" anions, due to the acidic character of the former species [4]. Nitrogen compounds, in the form of NO_x, also tend to accelerate atmospheric attack. The NO_x emission, largely from combustion processes, has been reported to have increased relative to SO2 levels [7]. However, measured deposition rates of these nitrogen compounds have been significantly lower than for SO2 [7], which probably accounts for the generally lower importance assigned to these.

The deposition of solid matter from the atmosphere can have a significant effect on atmospheric corrosion rates, particularly in the initial stages. Such deposits can stimulate atmospheric attack by three mechanisms:

1. Reduction in the critical humidity levels by hygroscopic action.
2. The provision of anions stimulating metal dissolution.
3. Micro galvanic effects by deposits more noble than the corroding metal (carbonaceous deposits deserve special mention in this context).

2.4.5 Temperature

The effect of temperature on atmospheric corrosion rates is complex in nature. An increase in temperature will tend to stimulate corrosive attack by increasing the rate of electrochemical reactions and diffusion processes. For a constant humidity, an increase in temperature would lead to a higher corrosion rate. Raising the temperature will, however, generally lead to a decrease in relative humidity and more rapid evaporation of surface electrolyte. By reducing the time of wetness in this manner, the overall corrosion rate would tend to diminish.

For closed-air spaces, such as indoor atmospheres, it has been pointed out that the increase in relative humidity associated with a drop in temperature has an overriding effect on corrosion rate [8].This implies that in air conditioning, a decrease in temperature requires additional dehumidification, to avoid accelerated atmospheric corrosion damage.

At temperatures below freezing, where the electrolyte film solidifies, electrochemical corrosion activity will drop to negligible levels in the absence of chloride contamination. The very low atmospheric corrosion rates reported in extremely cold climates are consistent with this effect [9].

Somewhat unexpectedly, relatively high corrosion rates have been measured in some coastal cold climates under the influence of salt deposition [10]. The well-known depression of the freezing point by salt may account for these results.

CHAPTER 3

METHODOLOGY

3.1 Process Flow

Methodology plays an important role in completing a project. It is an abstract representation of each system processes. The purpose of having methodology is to guarantee system is developed within the scope planned and ensure consistency of each process. Before the project begins, basic knowledge on the project was learned and was understood. This was done through reading text books, journal and thesis in the library or in the internet on the subject matter. The methodology starts with theory understanding and parameters acquisition as shown in Figure 2

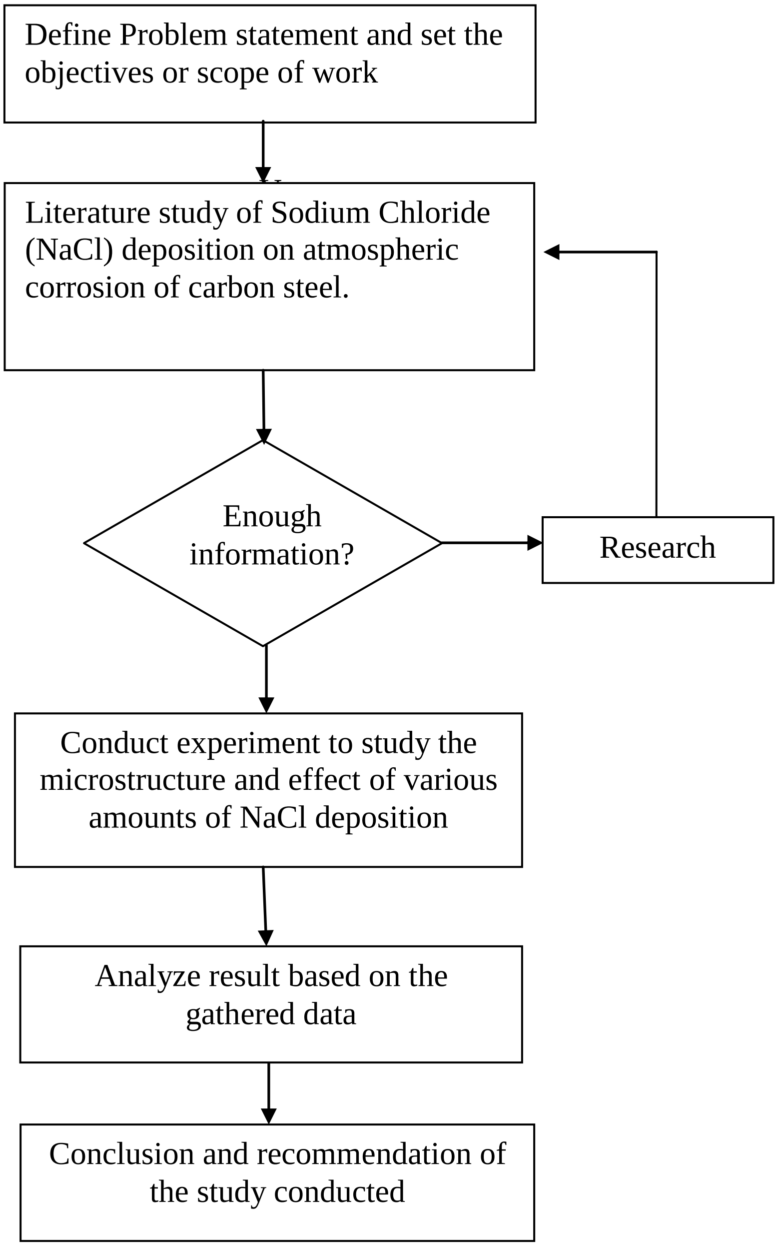
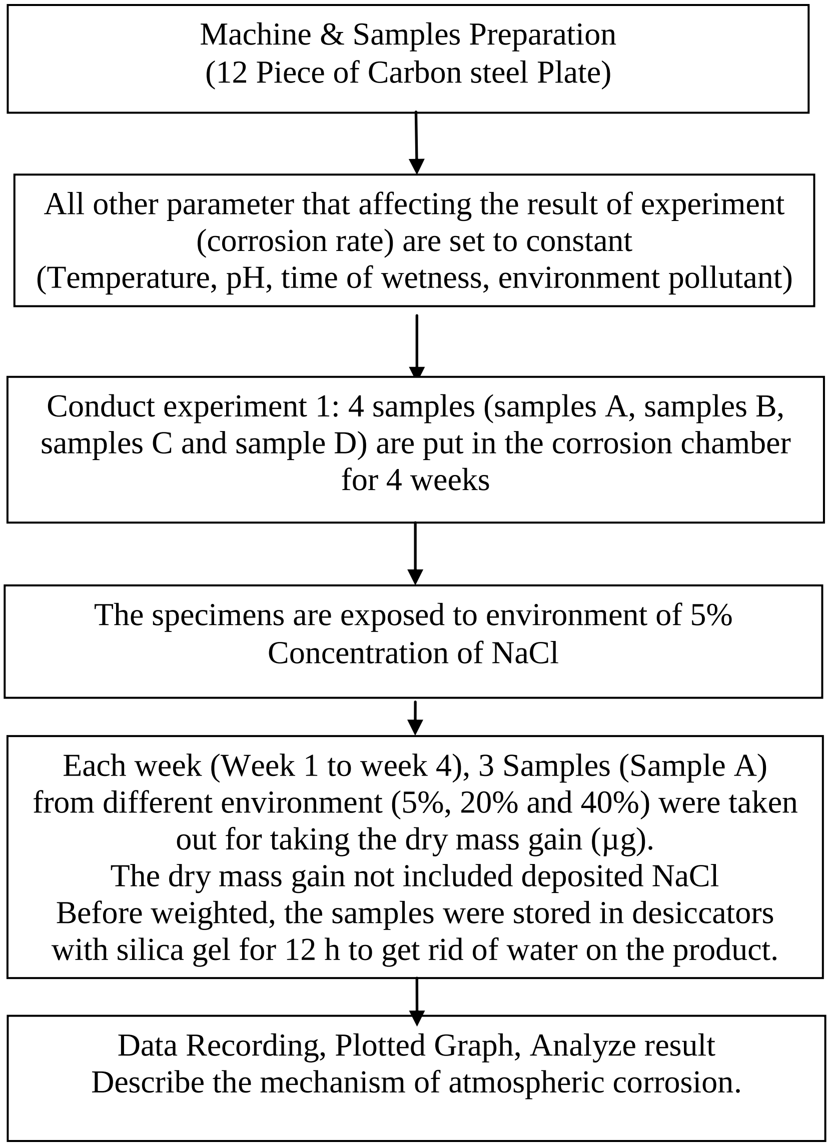


Figure 2: Project Workflow

3.2 Salts Spray Testing Procedure

The experiment was conducted based on ASTM B117, Standard Practice for Operating Salts Spray (Fog) Apparatus.

Test Specimen: Untreated Mild Carbon Steel



Machine & Samples Preparation
(12 Piece of Carbon steel Plate)

All other parameter that affecting the result of experiment (corrosion rate) are set to constant
(Temperature, pH, time of wetness, environment pollutant)

Conduct experiment 1: 4 samples (samples A, samples B, samples C and sample D) are put in the corrosion chamber for 4 weeks

The specimens are exposed to environment of 5% Concentration of NaCl

Each week (Week 1 to week 4), 3 Samples (Sample A) from different environment (5%, 20% and 40%) were taken out for taking the dry mass gain (µg).
The dry mass gain not included deposited NaCl
Before weighted, the samples were stored in desiccators with silica gel for 12 h to get rid of water on the product.

Data Recording, Plotted Graph, Analyze result
Describe the mechanism of atmospheric corrosion.

Figure 3: Salts Spray experimental procedure

3.2.1 Sample Preparation

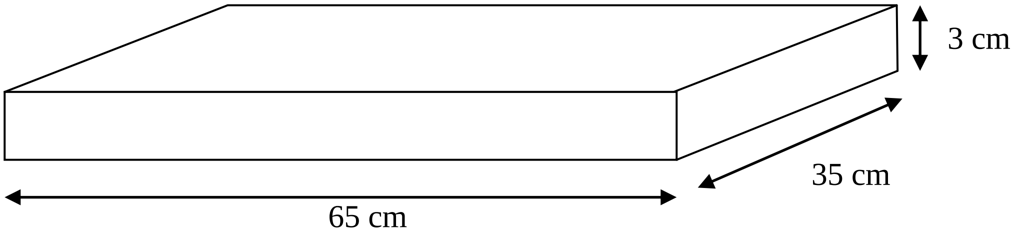


Figure 4: Dimension of test specimens

Metal sheets of Carbon steel were used as the specimens. Each metal sheet was cut to a dimension of 20mm x 7 mm x 1.5mm. Before weighing and exposure, test specimen must be cleaned from any contaminants and dirt. The sample were polished on Silicon carbon (SiC) paper to 1000 mesh and washed in ultrasonic bath (10 min) containing acetone, and then dried with hair dryer and store in desiccators with silica gel for 12 hour. Salt was deposited by spraying solution of different percentage of Sodium Chloride (NaCl) in the corrosion chamber.

3.2.2 Position of the specimen during exposure

The sample was supported or suspended between 15-30^{o} from the vertical and preferably parallel to the principal direction of flow of fog through the chamber, based upon the dominant surface being tested

3.2.3 Salts Solution

Different concentrations of salts solution were used in this experiment.

For 5% concentration of NaCl:
The solution consists of 95% of water + 5 % of NaCl. The mass of water is 1g for 1mL.
Mass of water: 1L of water = 1g x 1000 = 1000g
Because of the water is only 95% of the total mixture by mass
The total mass of the solution (water + NaCl) : 1000/0.95 = 1053 g
Mass of NaCl = 1053 g – 1000 g = 53 g
Multiplier of NaCl = 53/1000g = 0.053
The equation for 5% of NaCl Solution is: 0.053 x Mass of water = Mass of NaCl required.

In order to ensure that proper salts concentration was achieved during mixing the solution, the solution should be checked using salimeter hydrometer. For 5% concentration, the measurement should be 4 and 6% at 25^{o}C (77^{o}F).

3.2.4 pH of salts solution

The pH of the salts solution should be such that when atomized at 35^{o}C (95^{o}F) the collected solution would be in the pH range of 6.5 to 7.2. The method for achieving this pH is explained in the ASTM B117-03 section 8.2

3.2.5 Temperature

The temperature within the salts chamber must be controlled which can be accomplished by several methods. It is generally desirable to control the temperature of the surrounding of the salts spray chamber and to maintain it as stable as possible. This can be achieved by placing the apparatus in constant-temperature room

3.2.6 Air Supply

The compressed air supply to the Air Saturator Tower should be free of grease, oil and dirt. This air should be maintained at a sufficient pressure at the base of the Air Saturator tower to meet the suggested pressures of Table 2 (ASTM B117-03) at the top of the Air Saturator Tower. The careful attention should be given to the relationship of tower temperature to pressure since this relationship can have a direct impact to maintaining proper collection rate. It was also preferable to saturate the air at temperature above the chamber temperature as insurance of a wet fog as listed in the table.

Table 1: Suggested temperature and pressure guidelines for the top of air saturator tower for the operation test at 35^{o}C (95^{o}F).

Air Pressure, (kPa)	Temperature, (^{o}C)	Air Pressure, (PSI)	Temperature , (^{o}C)
83	46	12	114
96	47	14	117
110	48	16	119
124	49	18	121

3.2.7 Period of Exposure

The period of exposure of the carbon steel plate was 4 week for each experiment (with different % of NaCl).

3.2.8 Method to Analysis

To monitor the corrosion process during exposure, three different amount of NaCl deposition (µg.cm^{-2}) were respectively investigated in three experiments. Four samples were exposed to each experiment, and the exposure normally lasted 4 weeks. During the exposure, three samples were interrupted and weighted by means of equipment with sensitivity less than 1 µg once each week. Before weighted, the sample was stored in desiccators with silica gel for 12h to get rid of water on the product. The means of dry mass gain was used to minimize the experimental errors.

3.3 Tools and Equipment Required

For the experiment for salt spray test, the main equipment used is salts spray chamber. Detailed explanations of this equipment are as below.

3.3.1 Salt Spray (vertically down)

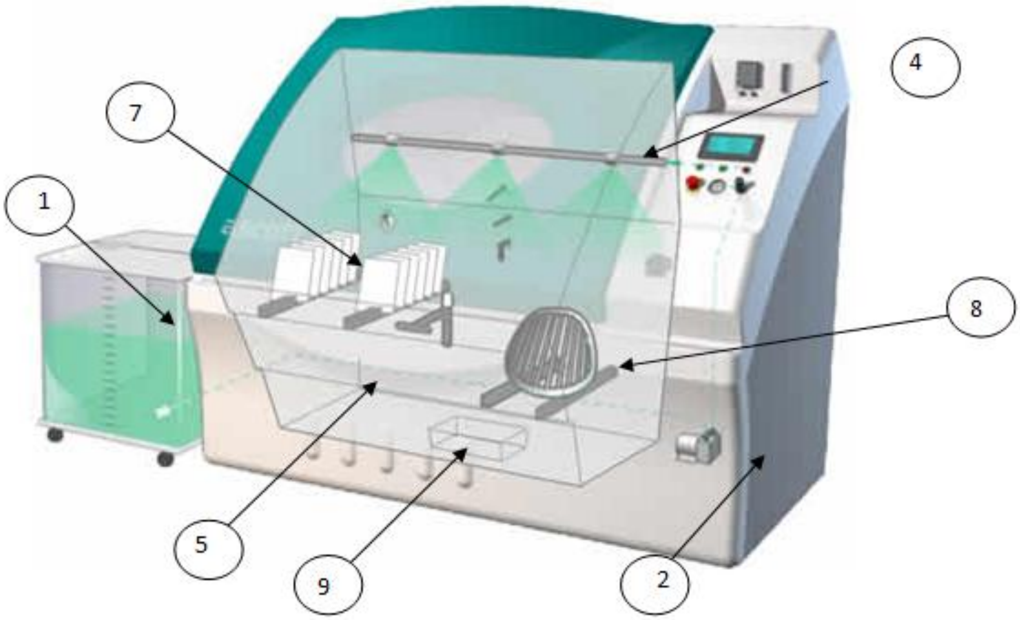


Figure 5: Salts Spray Chamber (Components)

This optional accessory comprises of a high level, multiple nozzle, salt spray rig, which sprays salt water directly down onto the samples under test. Spray time was adjustable and could be programmed to occur automatically at pre-determined point(s) during the test. The salt water was held in a separate holding tank, at ambient temperature.

The control system fitted to chambers enables the user to program whether salt spray (vertically down) is conducted alone, or in sequence with other climates, to form a cyclic corrosion test, for automatic execution by the chamber.

1) Salt solution reservoir

An additional 200L (52 US Gal) free standing, salt solution reservoir, was provided with this optional accessory. This stores the salt water to be sprayed down, at ambient temperature. The reservoir was mounted on castors for mobility and incorporates a transparent graduated sight glass for ease of monitoring the solution level inside.

2) Salt solution pump

A marine specification salt solution pump was built into the Salts Spray chamber. When required by the test program being run, this pump automatically delivered salt solution from the reservoir to the spray rig, at high pressure.

3) Multi-nozzle spray rig

Located high up on the back wall of the chamber is a spray rig which sprays salt water from a number of strategically located, fixed position spray nozzles (the number depends upon the chamber size). These nozzles generated a uniform spray pattern which covered the entire test area below. Test samples located in the test area would therefore be sprayed directly with salt water.

4) Control panel

Forming the center-piece of the ergonomically designed control panel is a state of the art, touch-screen, Human Machine Interface (HMI). It was here that the user controls and monitors the various chamber functions. The HMI incorporates alpha-numeric text messaging and digital displays of chamber variables such as temperature, humidity and time. Also included was a useful trend logging facility. This generates a graphical display of set values for temperature and humidity, over a 72 hour time period, and compares this to the actual temperature and humidity achieved inside the chamber, over the same period. All chamber control panels incorporate an emergency stop and other safety facilities.

5) Chamber canopy

The chamber canopy is effortlessly opened/closed using pneumatic cylinders, which are activated at the touch of a button on the control panel. An automatic purge facility is incorporated to minimize the risk of corrosive salt spray escaping into the laboratory when the chamber is opened.

6) Sensors

Strategically located sensors, mounted inside the chamber and air saturator, monitor the climate continuously and convey this information to the Human Machine Interface (HMI), where it was displayed digitally at the control panel. Temperatures were monitored by PT100 precision temperature sensors and displayed to a resolution of 0.1°C. Chambers was also equipped with a special design of corrosion resistant humidity sensor. This measures the relative humidity electronically inside the chamber and displays this at the HMI as %RH to a resolution of 1%RH.

7) Test samples

Test samples are accommodated within the chamber generally by placing on, or by suspending beneath, sample racks. Additional sample racks are also available as optional accessories.

8) Exhaust vent

This vents spent salt spray from inside the chamber to atmosphere. The chamber should therefore ideally be located adjacent to an outside wall, and a hole made through the wall to accommodate the exhaust pipe. The end of this pipe should be directed away from persons and property, and be shielded from wind to prevent any disturbance to the conditions inside the chamber.

9) Condensate drain

A floor level drain is required to remove used salt spray from inside the chamber to waste.

CHAPTER 4

RESULT & DISCUSSION

4.1 Salts Spray Testing

From this experiment, the dry mass gain (µg.cm^{-2}) of the sample exposed has been recorded. Three sets of readings were recorded and the average was taken to minimize the error. The table shows the result from the weighting the dry mass gain.

Table 2: Dry mass gain (µg.cm^{-2}) of the sample

Experiment	% of NaCl in solutions	Exposure time (Week)	Reading 1 (µg.cm^{-2})	Reading 2 (µg.cm^{-2})	Reading 3 (µg.cm^{-2})	Average (µg.cm^{-2})
1	5%	1	99	103	101	101
		2	199	197	198	198
		3	265	263	276	268
		4	295	301	304	300
2	20%	1	155	151	150	152
		2	273	278	274	275
		3	380	370	354	368
		4	401	404	404	403
3	40%	1	231	212	220	215
		2	355	357	353	355
		3	483	487	485	485
		4	533	527	530	530

Table 2 can be simplified as below:

Table 3: Simplified result for salts spray test and weighting

Experiment	Percentages of NaCI in salts solutions	Exposure time			
		1 Week	2 Week	3 Week	4 Week
		Weight Increases(μg.cm^{-2})			
1	5%	101	198	268	300
2	20%	152	275	368	403
3	40%	215	355	485	530

From the table above, the graph weight gain versus exposure time can be plotted in order to distinguish the relationship between exposure time and weight gain and also with different percentage of NaCl in the solution. This graph can further be analyzed to understand the relationship between percentages (%) of NaCl in solution with the corrosion rate of the sample.

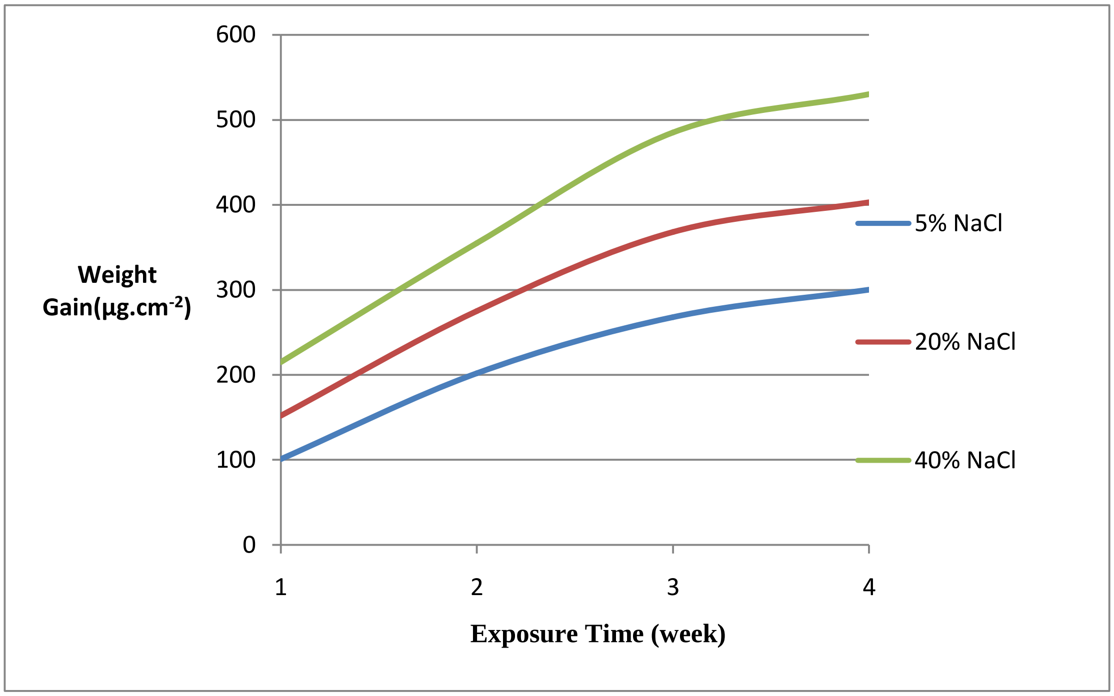


Figure 6: Weight gain (µg.cm^{-2}) versus exposure time (week)

Figure 6 above shows the result of Weight gain (µg.cm^{-2}) versus exposure time (week for 3 different environments. From the result, it is known that increasing the NaCl concentration would increase the corrosion rate. For example, in the exposure of 5% NaCl concentration, the weight gain for the exposure of 1 week is 101 µg.cm^{-2}, while for the exposure of 20% NaCl concentration, the weight gain is 152 µg.cm^{-2} and for the exposure of 40% NaCl concentration, the weight gain is 215 µg.cm^{-2}.

Based on literature review [11], it is basically with regards chemical reactions that take place between the surfaces of the untreated carbon steel with the environment. The weight increase is basically based on the increasing of the corrosion product or also known as rust. The chemical reaction when metallic iron (Fe) in the carbon steel reacts with water (H_20), carbon dioxide (CO_2) and oxygen(O_2) in the air to form iron oxide(Fe_2O_3, FeO,Fe_3O_4). In order for this reaction to occur, the electrons must be transferred from the iron to another molecule, allowing the iron (Fe) to become and ion, either Fe^{2+} or Fe^{3+}. The main function of sodium chloride (NaCl) in the solution is to further help with the electrons transfer. The NaCl breaks up into Na+ and Cl- which will then help to carry the electrons back and forth during the reaction. With the increasing of NaCl concentration, more ions NaCl involve in the reactions and further increase the electron transfer and eventually increase the rusting process.

In 3 different environment, the formation of rust decreases with the exposure time. For example in the exposure of 5% NaCl concentration, the slope of graph decrease with the exposure time. This is due to the decreasing of the corrosion rate of the carbon steel [11]. Further explanation will be discussed in paragraph 4.2 on corrosion rate.

4.2 Corrosion Rate

The corrosion rate, the rate of material removal as a consequence of chemical reaction could be express as the Corrosion Penetration Rate (CPR), or the thickness loss/increase of material per unit of time [2].

The formula for corrosion rate:

$$\text{CPR} = \frac{KW}{\rho A t} \quad \ldots\ldots.(4.1)$$

Where;

K = constant (8.76 for corrosion rate in mm/year or 534 for corrosion rate in mil/year (mpy)

W= Weight Loss (mg)

t = exposure time (hours)

ρ = density of the metal (g/cm^3)

For the analysis, the corrosion rate of carbon steel in 3 different environments was calculated and the example for the calculation is as below:

For the sample that was exposed to 5% of NaCl concentration, the calculation rates are calculated as follows:

Density of the mild steel = **7.85 g/cm^3** [23]
Exposure time: 1 week = 7 days x 24 hours/day = **168 hours.**
Weight Increase = Dry mass gain x Area ………(4.2)
= (101 μg.cm^{-2} x (65 cm x 35))/1000
= **229.775 mg**

While K = **8.76 (mm/year)** [2]

So, using the equation 4.2, the value can be substituted to calculate the CPR

$$\text{CPR} = \frac{KW}{\rho A t} \quad \text{…….(4.3)}$$

CPR = 8.76 x 229.775 / (7.85 g/cm^3 x 2275 cm^2 x 168 hours)
= **6.70 x 10^{-4} mm/year.**

Table 4, 5 and 6 show the calculated corrosion for the carbon steel in 3 different NaCl concentrations.

Table 4: Calculated Corrosion rate for carbon steel in 5% concentration of NaCl

5% of NaCl Concentration					
Constant K	Weight Loss /Increase (mg)	Density (ρ)	Area (cm^2)	Exposure time(hours)	Corrosion Rate (mm/year)
8.76	229.775	7.85	2275	168	0.000670883
8.76	450.45	7.85	2275	336	0.000657598
8.76	609.7	7.85	2275	504	0.000593388
8.76	682.5	7.85	2275	672	0.00049818

Table 5: Calculated Corrosion rate for carbon steel in 20% concentration of NaCl

20% of NaCl Concentration					
Constant K	Weight Loss/ Increase (mg)	Density (ρ)	Area (cm^2)	Exposure time(hours)	Corrosion Rate (mm/year)
8.76	345.8	7.85	2275	168	0.001009645
8.76	625.625	7.85	2275	336	0.00091333
8.76	837.2	7.85	2275	504	0.000814801
8.76	916.825	7.85	2275	672	0.000669222

Table 6: Calculated Corrosion rate for carbon steel in 40% concentration of NaCl

40% of NaCl Concentration					
Constant K	Weight Loss/ Increase (mg)	Density (ρ)	Area (cm^{-2})	Exposure time(hours)	Corrosion Rate (mm/year)
8.76	489.125	7.85	2275	168	0.001428116
8.76	807.625	7.85	2275	336	0.001179026
8.76	1103.375	7.85	2275	504	0.001073855
8.76	1205.75	7.85	2275	672	0.000880118

Table 4 shows the corrosion rate (mm/year) for difference exposure time when expose to environment with 5% of NaCl concentration while the table 5 shows the corrosion rate for the exposure environment of 20% NaCl concentration. For table 6, the obtained results are for the exposure in 40% NaCl concentration. The obtained results have been analyzed and graph exposure time versus corrosion rate (mm/year) has being plotted.

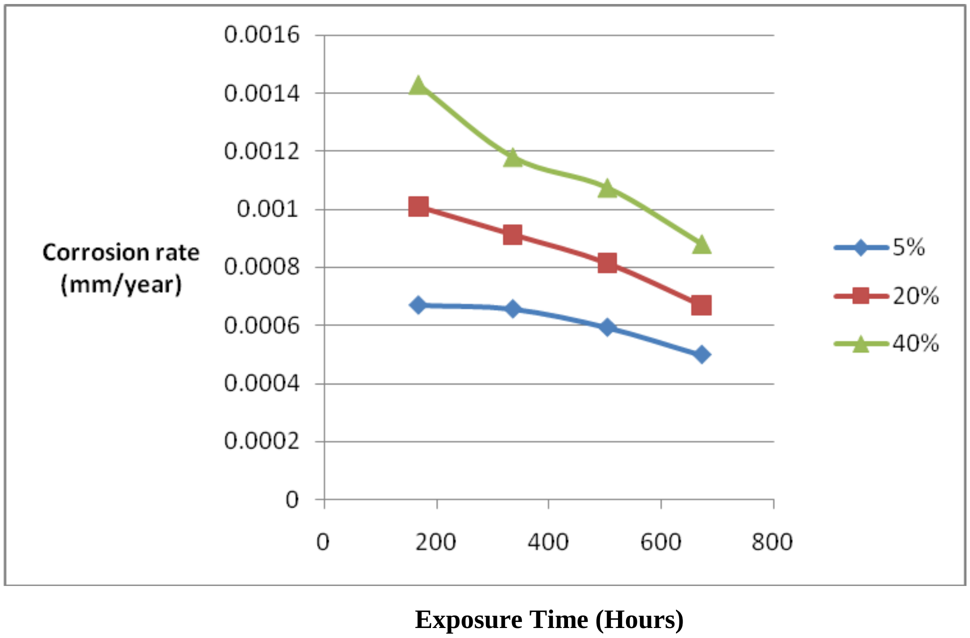


Figure 7: Corrosion rate versus exposure time for carbon steel

From Figure 7, it clearly indicates that the corrosion rate for 3 different environments is decreasing with the increasing of exposure time. In environment of 5% of NaCl concentration, the corrosion rate for one week or 168 hours exposure time is 0.000670883 mm/year while for 2 week (336 hours) of exposure time is 0.000657598 mm/year. For the 3rd week the corrosion rate decrease to 0.000593388 mm/year and further decrease after 4th week of exposure which was 0.00049818 mm/year. For the exposure in 20% of NaCl concentration also shows that the corrosion rate is decreasing from 0.001009645mm/year for exposure of 168 hours, 0.00091333mm/year for exposure in 336 hours, 0.000814801mm/year for exposure in 504 hours and also 0.000669222mm/year for exposure after 672 hours. Table 6 shows the obtained result for exposure in 40% of NaCl concentration and also shows that the corrosion rate is decreasing with the increasing of exposure time.

The decreasing of corrosion rate with the increasing of exposure time can be explained by using electrochemical reaction that takes places on the surface of the carbon steel [11]. In the early stages of the corrosion process, when the surface of the steel is wet, the anodic reaction which is the dissolution of iron metal is at the maximum level where the ions Na^+ and Cl^- helps in transferring the electrons. The reactions are:

$$\text{Anodic reaction: } Fe \rightarrow Fe_2 + 2e \ldots\ldots\ldots(4.4)$$

$$\text{Cathodic reaction: } \tfrac{1}{2} O_2 + H_2O + 2e \rightarrow 2OH- \ldots\ldots(4.5)$$

Furthermore, countless of electrochemical cells begins to form on the surface of sample, the water film on the steel would present with weak basicity while the iron hydroxide (OH^-) forms. The addition of NaCl may lead to the formation of electrolyte rather quickly and the conductivity of the electrolyte film increases with the amount of NaCl in solution. As shown in the Figure 6, the corrosion rate for exposure of 40% NaCl concentration is the highest at week 1 due to the highest conductivity of the electrolyte followed by exposure in 20% NaCl and in 5% of NaCl concentration.

With the reaction going on, cations, Na^+ , Fe^{2+} will migrate towards cathodic area while anions, e.g Cl^- and OH^- move towards anodic area while anions, e.g Cl^- and OH^- move towards anodic area. Thus the formation of iron hydroxide took place at anodic area. The reactions are:

$$Fe^{2+} + 2\,OH^- \rightarrow Fe(OH)_2 \ldots\ldots\ldots\ldots(4.6)$$

As it indicates in the figure, the corrosion rate is decreasing from week 1 to weak 4. This is basically because of the formation of iron oxide at the surface of the sample. FeOOH, Fe_2O_3, Fe_3O4 are the most common iron oxide that can be found at the surface based on the reaction below:

From the formation of iron (II) hydroxide $Fe(OH)_{2,}$ it would rapidly oxidized to form FeOOH when oxygen began to dissolved in the electrolyte layer[11]. The reaction involved is:

$$2Fe(OH)2 + \frac{1}{2} O_2 \rightarrow 2FeOOH + H_2O \;\ldots\ldots(4.7)$$

Then, FeOOH would gradually transformed to more stable substance, Fe_2O_3

$$2FeOOH \rightarrow Fe_2O_3 + H2O\ldots\ldots\;(4.8)$$

Furthermore, $Fe(OH)_2$ also could be slowly oxidized to magnetite

$$3Fe(OH)_2 +1/2\; O_2 \rightarrow Fe_3O4 + H_2O\ldots\ldots(4.9)$$

FeOOH, Fe_2O_3, and Fe_3O4 etc. are insoluble in weak basic solution thus it would form a barrier film that may counteract the further migration of the ions. Therefore, the electrochemical corrosion rate will slow down and the corrosion rate decreases.

CHAPTER 5

CONCLUSION

From the experiment, it can be concluded that:

- NaCl plays and important role in atmospheric corrosion as it helped in increasing the conductivity of the electrolyte by providing a medium of electron transfer.
- The dry mass gain of carbon steel would increase with the amount of NaCl Concentration.
- The corrosion rate would decrease with the increasing of exposure time.

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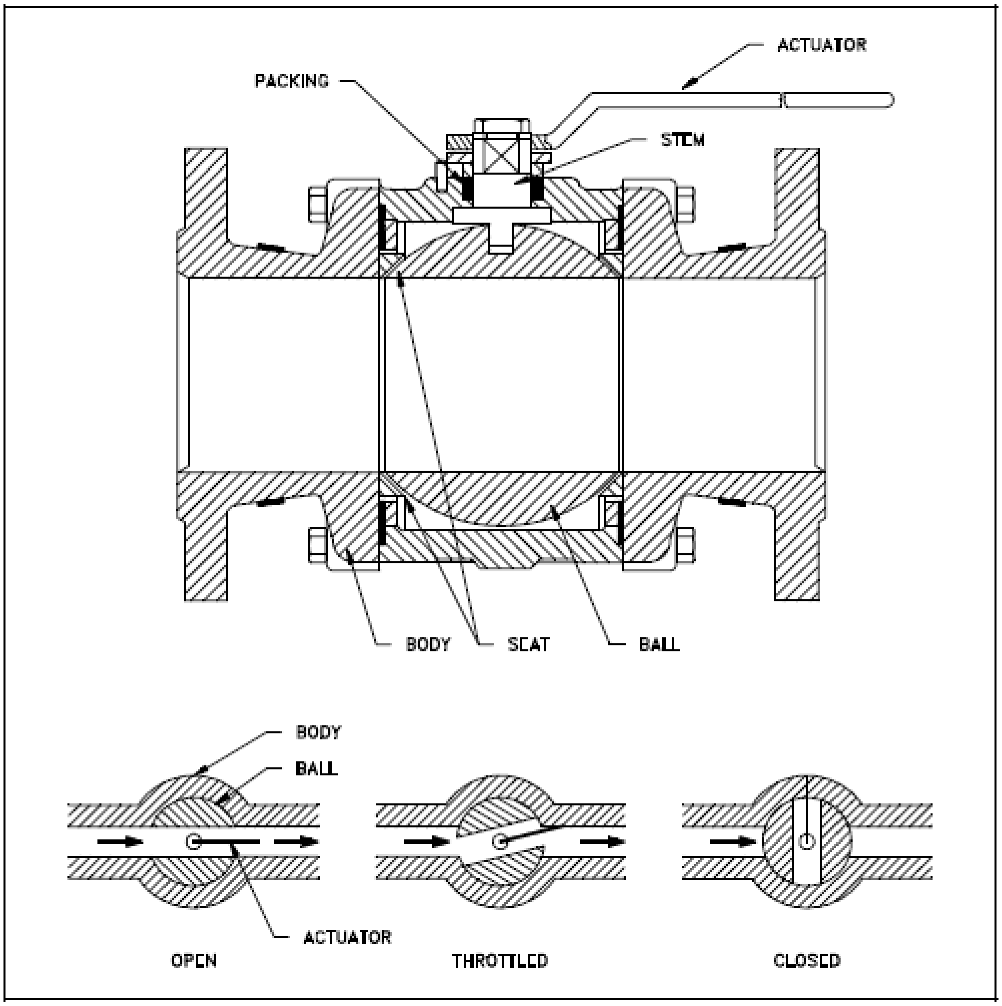
APPENDIX



Cross section of ball valve. [1]