EFFECT OF DIFFERENT SODIUM CHLORIDE (NaCl) CONCENTRATION ON CORROSION OF COATED STEEL

MOHD FIRDAUS BIN IBRAHIM

Report submitted in partial fulfillment of requirements
for award of the Degree of
Bachelor of Mechanical Engineering

FACULTY OF MECHANICAL ENGINEERING
UNIVERSITI MALAYSIA PAHANG

JUNE 2013

ABSTRACT

One of the ways to prevent the corrosion from occurs is coating or painting. Paint is used as protector to the materials such as mild steel that prevent the corrosion to occur. Besides that, the corrosion rate in different concentration of Sodium Chloride (NaCl) solution is different. This study is carried on the 5 sample of mild steel as specimen that immersed in different concentration of NaCl that is 0% of NaCl, 1.5% of NaCl, 2.5% of NaCl, 3.5% of NaCl and 4.5% of NaCl. This study is carried 6 days and the result is obtained by photo snapping at second day (2nd day), fourth day (4th day) and sixth day (6th day) continuously. The paint quality is analyzing from width of corrosion, peeling, wear off and changes in colour. After that, to obtain the corrosion rate, the mass loss experiment was carried out. The purpose of this study is to study the corrosion on coated steel in different concentration of NaCl solutions. Besides that, this study also to investigate the performance of protective coating on steel in different concentration of NaCl solutions. At the end of the experiment, we can conclude that the corrosion rate is increase when the concentration of NaCl solution is also increase. Other than that, the performance of the protective coating especially paint on steel is different when it immersed in the different concentration of NaCl that is the quality of paint in 4.5% of NaCl solution is most fast to decrease.

ABSTRAK

Salah satu cara untuk mengelakkan pengaratan adalah melalui pengecatan. Penggunaan cat ini adalah adalah sebagai pelindung kepada bahan tersebut contohnya keluli lembut daripada berlakunya kecacatan. Selain itu, kadar pangaratan adalah berbeza apabila berada di dalam larutan NaCl yang berbeza. Kajian ini dilakukan pada 5sampel keluli lembut atau specimen yang mana ia direndamkan di dalam larutan yang mempunyai kepekatan yang berbeza iaitu 0% NaCl, 1.5% NaCl, 2.5% NaCl, 3.5% NaCl dan 4.5% NaCl. Selepas itu, eksperimen dijalankan selama 6 hari dengan pengambilan foto pada hari ke-2, hari ke-4 dan hari ke-6 dilakukan dan berterusan. Kualiti cat dilihat berdasarkan nilai lebar pengaratan, pelepuhan, pengelupasan dan perubahan warna. Selepas itu, untuk mencari kadar hakisan, mass loss eksperimen dilalukan.Kajian ini adalah bertujuan untuk mempelajari tentang hakisan pada besi yang dilindung di dalam larutan NaCl yang berbeza. Selain itu, kajian ini adalah untuk menyelidik persembahan cat pada besi didalam larutan NaCl yang berbeza kepekatan. Pada akhir eksperimen ini, dapat disimpulkan bahawa pada larutan yang mempunyai kepekatan NaCl paling tinggi, kadar hakisan adalah lebih cepat berbanding dengan kepekatan NaCl yang lebih rendah. Selain itu, kualiti cat juga paling cepat menurun di dalam larutan NaCl yang paling tinggi kepekatannya iaitu 4.5% NaCl berbanding dengan larutan NaCl yang lebih rendah kepekatannya.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

%	Percentage
°C	Degree Celsius
cm	Centimeter
g	Gram
µ	Micro
ipm	Inches per month
ipy	Inches per year
m	Meter
mm	Millimeter
mpy	Mils per year
mmpy	Milimeters per year
pmpy	Picometers per year
s	seconds

LIST OF ABBREVIATIONS

A	Area
C	Carbon
Ca	Calcium
$CaCO_3$	Calcium Carbonate
Cl	Chlorine
Cr	Chromium
Cu	Copper
$CuSO_4$	Copper Sulphate
D	Density
e^-	Electron
$E_{eq,H}$	Hydrogen evolution
Fe	Ferum
$FeSO_4$	Ferrous Sulphate
H	Hydrogen
HCl	Hydrochloric Acid
H_2O	Hydrogen Oxide (Water)
H_2SO_4	Hydrogen Sulphate
K	Constant for corrosion rate
Mg	Magnesium
MgOH	Magnesium Hydroxide
Mn	Mangan
Na	Sodium
NaCl	Sodium Chloride
Ni	Nickel

O_2	Oxygen gas
OH^-	Hydroxyl
P	Phosphorus
S	Sulphur
Si	Silicon
T	Time of exposure
W	mass/ weight
Zn	Zinc

CHAPTER 1

INTRODUCTION

1.1 STUDY BACKGROUND

Mild steel is the combination of some metal elements and the carbon contains less than 0.18%. Due to the low carbon contain in the steel, mild steel cannot through the hardening process. Mild steel is known as alloy metal because it contains the quantity of alloy elements. Besides carbon, there are other elements that contain in this steel such as Mangan (Mg), Silicon (Si), and Phosphorus (P) that added to changes of the mechanical and physical properties of materials. There are two types of alloy steel that is low alloy steel and high alloy steel. The low alloy steel contains less than 5% of total element of metal alloy and the high alloy steel contains higher than 5% of total element of metal alloy also not contain the Carbon (C) element. Alloying is a method that very effective and the composition is to increase the strength of material also repairing the physical properties and whole characteristic of that alloy materials.

Corrosion can be defined as the changes of material as a result of chemical attack that caused by the environment of material. Besides that, corrosion also can be defined as the degradation of material in their environment. This is because the changes in environment that influenced by some factor that is weather and humidity rate. The corrosion had affected to the industry loss that caused by the requirement to change the part that has been corroded. It indirectly makes the life span of components or parts because the corrosion process. Because of that, some research have carried out to study and finding the steps that needed to protect the corrosion or decrease the corrosion rate per year.

Electrochemical reaction is a one process of electron transferring and chemical changes of materials. This electrochemical reaction will go through the two processes that is oxidation process (anode reaction) and reduction process (cathode reaction). Oxidation process is a chemical reaction process that produces the electron where as the reduction process is a chemical reaction process that will use the electron. There are three components that will make the corrosion occur that is water, oxygen and steel. The reaction this three components will produce the corrosion process that will cause the life span of the material is shorten and damage the physical and mechanical properties of material also the performance of that material.

The research and study about corrosion is interesting and need to proceed and continuous because nowadays, mostly industries still using steel and it alloy as the main material in the critical parts such as structural parts for oil platforms and structural for bridge. This is important to decrease the corrosion rate and the life span of material will longer. Corrosion prevention can be carried with many ways depends on the application in the industry.

This study will include the aspect of electrochemical for corrosion and the effect of the different concentration of sodium chloride (NaCl) on corrosion of coated mild steel that is the specimen that is used in this study and the factor that affect to the paint that used to coated the steel.

1.2 PROBLEM STATEMENT

There are many researches about the corrosion, the effect of corrosion and how to prevent the corrosion. This is because the mild steel and its alloys is a main material in the industry today either as the structure of a construction or as the raw material for manufacturing process of a product. However, due to material degradation with the environment that is corrosion process, it causes the life span of the material decrease and gives the effect on the mechanical and physical properties of the materials.

This research is important to find the steps that needed to decrease the corrosion rate especially in the sea water because the NaCl is the salt that have their salinity and can be representing as the sea water. From this, we can increase the life span of the material that is mild steel that used in industry.

This research will focus about the concentration of NaCl that will effect on the corrosion of coated steel. Nowadays, the real world problem why this experiment or research ii carried is because the corrosion is always happen in the sea water and this will make the ship easy to corrode.

There are several main reasons what the advantages are and why we should study about corrosion that is economics, safety, and conservation. To reduce the economic effect of corrosion, corrosion engineers and with the support of corrosion scientist should be purpose to reduce the material losses as well as the additional economic losses, that result from the corrosion of piping, tanks, metal components of machines, ships, bridges, marine structures and so on.

1.3 OBJECTIVES OF THE STUDY

The objectives of this study are:

1. To study the corrosion on coated steel in different concentration of NaCl solutions.
2. To investigate the performance of protective coating on steel in different concentration of NaCl solutions.

1.4 SCOPE OF STUDY

The scopes of this study are:

1. The materials that used in this experiment are coated mild steel.
2. The physical changes of coated steel after immersed in different NaCl solutions.
3. The analysis of the formation of rust on scratched coated steel in different solution of NaCl.
4. To calculate the corrosion rate, the mass loss experiment is carried.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Corrosion is the destructive attack of a metal by chemical and electrochemical reaction with its environment. Deterioration by physical causes is not called corrosion, but is described as erosion, galling, or wear. In some instance, chemical attack accompanies physical deterioration, as described by the following term that is corrosion-erosion, corrosive wear, and fretting corrosion. Non metal are not included in this definition of corrosion. Plastic may swell or crack, wood may split or decay, granite may erode, and Portland cement may leach away, but the term corrosion, in this book, is restricted to chemical attack of metals.

Rusting applies to the corrosion of iron or iron-base alloys with formation of corrosion products consisting largely of hydrous ferric oxides. Nonferrous metal, therefore, corrode, but not rust (Revie and Uhlig, 2008).

2.2 APPLYING PAINT COATINGS

The coating should be applied to the dry metal surface as soon as possible after the metal is cleaned in order to achieve a good bond. For the better one, the metal should first be given a phosphate coat, in which case the prime coat, if necessary, can be delayed for a short while. The advantages of a phosphate coat are it can give the better bond of paint to the metal and good resistance to undercutting of the paint film at scratches or other defects in the paint at which rust forms also progresses beneath the organic coating. For many years it has been standard practice to coat automobile bodies and electric appliances with phosphate first before painting (Hudson, 1961).

Only in unusual cases paint should be applied through damp or wet surface because poor bonding of paint to steel results under these conditions. A second coat can be applied after the first has dried, or a sequence of top coats can follow. A total of four coats with combined thickness of not less than about 0.13 mm are considered by some authorities to be the recommended minimum for steel that will be showing to corrosive atmospheres (Hudson, 1961).

One of the advantages of this process compared to spraying is that it results in a uniform, thin coating that is about 25 μm thick with coverage on both exterior and interior cavity surfaces. In addition, this process is controllable, automated, efficient, and environmentally acceptable (John, 1992).

2.3 EFFECT OF CHLORIDE ION CONCENTRATION ON CORROSION

Unlike pH, the chloride ion concentration can significantly be different between bodies of water and effects of chloride ion concentration on corrosion processes are of importance due to the abundance of salt present in the environment. The average salinity level of the sea is 3.5%. Although Sodium chloride (NaCl) is found in abundance, other salts are also present whereby the composition includes a variety of ions listed from highest to lowest concentrations: chloride (Cl), sodium (Na), sulphates (SO_4), magnesium (Mg), calcium (Ca), potassium (P), carbonate (CO_3) and bromide (Br). This study is researched by some people and has been written in their book respectively. They are Agency (2001) and then proceed again by Mobin and Malik, 2007.

The rate of corrosion is usually higher in salt versus fresh water as researched by Ardagh et. al., 1933. This can be explained by the presence of chloride ions, which is it known to substantially decrease the ability of the passive film to negative metal oxidation or dissolution. The small size and negative charge of the chloride ion penetrates through the passive layer to the positively charged metal cation destroying the protective function of the passive film (Ibrahim et. al., 2009). Metals heavily affected by the breakdown of the passive film that are stainless steels and aluminum. This already stated by Malik (1999) and then by Dexter (2006). With the breakdown of the passive film, pitting corrosion of stainless steels is commonly observed, particularly in seawater.

For items of metallic facts, which are retrieved from the water, the presence of chloride ions is expected to increase the rate of corrosion. This factor is important for forensic investigators to characterize (especially for crime laboratories located along ocean coastlines) in order to appropriately assess the rate of corrosion.

2.4 CORROSION OF STEEL MECHANISM IN SOLUTION

At the medium of steel or mild steel (specimen), the reaction of corrosion that occurs is:

$$Fe + H_2O \rightarrow Fe(H_2O)_{ads} \tag{2.1}$$

$$Fe(H_2O)_{ads} \rightarrow Fe(OH^-)_{ads} + H^+ \tag{2.2}$$

$$Fe(OH^-)_{ads} \rightarrow Fe(OH)_{ads} + e^- \tag{2.3}$$

$$Fe(OH)_{ads} \rightarrow Fe(OH)^+ + e^- \tag{2.4}$$

$$Fe(OH)^+ + H^+ \rightarrow Fe^{2+} + H_2O \tag{2.5}$$

When steel is immersed in the water, H_2O the steel (Ferum) atom will lose their electrons and become the positive ion that will dissolve to the electrolyte while the cathode reaction will produce the reduction reaction at H^+ in the water solution until the hydrogen gas, H_2 will formed. The complete reaction for anode and cathode is as shown in equation 2.6 and 2.7.

Anode: $Fe \rightarrow Fe^{2+} 2e^-$ (2.6)

Cathode: $2H^+ + OH^- \rightarrow H_2$ (2.7)

In the solution of water, there are hydroxyl ions (OH^-) that come from the dissociation reaction of water as shown in the equation 2.8.

$$H_2O \rightarrow H^+ + OH^- \quad (2.8)$$

The hydroxyl ions will react with the iron (Fe) ions and becomes like the equation 2.9 shown

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \quad (2.9)$$

When there is excess of substance of oxygen in the solution, it will form hydroxide ion at the cathode as shown in the equation 2.10.

$$2H_2O + O_2 + 4e^- \rightarrow 4(OH^-) \quad (2.10)$$

Then, this will make the corrosion process faster and produces rusting. This will be shown by equation 2.11 below.

$$Fe(OH)_2 + OH^- \rightarrow Fe(OH) + H_2O \quad (2.11)$$

Then, the full reaction is written as the equation 2.12 that show the reaction of corrosion process in the presence of water.

$$4Fe + 3O_2 + 6H_2O \rightarrow 4Fe(OH)_2 \quad (2.12)$$

Chloride ion is a negative charge ion (anion). From researched have been made by Brasher, he stated that the concentration of anion in the electrolyte is important to concerns the electrolyte behavior on protector (the layer of protector oxide that formed at the top of steel surface). Chloride anion in the electrolyte assumed as too aggressive towards that oxide layer. Therefore, chloride ion is too sensitive to metal that contain iron.

As we know, at the cathode, the reduction of oxygen will occur and it shown in the reaction 2.13.

$$2H_2O + O_2 + 4e^- \rightarrow e^- + 4OH^- \qquad (2.13)$$

Whereas, at the anode, the oxidation reaction will occur because the Fe ion will lose their electrons and the equation 2.14 can be produced.

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (2.14)$$

The increase of dissolved oxygen in the solution will make the reduction of oxygen increase to become the hydroxyl ion. This reaction use electrons that produced from oxidation reaction that happen at the steel. So, the increases the number of oxygen reduction will cause the electrons that needed is increase. That why when the oxygen dissolve in solution is more, it will make the corrosion on steel is increases also. All of this information has stated by Sponas (1998) from the research about the effect of industrial composition variation on the transformation behavior of ultralow carbon steel.

2.5 EFFECT OF DISSOLVED SALTS ON CORROSION

The effect of sodium chloride concentration on corrosion of iron in air saturated water at room temperature is shown in Figure 2.1. The corrosion rate increases first with salt concentration and then decreases, with the value falling below that for distilled water when saturation is reached (26% NaCl).

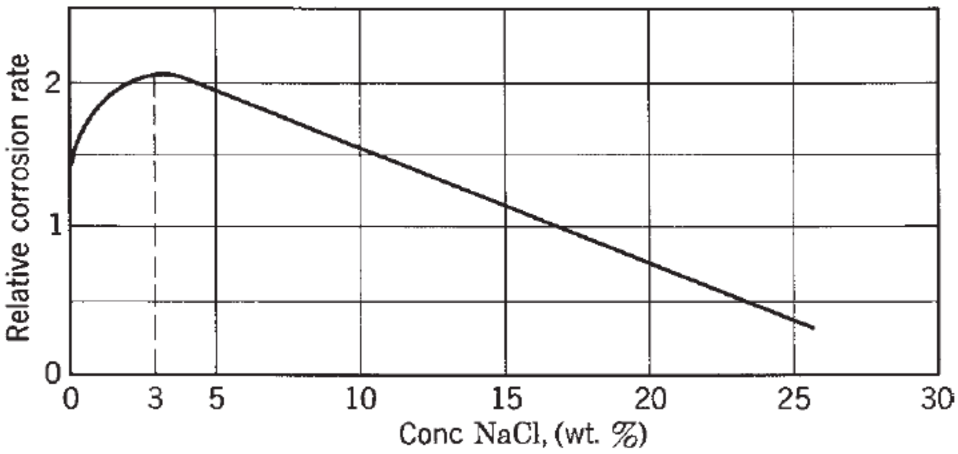

Figure 2.1: Effect of sodium chloride concentration on corrosion of iron in aerated solutions, room temperature (composite data of several investigations). (Borgmann, 1937)

Since oxygen depolarization controls the rate throughout the sodium chloride concentration range, it is important to understand why the rate first increases, reaching a maximum at about 3% NaCl (seawater concentration), and then decreases. Oxygen solubility in water decreases continuously with sodium chloride concentration, explaining the lower corrosion rates at the higher sodium chloride concentrations. The initial rise appears to be related to a change in the protective nature of the diffusion - barrier rust film that forms on corroding iron. In distilled water having low conductivity, anodes and cathodes must be located relatively near each other (Borgmann, 1937).

In sodium chloride solutions, on the other hand, the conductivity is greater; hence, additional anodes and cathodes can operate much further removed one from the other. At such cathodes, NaOH does not react immediately with $FeCl_2$ formed at anodes; instead, these substances diffuse into the solution and react to form $Fe(OH)_2$ away from the metal surface. Any $Fe(OH)_2$ so formed does not provide a protective barrier layer on the metal surface. Hence, iron corrodes more rapidly in dilute sodium chloride solution because more dissolved oxygen can reach cathodic areas. Above 3% NaCl, the continuing decreased solubility of oxygen becomes more important than any change in the diffusion that is barrier layer. Hence, the corrosion rate decreases (Borgmann, 1937).

2.6 FORMS OF CORROSION

There are many types or forms of corrosion that occur in the structure. From Figure 2.2, it has shown the forms of corrosion that occur to the metal structure. The several type or forms of corrosion are pitting, exfoliation, erosion and more (Jones, 1982).

i. General corrosion: General corrosion or rusting is the most familiar form of steel corrosion. It can be considered a uniform corrosion process in which numerous micro corrosion cells are activated at the corroded area. The cells could be minute grains where the boundary tends to be the anode, for example in atmospheric exposures, oxygen in the air is the usual oxidizing agent, and the water necessary for the reaction is readily available in the form of rain, condensation (dew, for example), or humidity (water vapor in the air). In the rusting of ordinary steel, the corrosion product (rust) does not form an effective barrier to further corrosion, but permits reactants to penetrate to the steel surface beneath and continue the rusting cycle.

ii. Pitting corrosion: A no uniform, highly localized form of corrosion that occurs at distinct spots where deep pits form. (A pit is a small electrochemical-corrosion cell, with the bottom of the pit acting as the anode.) Chloride-induced corrosion is of this type and can be seen frequently in structures exposed in coastal areas.

iii. Galvanic corrosion: When two metals of different electrochemical potential are joined or coupled electrically in the presence of moisture or an aqueous solution, one will act as the anode and corrode; the corrosion of steel when it is in contact with copper is a familiar example. This principle is used to advantage when steel is protected by galvanic methods (for example, galvanized steel or the use of other sacrificial anodes).

iv. Stress-corrosion: Under stress, corrosion processes proceed much faster and can lead to brittle failure as corrosion tends to be localized. Corrosion of this kind can occur in prestressing tendons in concrete.

v. Crevice corrosion: This form occurs when moisture and contaminants retained in crevices accelerate corrosion.

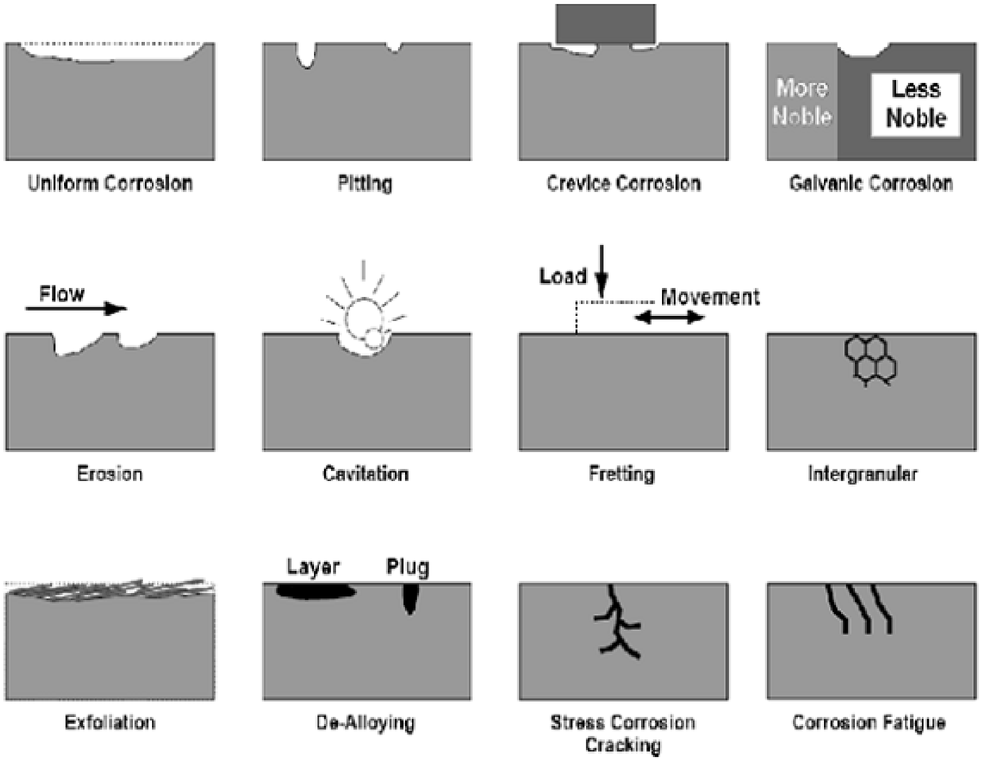

Figure 2.2: Forms of corrosions. (Jones et. al., 1982).

2.7 BLISTERING AND DELAMINATION PROCESSES ON COATED STEEL.

When a coating is exposed to an aggressive medium, such as that found in a marine environment, the associated failure mechanisms of blistering and delamination are amongst the most important to be considered. These two modes of failure are often treated separately, but have so many common features that it could be argued that the differences are a matter of degree rather than type. There is a general consensus over the integrity of a typical coating and it is fair to assume that one will find defects, due to porosity or damage in service. Therefore the following considers the situation of an organically coated steel structure containing a defect, which is subjected to aggressive, immersed conditions (Scantlebury, 2001).

Due to the presence of imperfections in the coating, the steel substrate is directly exposed to its surroundings. This initiates a corrosion process, with the anodic reaction occurring at the defect, this reaction follows that shown in equation 2.6.

$$Fe \rightarrow Fe^{2+} + 2e \qquad (2.6)$$

In order to maintain electroneutrality within the system, this reaction is balanced by a cathodic reaction. In most naturally occurring situations, this reaction will be oxygen reduction, as illustrated in equation 2.7. These two reactions initially take place adjacent to each other but separate as the process continues with the cathode moving under the coating.

$$O_2 + 2H_2O + 4e^- = 4OH^- \qquad (2.7)$$

The ferrous ions produced in equation above go into solution and react to produce electrically neutral compounds through combination with cations in the medium. This leaves us with a charge imbalance. The environment has a surfeit of positive charge, in the form of whatever cations are present and the environment at the cathode is producing hydroxyl ions, resulting in an excess of negative charge. In the case of uncoated steel, the route for the counter-cations is straightforward. However, when the steel is coated the situation becomes more complicated. The path from the exposure environment to the cathodic site is either restricted or blocked completely.