A STUDY OF ATMOSPHERIC CORROSION INDOOR AND OUTDOOR

MOHD FAHIES BIN ISMAIL

A report submitted in partial fulfilment of the requirements For the award of the degree of Bachelor of Mechanical Engineering Pure

Faculty of Mechanical Engineering
UNIVERSITI MALAYSIA PAHANG

NOVEMBER 2009

UNIVERSITI MALAYSIA PAHANG
FACULTY OF MECHANICAL ENGINEERING

We certify that the project entitled "A Study of Atmospheric Corrosion Indoor and Outdoor "is written by Mohd Fahies bin Ismail. We have examined the final copy of this project and in our opinion; it is fully adequate in terms of scope and quality for the award of the degree of Bachelor of Engineering. We herewith recommend that it be accepted in partial fulfillment of the requirements for the degree of Bachelor of Mechanical Engineering.

Examiner Signature

SUPERVISOR'S DECLARATION

I hereby declare that I have checked this project and in my opinion, this project is adequate in terms of scope and quality for the award of the degree of Bachelor of Mechanical Engineering.

Signature
Name of Supervisor:
Position:
Date:

STUDENT'S DECLARATION

I hereby declare that the work in this project is my own except for quotations and summaries which have been duly acknowledged. The project has not been accepted for any degree and is not concurently submitted for award of other degree.

Signature
Name: MOHD FAHIES BIN ISMAIL
ID Number: MA06085
Date:

Dedicated to my parents

ACKNOWLEDGEMENTS

First of all, grateful to Allah S.W.T, after a year of struggle and hard work, with His will, this thesis is completed. Thanks to Allah for giving me the strength to complete this project and the strength to keep on living.

To my supervisor, Madam Juliawati binti Alias. Thanks a lot for the guidance you gave in completing this thesis. All advises and help you gave, academically or non-academically, are really helpful and never be forgotten. Not forgotten, for my new supervisor Madam Dayangku Noorfazidah. All the knowledge and idea that you gave are really helpful as a guide for me to complete this thesis.

To my mom Wan Mara binti Awang Besar, dad Ismail Bin Husin thank you for all the support you gave to me. Your sacrifice is too great to be measured. You’ll never be forgotten. Also to my sisters, Nor Suriati and Nor Farahim, my brothers Mohd Hafies and Mohd Nahies, thanks a lot for your support in all aspects.

To Siti Azmal Azzah binti Abdullah Halim and family. Thanks a lot for patience and help.

ABSTRACT

Atmospheric corrosion may cause serious damage to metallic structures and equipments. Because of the huge impact of corrosion, it is imperative to have a systematic approach to recognizing and justifying corrosion problems as soon as possible after they become apparent. In this study, the impact of atmospheric corrosion on aluminum, copper and zinc was investigated by exposing the sample in indoor and outdoor atmosphere. Each sample undergoes environmental exposure for 28 days before the surface morphology investigation was conducted. Then the cleaning process follows prior to the final analysis. Scanning Electron Microscope (SEM) was used to study the surface morphology. Corrosion rate was determined for all samples. In indoor environment, it was found that zinc possess the highest corrosion rate; 1.440 mpy while aluminum is the less corrosive sample with only 0.2645 mpy. The outdoor environment investigation yield similar polar of result where the value increase in almost double the result from indoor investigation. Corrosion rate of zinc is 2.103 mpy and the less corrosive sample; aluminum is 0.417 mpy. Any features of corrosion failure give significant clue of the possible corrosion factor. This article details a proven approach to properly determining the effects of the environment and material types to the corrosion rate, and includes surface microstructure of the most common corrosion types, including general corrosion, pitting, and erosion. In conclusion, properties of outdoor and indoor influence the corrosion rate. Indoor environment shield the samples from rain and dew hence decrease the corrosion rate compare to open or outdoor environment where the samples subjected to the dynamicity of weather. Aluminum proves to be the most protective sample and corrosion durable. Hence it may suggest that for both indoor and outdoor application, aluminum is highly recommended.

ABSTRAK

Kakisan boleh memberikan kesan yang serius terhadap struktur dan peralatan besi. Disebabkan oleh kesan yang ketara ini, adalah wajar bagi mengesan dan menjustifikasikan seawal mungkin kemunculan karat dengan menggunakan pendekatan sistematik. Dalam penyelidikan ini, kesan kakisan atmosfera ke atas aluminium, kuprum and zink dikaji dengan mendedahkan sampel kepada persiktaran terbuka dan tertutup. Setiap sampel didedahkan selama 28 hari sebelum analisis morfologi permukaan dijalankan. Proses pembersihan dilakukan sebelum analisa akhir. “Scanning Electron Microscope (SEM)” atau mikroskop imbasan elektron digunakan dalam kajian morfologi permukaan. Kadar pengaratan ditentukan bagi setiap sampel. Bagi persekitaran tertutup, zink mengalami kadar kakisan tertinggi iaitu 1.440 mpy manakala aluminium mengalami kadar kakisan terendah iaitu sebanyak 0.2645 mpy. Persekitaran terbuka pula memberikan polar keputusan kajian yang sama tetapi dengan nilai kadar kakisan hampir mencecah dua kali ganda kadar pengaratan persekitaran tertutup. Kadar kakisan zink ialah 2.103 mpy dan aluminium pula ialah 0.417 mpy. Sebarang ciri pengaratan mendedahkan faktor penyebab kakisan itu. Artikel ini memberikan pendekatan yang terbukti dalam menentukan secara tepat kesan persekitaran dan jenis bahan terhadap kadar kakisan. Ini termasuk strutur mikro kakisan seperti kakisan umum, pitting dan kakisan kimia. Kesimpulannya, ciri-ciri persekitaran mempengaruhi kadar kakisan. Bagi persekitaran tertutup, kadar kakisan adalah rendah kerana sampel terlindung daripada hujan dan embun. Persekitran terbuka pula memberikan bacaan hampir dua kali ganda kerana wujudnya faktor cuaca. Aluminium terbukti sebagai sampel yang mempunyai daya tahan kakisan tinggi. Oleh itu, penggunaan aluminium dalam aplikasi di ruangan terbuka dan tertutup adalah sangat disyorkan.

TABLE OF CONTENTS

CHAPTER 1 INTRODUCTION

CHAPTER 2 LITERATURE REVIEW

CHAPTER 3 METHODOLOGY

CHAPTER 4 RESULTS AND DISCUSSION

CHAPTER 5 CONCLUSION AND RECOMMENDATIONS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

P	Pressure
$^{\circ}C$	Degree Celsius

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Nowadays, the defects and losses that cause by atmospheric corrosion always are topics of conference and discussion. Atmospheric corrosion of metal is most commonly observed phenomena in our life. However, the mechanism of atmospheric corrosion of metal has not been clarified because of the difficulty in experimental work.

From the standpoint of economics, safety, and aesthetics, the importance atmospheric corrosion and its control is well recognized. More structure and material are exposed to the atmosphere than to any other environment. It is not surprising, therefore, that a vast body of exists on the performance of materials in the atmosphere and the characterization of such environments. Society interests in the performance of material in the atmosphere were active well before the formation of committee G-1 on corrosion of metal in 1964. The International Organization standardization (ISO) has also been very active in the development of standards for atmospherics testing methods and classification of atmospheres. It seemed a natural follow-up for subcommittee G 01-04 to organize another symposium on atmospheric corrosion, held in November 1993 in Dallas, Texas.

Atmospheric corrosion is the interaction of any material, commonly a metal, with the surrounding atmospheric environment. A well-known example is the rust formation on cars and other vehicles, but also electronic devices, construction materials, our cultural heritage and military equipment, to mention a few examples, are subjected to atmospheric corrosion. Additionally, this kind of corrosion is important to many naturally occurring processes. Due to the massive economical impact corrosion has on society, a good knowledge of the fundamental processes involved is essential in the search for new preventative measures. Since atmospheric corrosion involves many physical and chemical processes, it requires a good knowledge in several scientific areas, and can thus be considered a truly interdisciplinary field.

The corrosion of a metal, and its transformation to the mineral it was extracted from, has been known for a long time, but it was not until the 1920's that scientific investigations of corrosion phenomena commenced. This new work was performed by Vernon, who examined the corrosion products formed upon exposure of a metal surface to corrosive gases, such as carbon dioxide (CO_2) and sulfur dioxide (SO_2)(Vernon, 1923,1927). The researcher studied the influence of relative humidity on the corrosion rate, and realized the importance of water in atmospheric corrosion. During the following decades, the central role of electrochemical reactions was discovered. In the 1960's, instruments capable of analyzing the chemical composition of the corroded surface started to emerge, and X-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy (AES) became work-horses as surface analytical tools. Year by year, the technology to investigate the corrosion have been developed in order to analyses corrosion propagations and find the ways to prevent it.

1.2 COST OF ATMOSPHERIC CORROSION

Atmospheric corrosion may cause serious damage to metallic structures and equipments. The effect is so serious that the annual cost of atmospheric corrosion is approximately half the total annual cost of all types of corrosion of metals (W. Ke, 2003**)**. It has been reported that more than half of the national cost of corrosion, which has been estimated at close to 4% of a nation's gross domestic product, is a result of atmospheric corrosion (J. H. Payer, 1980). As another example, around 20% of failures of aircraft electronics are thought to be due to corrosion-related causes (B. Dobbs and G. Slenski, 1984). It is difficult to estimate the cost of direct or indirect consequences caused by atmospheric corrosion on materials exposed in our environments (C. Leygraf and T. E. Graedel, 2000). It has become evident that acid deposition through rain, snow, fog, or dew has resulted in substantial deterioration of artistic and historic objects, including old buildings and structures of historic value, statues, monuments and other cultural resources.

1.3 PROBLEM STATEMENT

Atmospheres are often classified as being rural, industrial or marine in nature. Two decidedly rural environments can differ widely in average yearly temperature and rainfall patterns, mean temperature, and perhaps acid rain, can make extrapolations from past behavior less reliable.

The corrosion of metal in the atmosphere and in many aqueous environments is best understood from a film formation and brake down standpoint. It is an inescapable fact that iron in the presence of oxygen and water is thermodynamically unstable with respect to its oxides. Because atmospheric corrosion is an electrolytic process, the presence of an electrolyte is required. This should not be taken to mean that the metal surface must be awash in water; a very thin adsorbed film of water is all that is required.

During the actual exposure, the metal spends some portion of the time awash with water because of rain or splashing and a portion of the time covered with a thin adsorbed water film. The portion of time spent covered with the thin water film depends quite strongly on relative humidity at the exposure site. This fact has led many corrosion scientists to investigate the influence of the time of wetness on the corrosion rate.

Atmospheric corrosion recovers the corrosion that happen in many places such as under sea water, indoor and outdoor. Different environment have different surrounding compositions and parameter such as pH. Therefore, different environment and types of material will give the variation corrosion rate and types that will discuss in this thesis.

1.4 OBJECTIVE OF STUDY

The objectives of this study are:

i. To study the atmospheric corrosion in outdoor and indoor environment.
ii. To investigate the effect of atmospheric corrosion to the surface and microstructure of each material.
iii. To study the effect of different environments and materials to the corrosion rate analysis of copper, aluminum, and zinc.

1.5 SCOPES OF PROJECT

The scope of this study includes:

i. Sample preparations process including cutting, drilling and initial cleaning
ii. Exposure of specimen indoor and outdoor
iii. Cleaning process using specific chemicals
iv. Corrosion analysis which will be done by weight loss method (corrosion rate) and surface observation (SEM)

1.6 SIGNIFICANCE OF STUDY

Conducting this study can contribute to the existing data on the atmospheric corrosion study and can be used as the reference in future research. Moreover, this study can contribute in order to avoid the corrosion or reduce the maintenance costs due to the further understanding about the atmospheric corrosion.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

The word corrosion is derived from the latin corrosus which means eaten away or consumed by degrees; an unpleasant word for an unpleasant process (Trimgham T.C.E, 1958). Corrosion is defined as the destruction of materials caused by chemical or electrochemical action of the surrounding environment. This phenomenon is experienced in day to day living. The most common examples of corrosion include rusting, discoloration and tarnishing (Speller F.N., 1951). Corrosion is an ever occurring material disease. It can only be reduced it cannot be prevented because thermodynamically it is a spontaneous phenomena.

Corrosion is an electrochemical process whereby a material reacts to the environment in which it is placed. Generally, this process results in the loss of properties of the material, causing economic losses, affecting safety, and raising 1environmental concerns. Metals corrode for a variety of reasons. Most metals are found in nature as ores and oxides, and the extraction of metals from their ores requires a considerable amount of energy. Energy is required for the alloying process and it is introduced in the form of heat.

2.2 CLASSIFICATION OF CORROSION PROCESS

Corrosion process can be conveniently classified into chemical and electrochemical corrosion as follows Figure 2.1.

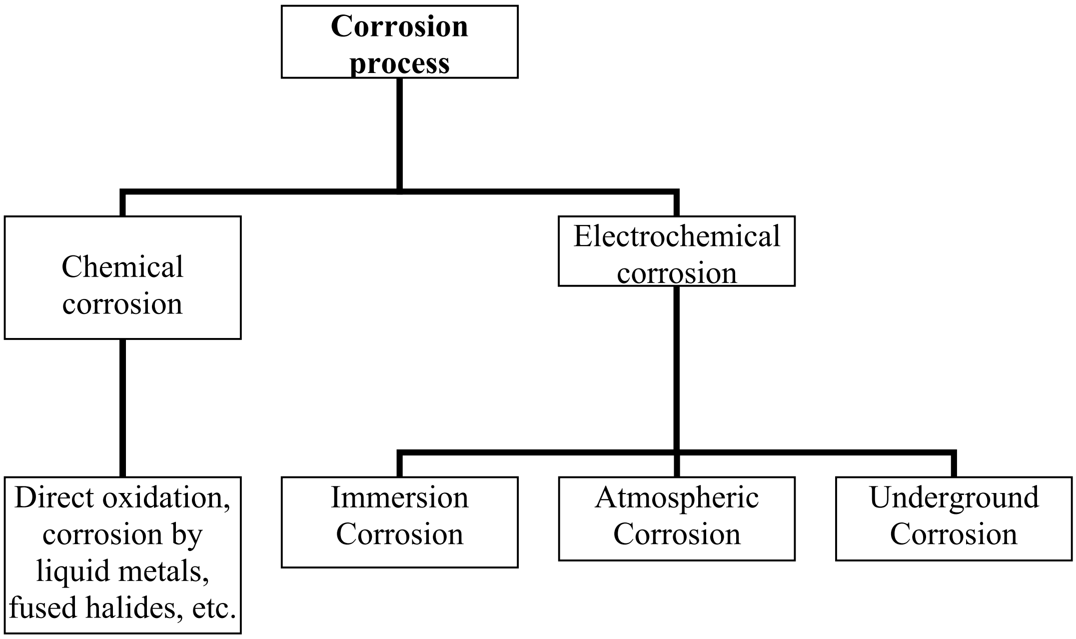


Figure 2.1: Corrosion process

Source: Natesan M, 1995

This study only focused on the atmospheric corrosion. This chapter will discuss the atmospheric corrosion including the atmosphere classification, corrosion mechanism, factors affecting corrosion and the types of corrosion.

2.3 ATMOSPHERIC CORROSION

The term “atmospheric corrosion” comprises the attack on metal exposed to the air as opposed to metal immersed in a liquid. Atmospheric corrosion is the most familiar type of corrosion for common metals (Naixin et al., 2002). Atmospheric corrosion is a subject of global concern because of its importance to the service life of equipment and durability of the structural materials. While there is a general agreement on the possible types of parameters that may lead to corrosion, these studies suffer severely from the lack of generality in the sense that their predictive capability is extremely poor.

Conventional atmospheric parameters that may lead to metal corrosion comprise of weathering factors such as temperature, moisture, rainfall, solar radiation, wind velocity, etc. Air pollutants such as sulphur dioxide, hydrogen sulphide, oxides of nitrogen, chlorides have also been found to contribute to atmospheric corrosion (Brown P.W and Masters L.W, 1982). Atmospheric corrosion can further be conveniently classified into dry, damp and wet categories. Dry oxidation takes place in the atmosphere with all metals that have a negative free energy of oxide formation. The damp moisture films are created at a certain critical humidity level, while the wet films are associated with dew, ocean spray, rainwater, and other forms of water splashing. By its very nature, atmospheric corrosion has been reported to account for more failures in terms of cost and tonnage than any other form of corrosion.

2.3.1 Types of Atmosphere

Atmospheric corrosion severity tends to vary significantly in different locations and, historically, it has been customary to classify environments as rural, urban, industrial, marine, or combinations of these. These types of atmosphere have been described as follows (K. L. Money, 1987):

i. Rural - This category is generally the least corrosive and normally does not contain chemical pollutants, but does contain organic and inorganic particulates. The principal corrodents are moisture, oxygen and to a lesser extent carbon dioxide. Arid or tropical types represent special extreme cases in the rural category.

ii. Urban - Similar to the rural type of atmosphere, in urban there is little industrial activity. Additional Contaminants are of the SO_x and NO_x variety, from motor vehicle and domestic fuel emissions.

iii. Industrial - These atmospheres are associated with heavy industrial manufacturing facilities and can contain concentrations of sulfur dioxide, chlorides, phosphates, and nitrates.

iv. Marine - Fine windswept chloride particles, deposited on surfaces, characterize this type of atmosphere. Marine atmospheres are usually highly corrosive, and the corrosivity tends to be significantly dependent on wind direction, wind speed, and distance from the coast.

2.3.2 Theory of Atmospheric Corrosion

The atmospheric corrosion of metals is an electrochemical process in which a metal reacts with its environment to form an oxide or other compounds. To cause this process, there are four essential constituents: an anode, a cathode, the metal itself and an electrically conducting solution. Simply, the anode is the site at which the metal is corroded; the electrolyte solution is the corrosive medium; and the cathode forms the other electrode of the cell and is not consumed in the corrosion process. At the anode the corroding metal passes into solution as positively charged ions, releasing electrons that participate in the cathodic process. The distribution of anodic and cathodic areas is one of the most important factors determining the type of corrosion that occurs. But in the simplest case, general corrosion, the corrosion cells are very small and numerous, and distributed in a random manner over the surface of the metal, and the effect is more or less a uniform attack on the surface (Materials Science and Engineering, 2001, 2002).

$$M + H_2O(1) \rightarrow M(OH)_2(s) \tag{2.1}$$

In addition, and unfortunately, the rate of wet corrosion may often be very high compared with dry corrosion on the same metal at the same temperature. There are two underlying reasons for this:

i. The dipolar water molecule stabilizes the free (dissociated) metal ions in solution

ii. The metallic structure and water in contact with it can both conduct electric current.

This enables reaction (2.1) to proceed through the coupling of two primary corrosion reactions that is at anode and cathode.

For the most corrosion processes, the anodic and cathodic reactions are the following (K. Barton, 1976):

$$M \rightarrow Mn^{+} + ne^{-} \quad \text{(Anodic reaction)} \tag{2.2}$$

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \quad \text{(Cathodic reaction)} \tag{2.3}$$

However, at low pH environment, hydrogen evolution may take place as cathodic reactions on the metal surface which it is assumed that the surface electrolyte in extremely thin layers is neutral or only slightly acidic, then the reaction can be ignored for atmospheric corrosion of most metals and alloys.

$$2H^{+}\ 2e^{-} \rightarrow H_2(g) \tag{2.4}$$

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 following oxygen reduction reaction is the most likely

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \tag{2.5}$$

Two reaction steps may actually be involved (K. Barton, 1976), with hydrogen peroxide as an intermediate species, according to

$$O_2 + 2H_2O + 2e^{-} \rightarrow H_2O_2 + 2OH^{-} \tag{2.6}$$

$$H_2O_2 + 2e^{-} \rightarrow 2OH^{-} \tag{2.7}$$

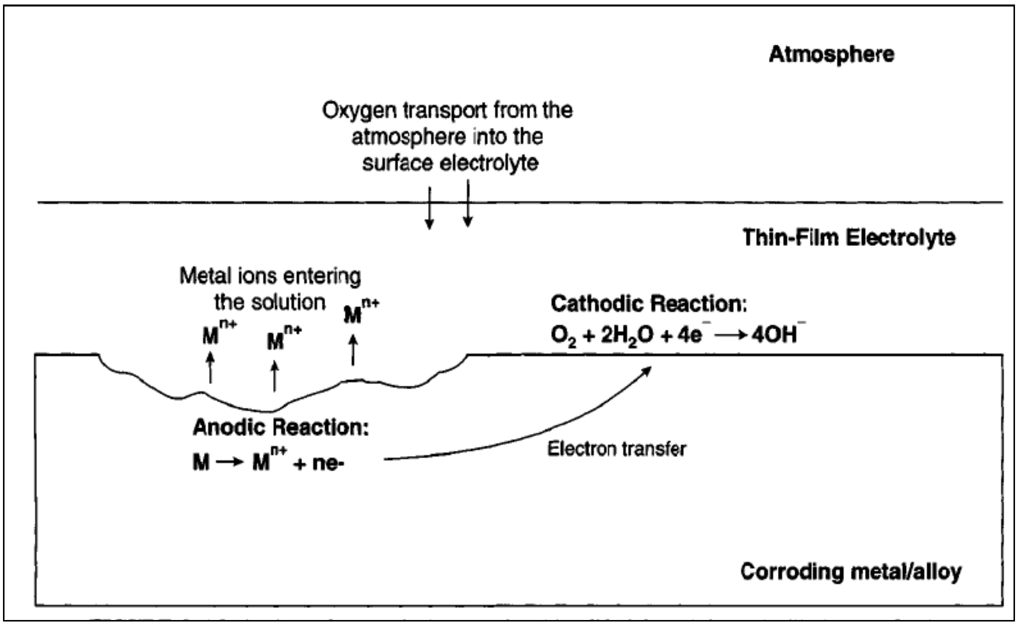


Figure 2.2: Mechanism of atmospheric corrosion

Source: Pierre R. Roberge (1999)

Figure 2.2 show the illustration on the mechanism of the atmospheric corrosion. Metals exposed in the environment will absorb water forming a thin water layer on the surfaces. The amount of water adsorbed by the metal surface is very important for the atmospheric corrosion process and most metals rapidly adsorb the first monolayer of water by forming a surface hydroxyl layer. Subsequent water adsorption is similar for many metals and oxides, and the water is absorbed in the molecular form. At 20% RH there will be about one monolayer of water and at 75% RH there will be about five monolayers adsorbed on the metal surface (B. G. Callaghan, 1993). Adsorbed water films, which are thicker than three monolayers have properties similar to bulk water (Shreir et al., 1994). Airborne salt particles, deposited on the surface of metals, will dissolve into this water adlayer and form thicker electrolyte layers or droplets. Oxygen (O_2), carbon dioxide (CO_2), and gaseous pollutants, such as SO_2, O_3 and NO_2, dissolve into the adlayer and affect the corrosion process. Unevenly distributed water films lead to the formation of local electrochemical corrosion cells with spatially separated anodes and cathodes. The mechanism is show in Figure 2.3.

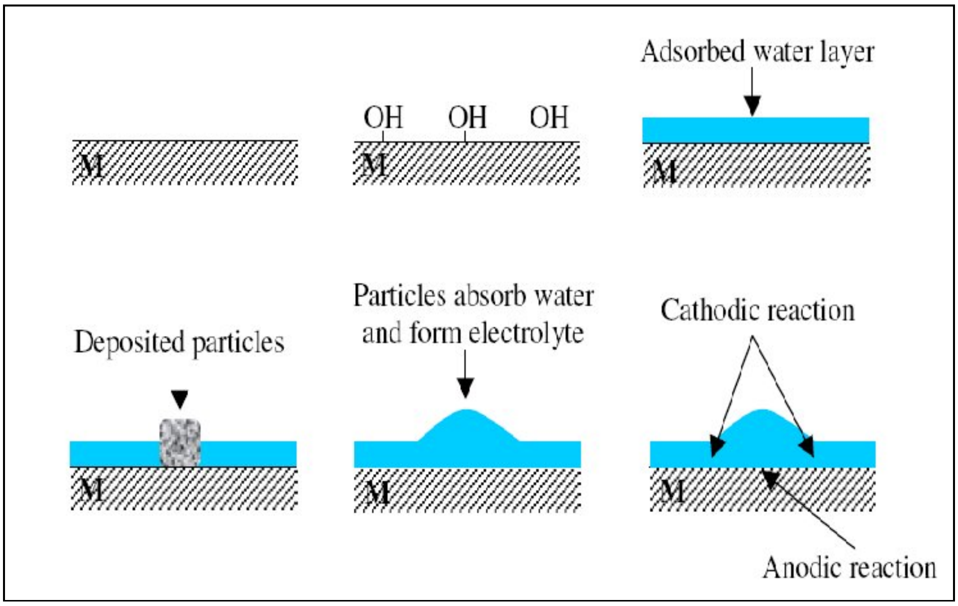


Figure 2.3: Schematic picture of salt particle induced atmospheric corrosion

Source: Pierre R. Roberge (1999)

2.3.3 Atmospheric Environment

Many atmospheric gaseous pollutants that occur in our everyday environment can act as corrosion stimulators. Several gaseous pollutants known to accelerate corrosion attacks are produced by human activities and are, thus, present in larger amounts in urban and industrial areas. Sulphur dioxide (SO_2), nitrogen dioxide (NO_2) and ozone (O_3) are most important gaseous pollutants for the atmospheric corrosion of metals. SO_2, O_3 and NO_2 present in the air can dissolve into the water layer formed on the metal surface, resulting in destabilization of surface oxides and initiation of corrosion.

2.3.4 Oxygen (O_2)

Oxygen is a natural constituent of air and is readily absorbed from the air into the water film on the metal surface, which may be considered saturated, thus promoting any oxidation reactions. Serious corrosive damage to iron alloys can be caused by 8-15% of oxygen at temperature of 3-500^oC (Karlsson A et al., 1990).

2.3.5 Carbon Dioxide (CO_2)

The concentration of carbon dioxide (CO_2) in the ambient atmosphere is about 350 ppm. Most of the CO_2 results from the combustion of organic matter if sufficient amounts of oxygen are present. Dissolved CO_2 in the water forms weak carbonic acid (H_2CO_3) and the carbonic acid in turn dissociates partly to form bicarbonate (HCO_3^-) and carbonate ions (CO_3^{2-}). CO_2 is one of the most important parameters in determining corrosivity of an oil/gas production environment. The most important role of CO_2 on atmospheric corrosion is to participate in the formation of secondary products, especially on non-ferrous metals. The dissolution of CO_2 gave an electrolyte pH of between 5 and 5.6 (Lindström, 2000). If oxygen is present in excess, the cathodic reaction will not change at this pH from oxygen reduction to hydrogen reduction. CO_2 has a strong effect on the NaCl-induced atmospheric corrosion of metals (Chen et al., 1993), and the corrosion was considerably lower at low CO_2 concentrations than at ambient. In reality, the supply of CO2 can be restricted under certain conditions such as in crevices and confined surfaces and under paint films which could lead to high corrosion rates in these locations. The ambient concentration of CO_2, 350 ppm, inhibits the NaCl-induced corrosion of metals.

2.3.6 Sulfur Dioxide (SO_2)

Sulfur dioxide, a product of the combustion of sulfur containing fossil fuels, plays an important role in atmospheric corrosion in urban and industrial 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 in accordance with Eq. (2.8) (K.Barton, 1976).

$$SO_2 + O_2 + 2e^- \rightarrow SO_4^{2-} \tag{2.8}$$

The required electrons are thought to originate from the anodic dissolution reaction and from the oxidation of ferrous to ferric ions. It is the formation of sulfate ions that is considered to be the main corrosion accelerating effect from sulfur dioxide.

For iron and steel, 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 expressed by Eq. (2.9).

$$FeSo_4 + H_2O \rightarrow FeOOH + SO_4^{2-} + 3H^+ + e^- \qquad (2.9)$$

The corrosion-stimulating sulfate ions are liberated by this reaction, leading to an auto-catalytic type of attack on iron. The acidification of the electrolyte could arguably also lead to accelerated corrosion rates, but this effect is likely to be of secondary importance because of the buffering effects of hydroxide and oxide corrosion products. In nonferrous materials such as zinc, sulfate ions also stimulate corrosion, but the auto-catalytic corrosion mechanism is not easily established. The important of pollution due to SO_2 can be further highlighted by the result of Figure 2.4.

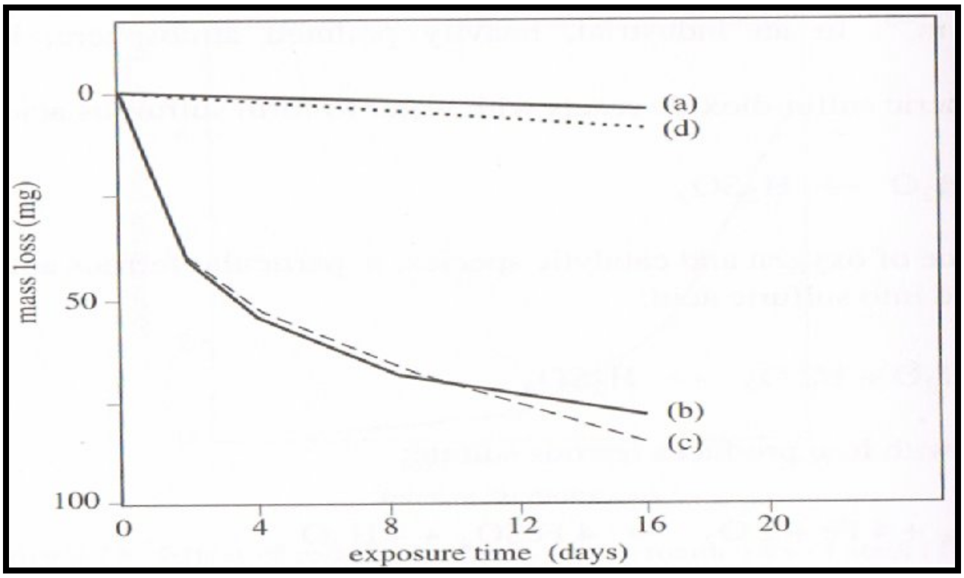


Figure 2.4: Effect of so_2 to weight loss of iron

Source: U. R. Evans, (1972)

Figure 2.4 present the weight loss measured on iron samples exposed to air with relative humidity of 95% under laboratory conditions: (a) in the presence of $SO_{2;\ \mathrm{and}}$ (b) in the absence of SO_2. The curve (c) represents the result obtained by exposing a precorroded sample in the presence of SO_2 and therefore contaminated by sulfates to and atmospheres without SO_2. The curve (d) represents the same kind of test as (c), except that the sample had been rinsed with water before the corrosion test (U. R. Evans, 1972). This shows that the corrosion acceleration will increase in the present of SO_2.

Corrosion rate varies in the different environments. Previous study clearly shown that corrosion rate increases in order of rural, urban, and industrial atmosphere.

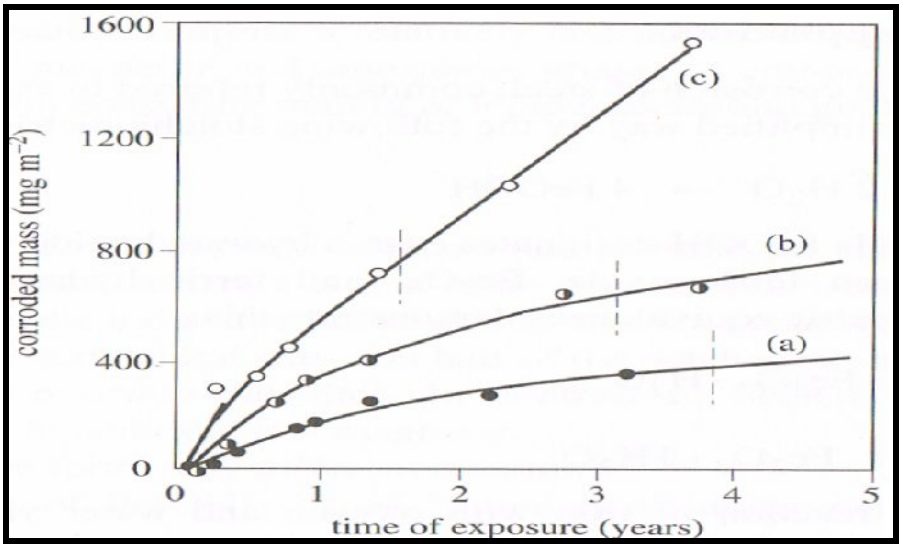


Figure 2.5: Corroded Mass of Steel Expose to Different Atmosphere

Source: K. Barton, (1973)

Figure 2.5 present the corroded mass of steel sample (a) exposed to the rural atmosphere; (b) to an urban atmosphere; and (c) an industrial atmosphere for a period of several years. The dashed lines indicate the time required to reach the steady-state corrosion rate (K. Barton, 1973). This shows that varies atmosphere contaminants will affect the corrosion acceleration.

2.3.7 Chlorides (Cl^-)

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 (K. Barton, 1976). 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 (K. Barton, 1976), consistent with practical experience.

2.3.8 Other Atmospheric Contaminants

Hydrogen sulfide, hydrogen chloride 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 (K. Barton, 1976). 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 (K. Barton, 1976). Nitrogen compounds, in the form of NOx, tend to accelerate atmospheric attack. The NOx emission, largely from combustion processes, has been reported to have increased relative to SO_2 levels (V. Kucera, 1987). However, measured deposition rates of these nitrogen compounds have been significantly lower than for SO_2 (V. Kucera, 1987), 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:

i. Reduction in the critical humidity levels by hygroscopic action.

ii. The provision of anions stimulating metal dissolution.
iii. Microgalvanic effects by deposits more noble than the corroding metal

2.4 FACTORS INFLUENCING CORROSION

Figure 2.6 shows the several factors that influencing corrosion.

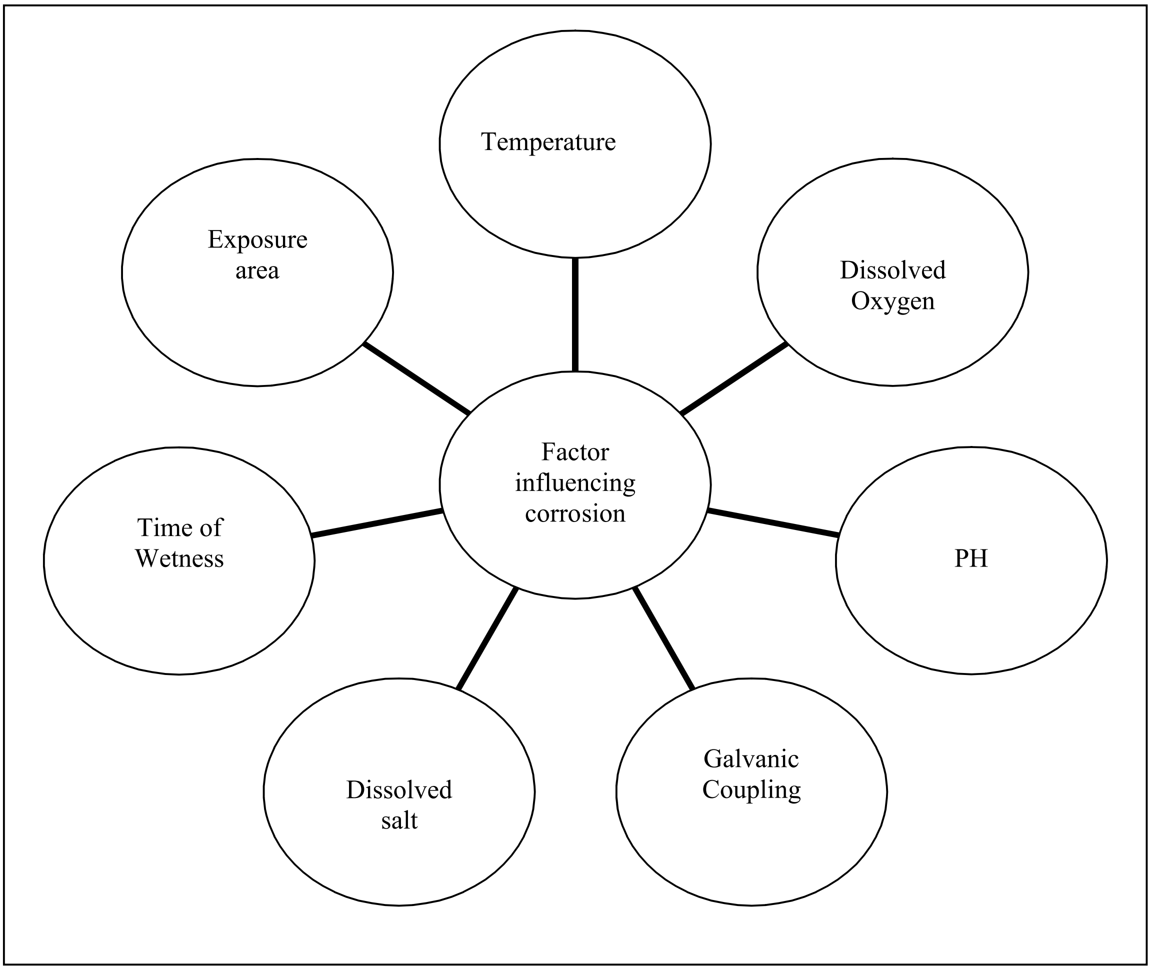


Figure 2.6: Factor Influencing Corrosion

2.4.1 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. 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 (H.H.Uhlig, 1984). Somewhat unexpectedly, relatively high corrosion rates have been measured in some coastal cold climates under the influence of salt deposition (G. A. King, 1998). The well-known depression of the freezing point by salt may account for these results.

2.4.2 Galvanic Attack

The corrosion potentials (E_{corr}) of metals play a crucial factor in galvanic corrosion. It is from these corrosion potentials that one can identify the anode and the cathode when two different metals are placed in electrical contact in a solution. The Galvanic Series is a very important tool used in engineering to determine which metals will be more anodic (active) or cathodic (noble) in a galvanic reaction.

The arrangement of metal alloys in order of their tendencies to be anodic (or order of their corrosion potentials) can be refer in galvanic Series as shown in Figure 2.7. The electrolytic current in the couple is proportional to the rate of galvanic corrosion so the most active or negative alloy in a couple is always attacked preferentially by galvanic corrosion. Selection of alloys with a minimum potential difference will minimize corrosion in galvanic couples so in general, the farther apart these metals are in the Galvanic Series, the greater the potential is for corrosion to occur.

The galvanic series, lists the corrosion potentials formed by the polarization of two or more half-cell reactions to a common mixed corrosion potential, E_{corr}, and are measured in real or simulated application conditions with respect to a secondary reference electrode.

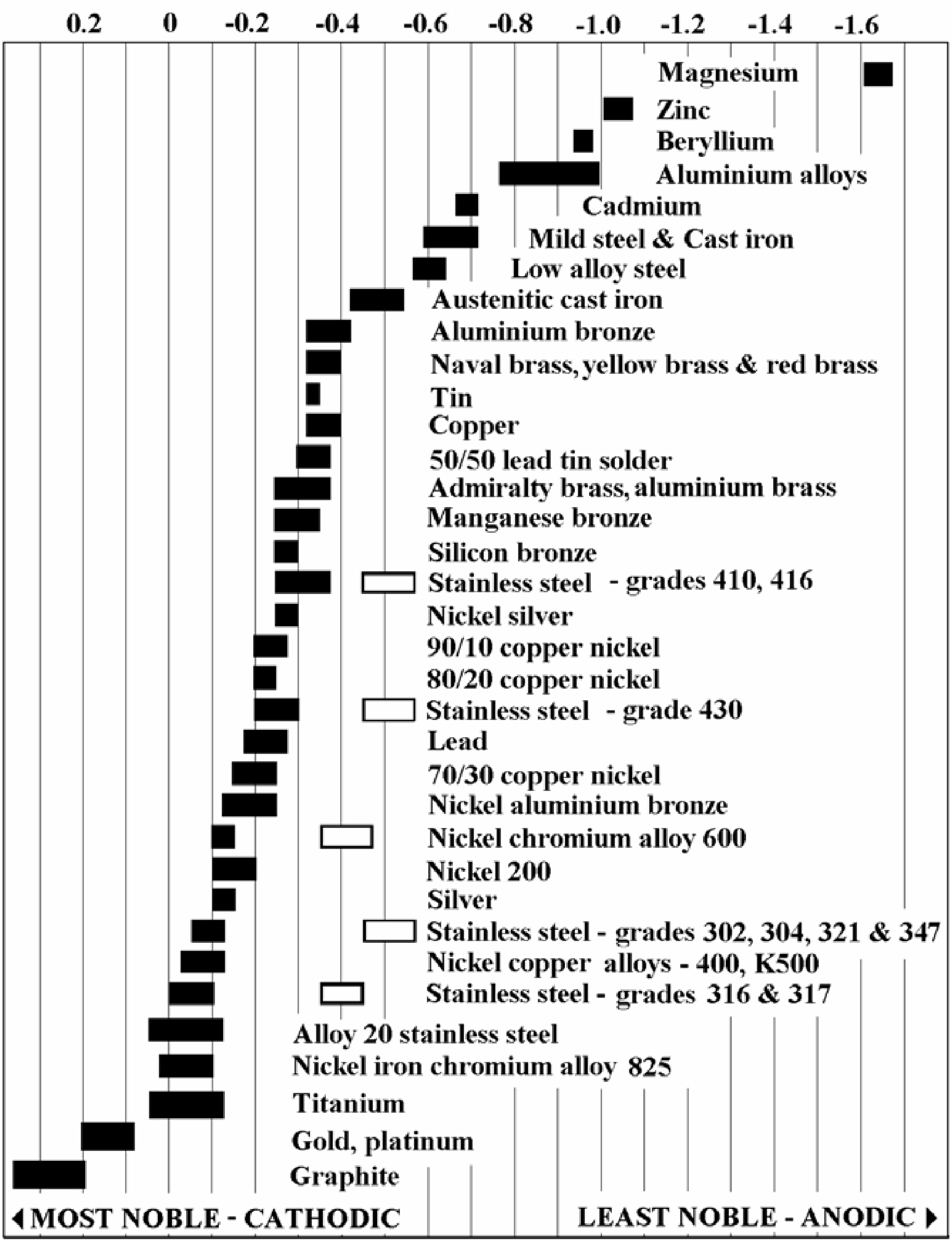


Figure 2.7: The galvanic series

Source: Atlas Specialty Metals (2006)

2.4.3 Relative Humidity

The relative humidity (RH) in the atmosphere plays an important role and affects directly the amount of water on the metal surface (Phipps and Rice, 1979). The absolute humidity (g/m^3) indicates the mass of water contained in cubic meter of gas, whereas the relative humidity represents the ratio between the vapor pressure and the saturation pressure. The atmospheric corrosion rate of metals increases with the relative humidity during the environmental atmosphere exposure (B. I. Rickett, 1995). The presence of water is necessary for the atmospheric corrosion process and the water layer acts as a medium for electrochemical reactions as well as a solvent for atmospheric constituents. By definition, when relative humidity is 100%, the air is saturated with water. If the water content in the air is increased the air will be super-saturated and water condensation will occur on any surface present, assuming that the surfaces are at the same temperature as the air. The amount of water on the surface was only weakly dependent on the temperature (S. Lee and R. W. Staehle, 1997).

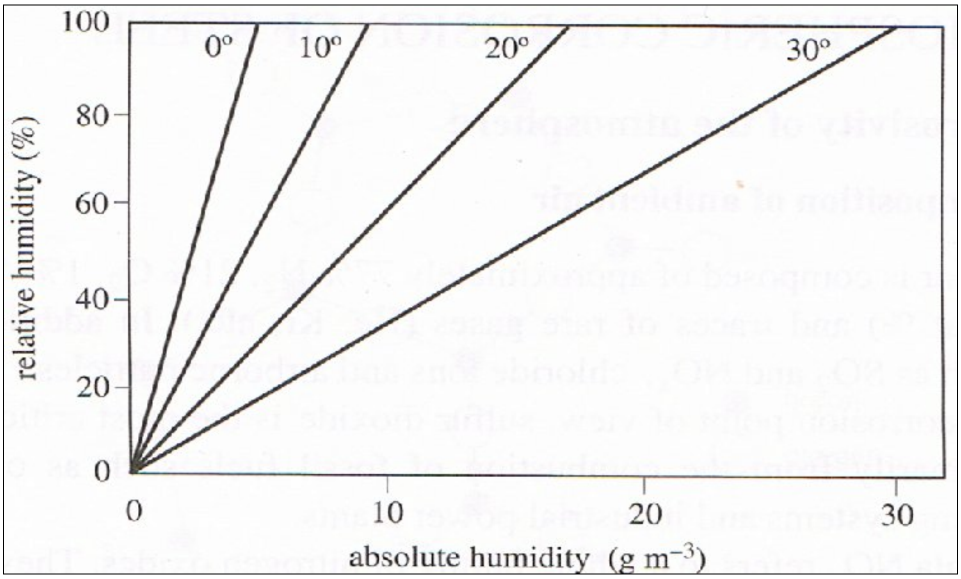


Figure 2.8: Relative humidity as a function of absolute humidity for different

Source: S. Lee and R. W. Staehle, (1997) On the other hand, the corrosion rate of steel increases markedly as soon as the relative humadity exceeds 80%. The presence of hygroscopic salt particles leads to absorption of water and formation of bulk electrolyte layer on the surface. This is usually accompanied with an abrupt increase in the corrosion rate of the metal. When a substance is dissolved in a solvent, such as water, a decrease in the vapour pressure of the solvent is observed:

$$P_{solvent} = a_{solvent}P^{0}_{\ solvent} \qquad (2.10)$$

The vapour pressure of the solvent (Psolvent) is equal to the vapour pressure of the pure solvent (P^0 solvent) multiplied by the activity of the solvent in the solution (asolvent). The vapour pressure lowering has very important consequences for the formation of surface electrolyte layers on metal surfaces.

The water in a solution in contact with air with a certain relative humidity will try to reach the activity corresponding to that of the surrounding air. The concentration of a solution and the thickness of the surface film will therefore change with the relative humidity for given amount of salt on a surface. Salts such as NaCl will form solutions above a certain critical relative humidity called the deliquescence point. The deliquescence point at a given temperature is defined as the water activity of a single electrolyte solution that is in equilibrium with its salt precipitate. This is very important under field conditions when mixture of pollutants can be present.

Figure 2.9 and Figure 2.10 shows the effect of relative humidity on the corrosion rate and the corroded mass of the steel. This shows that the corroded mass and the corrosion rate of the steel increase with the increasing of the relative humidity.

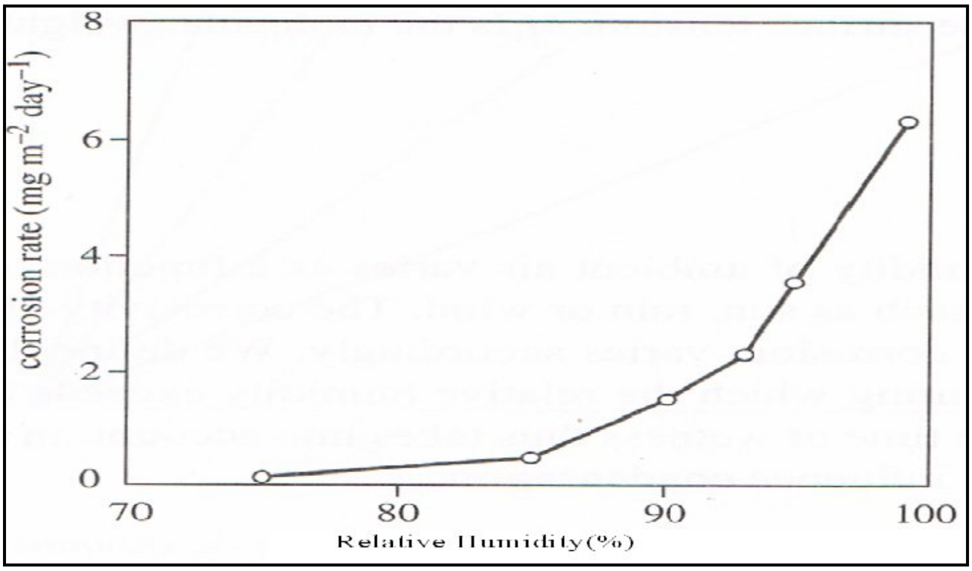


Figure 2.9: Effect of relative humidity on corrosion rate of the steel

Source: W. H. Vernon, (1935)

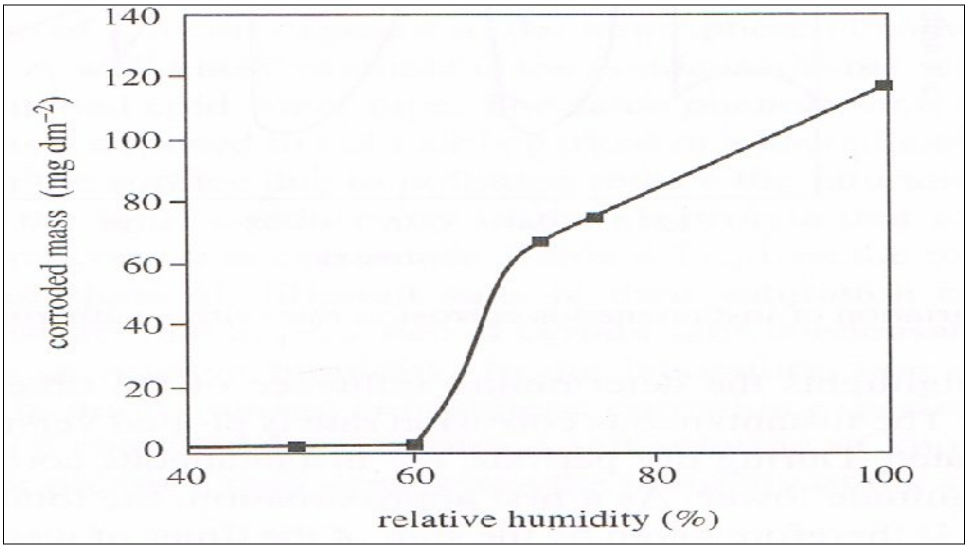


Figure 2.10: Effect of relative humidity on corroded mass of the steel

Source: W. H. Vernon, (1935)

2.4.4 Time of wetness

The time of wetness is obviously strongly dependent on the critical relative humidity. We define the time of wetness as the period of time during which the relative humidity exceeds 80% at a temperature above 0^oC(Norm ISO N. 9223, 1989).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. 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). 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. Figure 2.11 shows the variation of corrosion rate with weathering conditions.

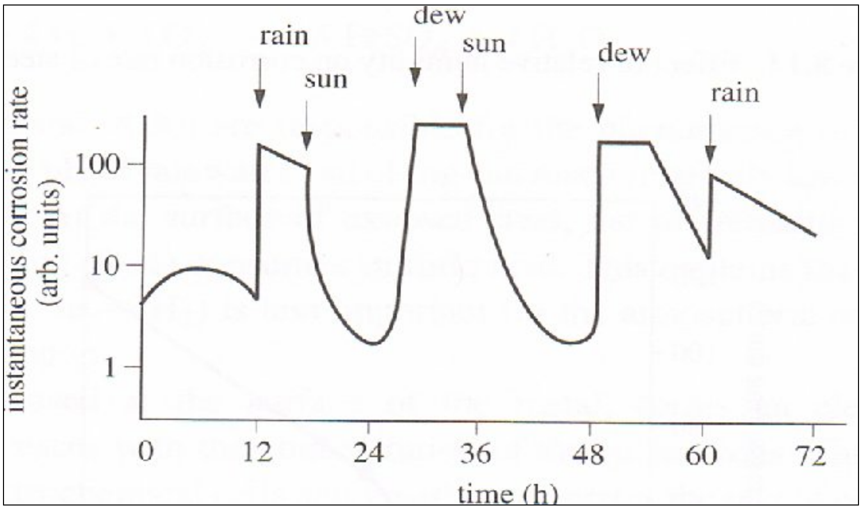


Figure 2.11: Variation of instantaneous corrosion rate with weathering conditions

Source: V.Kucera, (1987)

2.5 FORM OF CORROSION

Figure 2.12 shows the illustration of the corrosion types including uniform corrosion, pitting, crevice corrosion, galvanic corrosion, erosion, cavitation, fretting, intergranular, exfoliation, de-alloying, stress corrosion cracking and corrosion fatigue.

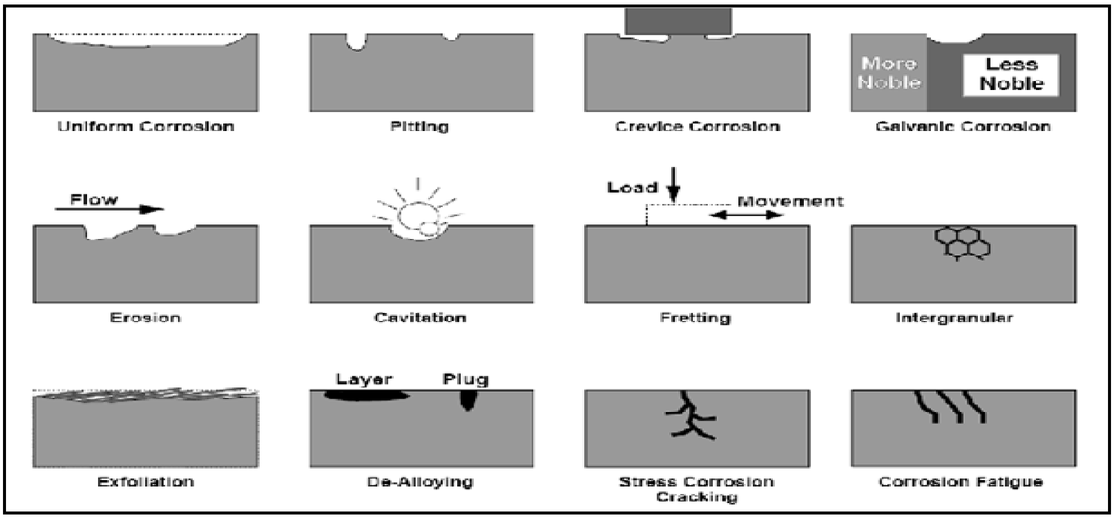


Figure 2.12: Type Of Corrosion

Source: Pierre R. Roberge (1999)

The common corrosion types formed on the metals surface when exposed to the atmosphere are general corrosion, pitting, galvanic, crevice, and erosion corrosion.

2.5.1 General Corrosion

General corrosion or rusting as show in Figure 2.13 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.

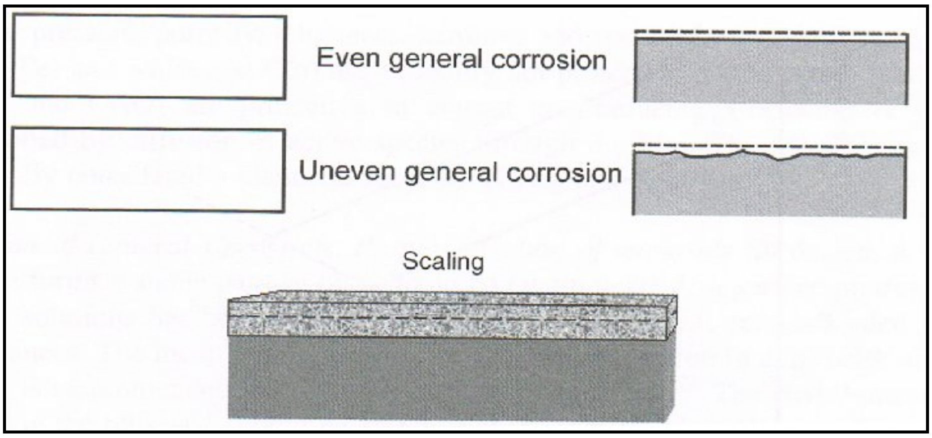


Figure 2.13: General Corrosion

Source: Pierre R. Roberge (1999)

2.5.2 Pitting Corrosion

Pitting corrosion as shown in Figure 2.14 is a nonuniform, 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.

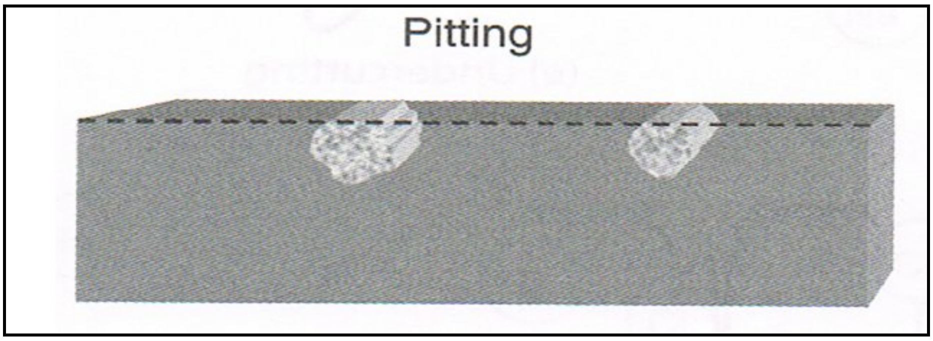


Figure 2.14: Pitting corrosion

Source: Pierre R. Roberge (1999)

2.5.3 Galvanic Corrosion

Galvanic corrosion as shown in Figure 2.15 formed 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 surficial anodes).

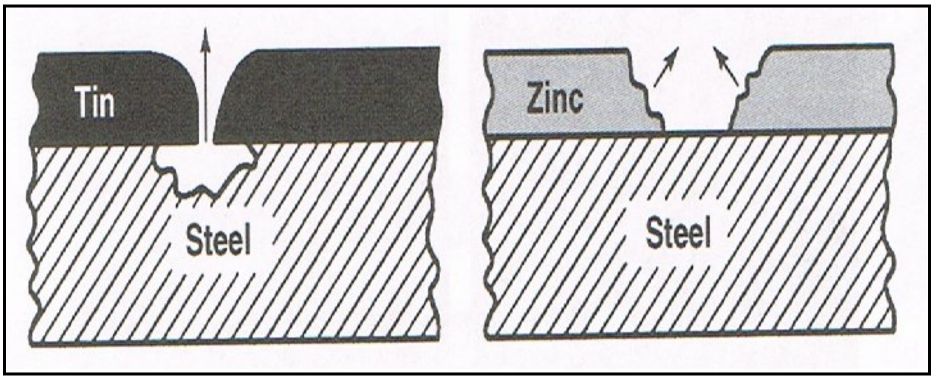


Figure 2.15: Galvanic Corrosion

Source: Pierre R. Roberge (1999)

2.5.4 Crevice Corrosion

Crevice Corrosion as shown in Figure 2.16 occurs when moisture and contaminants retained in crevices accelerate corrosion. When crevices are present between a metal surface and another component, the environment within the crevice can differ significantly from the environment in the boldly exposed areas, mostly due to differences in the amounts of available oxygen. Furthermore, the absence of oxygen impairs development of a protective oxide film within the crevice. As a result of these factors, localized corrosive attack occurs to the metal surface within the crevice.

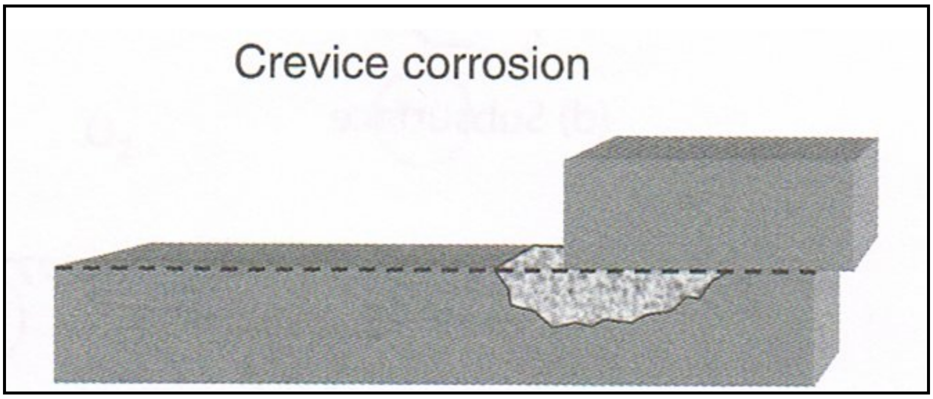


Figure 2.16: Crevice Corrosion

Source: Pierre R. Roberge (1999)

2.5.5 Erosion Corrosion

Virtually all metals are susceptible to erosion corrosion as shown in Figure 2.17, which is the simultaneous action of erosion (wear) and corrosion. This phenomenon can occur in a variety of environments, but is commonly seen in corrosive liquids containing abrasive particles. In recirculating systems, initial corrosion of components and piping can lead to erosion corrosion as oxide particles are generated.

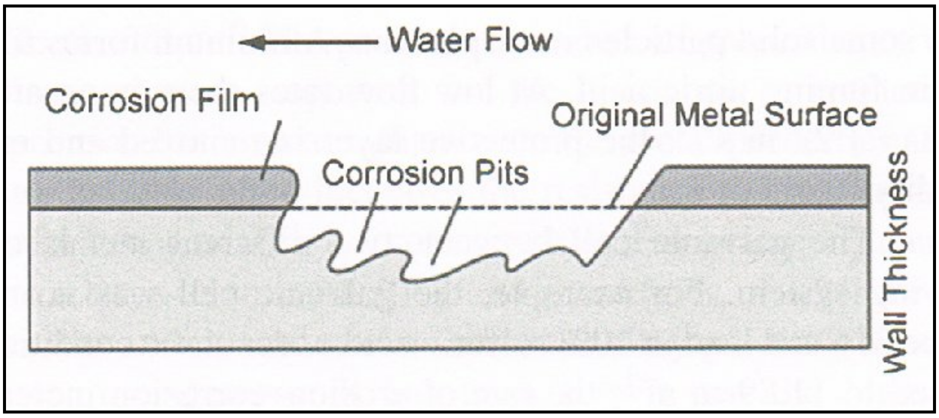


Figure 2.17: Erosion Corrosion

Source: Pierre R. Roberge (1999)

2.6 CORROSION RATE EXPRESSIONS

Mostly the rates of corrosion of metals are expressed as mpy or mmpy.

i. Safe: Less than 5mpy or 0.125 mmpy
ii. Moderate: 5 mpy to 50 mpy or 0.125 mmpy to1.25mmpy.
iii. Severe: Greater than 50 mpy or 1.25 mmpy.

Average corrosion rate may be obtained as follows (ASTM Standards, G 1 – 03):

$$Corrosion\ Rate = \frac{(K \times W)}{(A \times T \times D)} \tag{2.10}$$

where
W=weight loss, mg;
D=density of specimen,g/cm3;
A= Area of specimen, cm^2 and
T= exposure time, hr

Many different units are used to express corrosion rates. The corrosion rate can be calculated rate can be calculated in a variety of units with the following appropriate value of K:

Table 2.1: Corrosion rate units and value of K

Corrosion rate units desired	Constant (K) in corrosion rate equation
Mils per year (mpy)	3.45×10^6
Inches per year (ipy)	3.45×10^3
Inches per month (ipm)	2.87×10^2
Milimetres per year (mm/y)	8.76×10^4
Micrometres per year (um/y)	8.76×10^7
Picometres per second (pm/s)	2.87×10^6

Table 2.1:Continued

Grams per square meter per hour ($g/m^2.h$)	$1.00 \times 10^4 \times D$
Milligrams per square decimeter per day (mdd)	$2.40 \times 10^6 \times D$
Micrograms per square meter per second ($\mu g/m^2.s$)	$2.78 \times 10^6 \times D$

Source: (ASTM Standards, G 1 – 03)

To convert a corrosion rate in units X to a rate units Y, multiply by Ky/Kx; for example:

$$15mpy = \frac{15(2.78 \times 10^6)}{3.45 \times 10^6} pm/s$$

CHAPTER 3

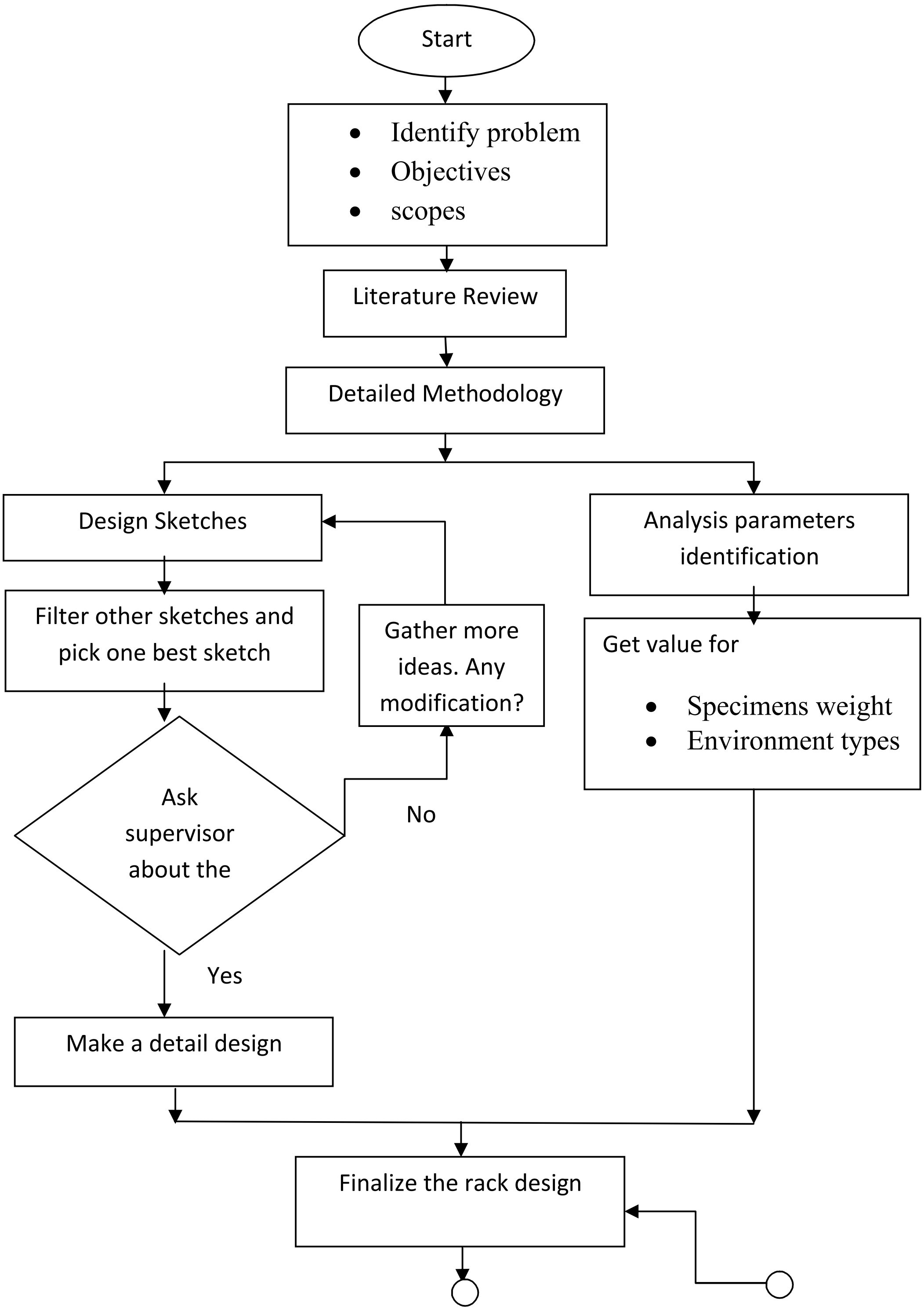
METHODOLOGY

3.1 INTRODUCTION

This chapter is discussed about the methodology used for this study. In this study, the metals have been exposed to the two types of environments which are, indoor and outdoor. The steps in this research was referred from the ASTM standard depends on the suitability, which referred to the tool and material available in the university. The materials used are zinc, aluminums alloy, and copper. The general procedures are including sample preparations, test the initial condition of the specimens, exposure to the environments, cleaning, and test the specimens condition after the exposure time and the last procedure is carried out the assessment of corrosion damage.

3.1.1 Project Process Flow

Figure 3.1 show the whole project process flow including methodology and result analysis.



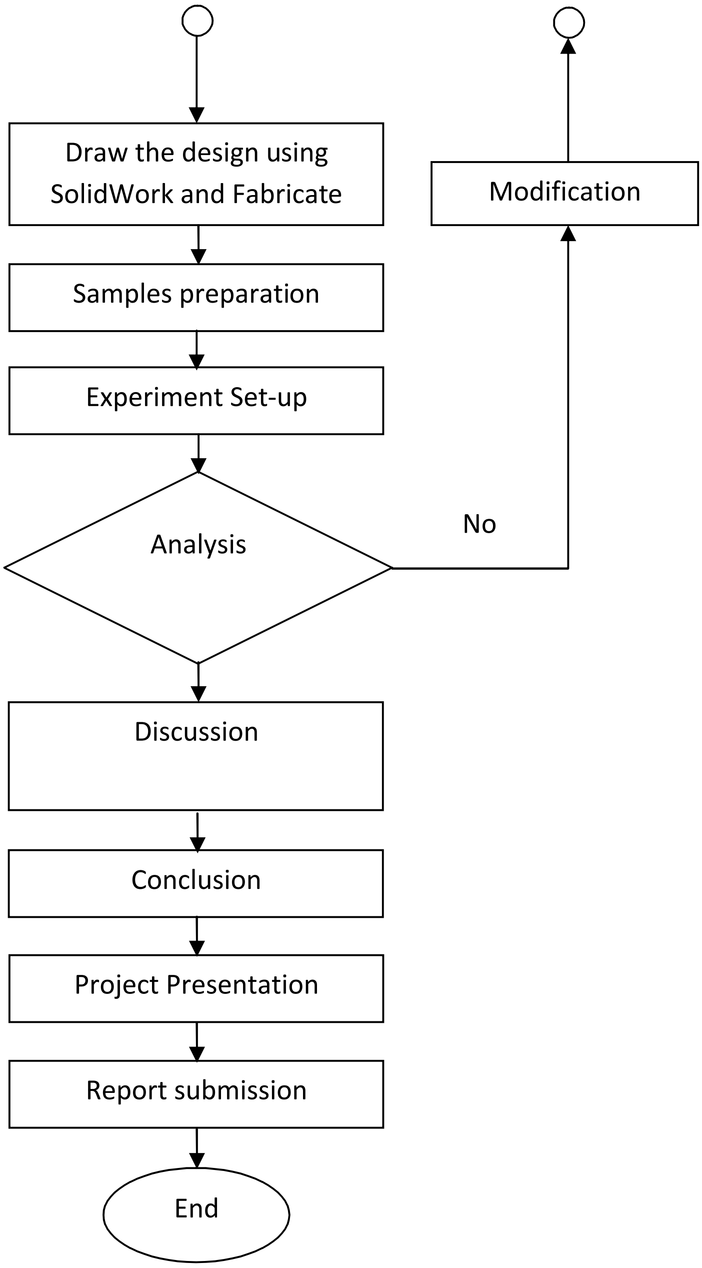


Figure 3.1: Process Flow Chart

3.2 DESIGN AND FABRICATE THE EXPOSURE RACKS

In this project, initially, it is started by designing and fabricating the exposure racks which is used to place the specimens. Here, the rack was designed as shown in Figure 3.2 using Solid Work software.

Exposure racks was designed to place the material in order to give the full effects of atmosphere at the location of the test site. The test racks must be constructed using material that will remain intake for the entire proposed period of exposure at the same times did not affect the result of the experiments. In this research, the racks are constructed by using the wood.

In order to hold the specimens on the racks, the galvanic relationships between the specimens and the material that has been used to build the racks must be considered. The racks are designed using wood that not gave the galvanic effects to the specimens, but in order to build the rack the nails were used. The nails were made by using the steel that can affect the result of the experiment cause by the galvanic relationship between the nails, screws and the specimens. After take the consideration about all of this, the insulator should be used as the specimen's holder. The holder that was used in this rack design is ropes.

For this research, the dimensions of the rack as shown in Figure 3.3 are higher than 760mm in order to make sure that the lowest specimens are at least 760mm from the ground or base. The exposure angle of this rack is 30 degree from the horizontal to yield the lowest corrosion rates.

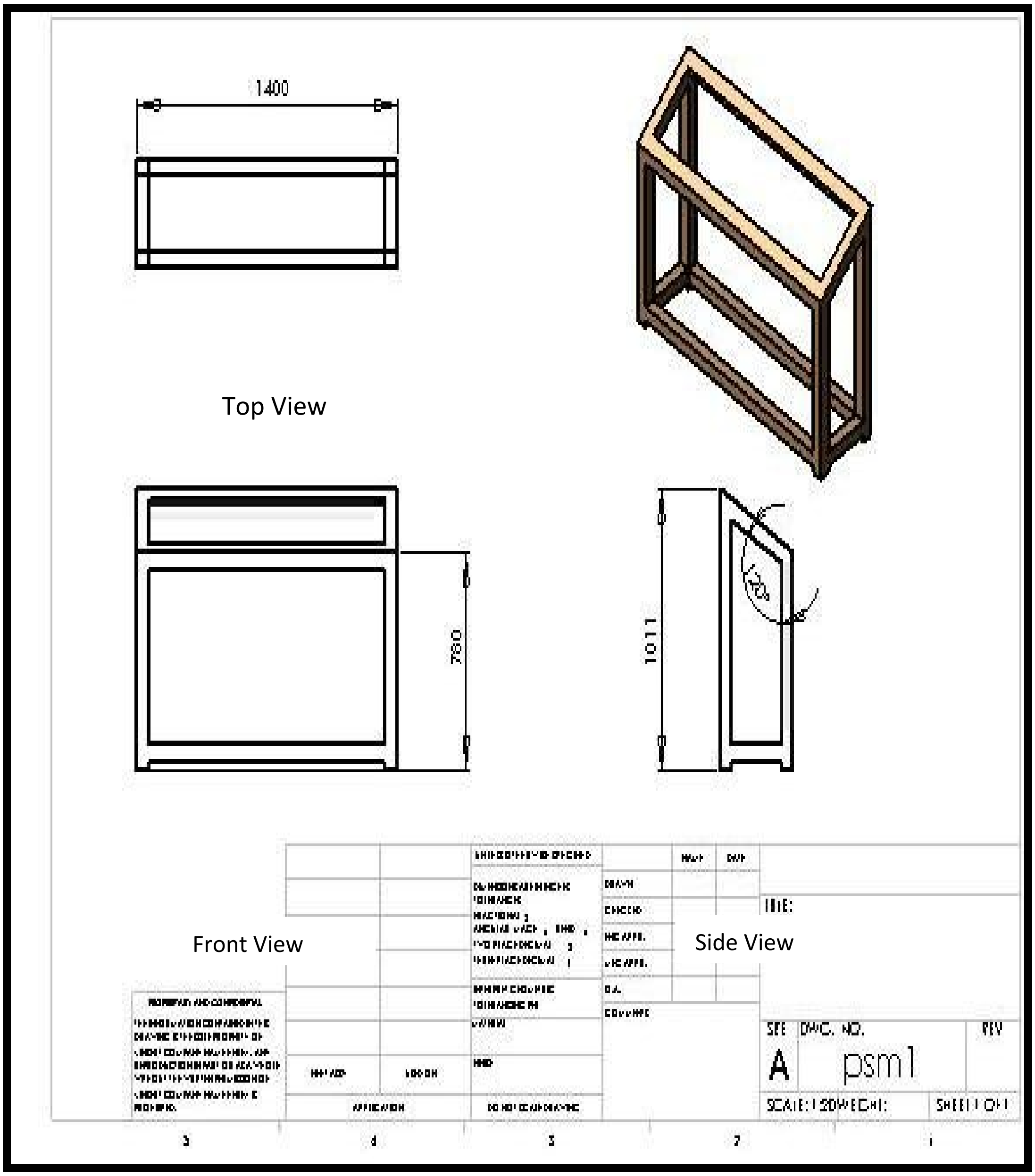


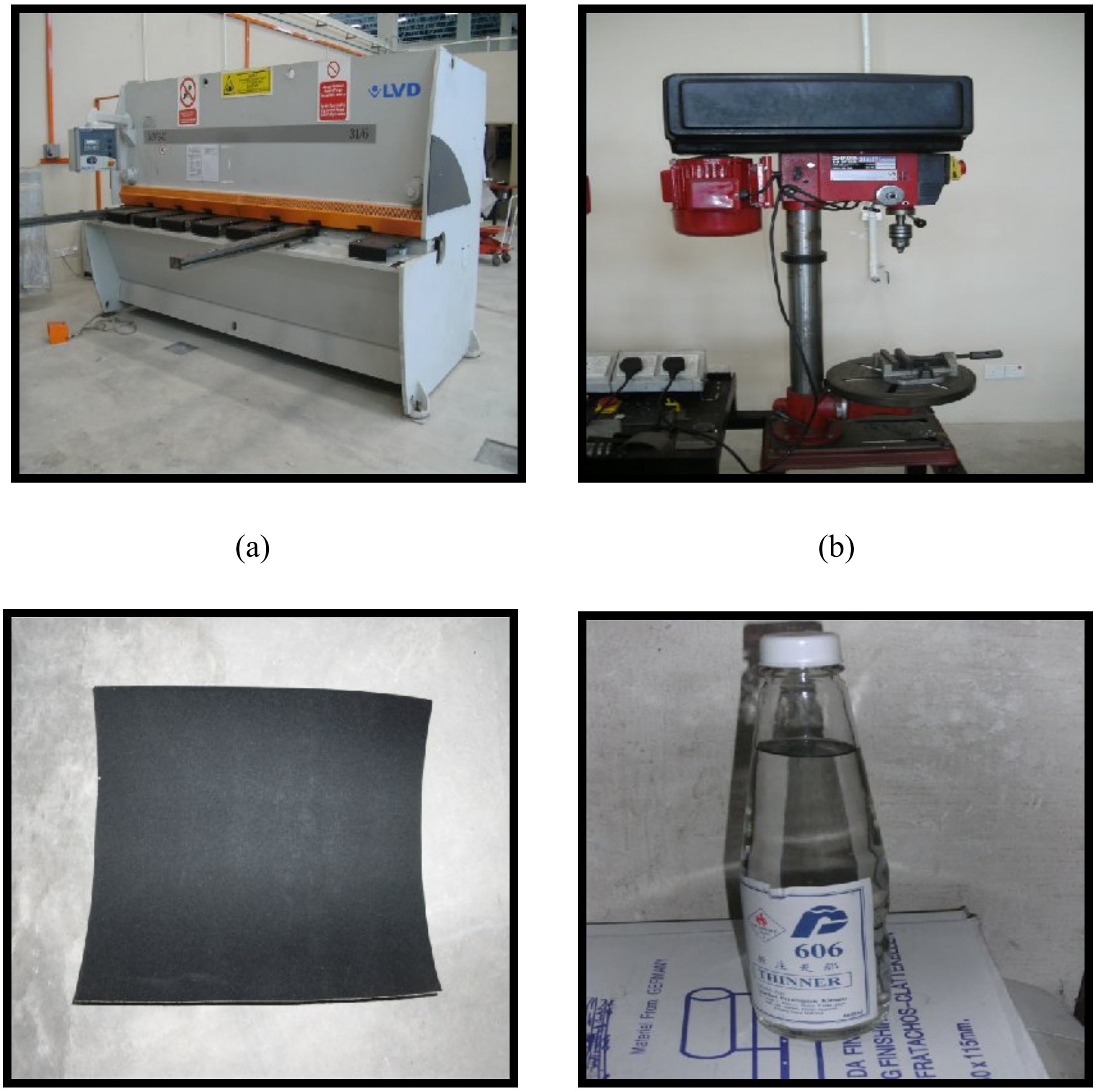
Figure 3.2: Rack design

(a) (b)

Figure 3.3: Rack in (a) Indoor Environment and (b) Outdoor environment

3.3 SAMPLE PREPARATIONS

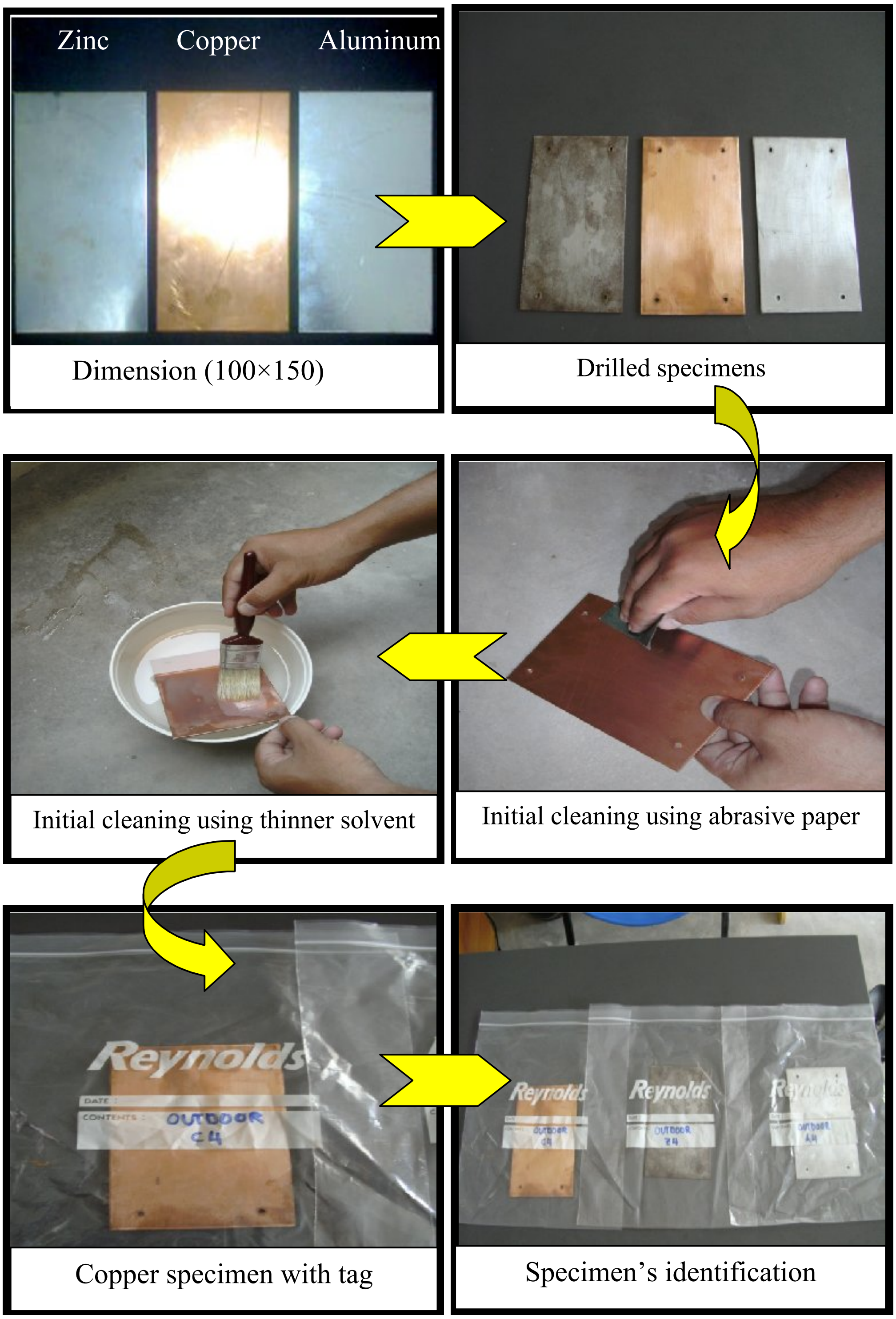
In this research, the sheet metal was used as the specimens which the dimension was (100×150) mm referred to ASTM standard G1-03. Sheet metal was cut using the hydraulic shear machine model MVS-C 31/6-40/6-31/13 as shown in Figure 3.4(a) and followed by drilled using Pillar Drill (Model No GDM120BX) as shown in Figure 3.4(b) to make four holes for each specimen. Secondly, the initial corrosion product has been removed using abrasive paper grade 700 as shown in Figure 3.4(c). After that, the oil, grease and dirt are removed with solvent and preceded by light brush. Thinner was used as degreasing agent that used in this process. Then, the specimens have been put into sealed storage bags with tag for specimen's identification.



(a) (b)

(c) (d)

Figure 3.4: Tools used (a) Hydraulic Shear Machine (b) Pillar Drill (c) Abrasive Paper (Grade 700) (d) Thinner



Dimension (100×150)

Drilled specimens

Initial cleaning using thinner solvent

Initial cleaning using abrasive paper

Copper specimen with tag

Specimen's identification

Figure 3.5: Samples Preparation Processes

3.4 WEIGHING BEFORE TESTING

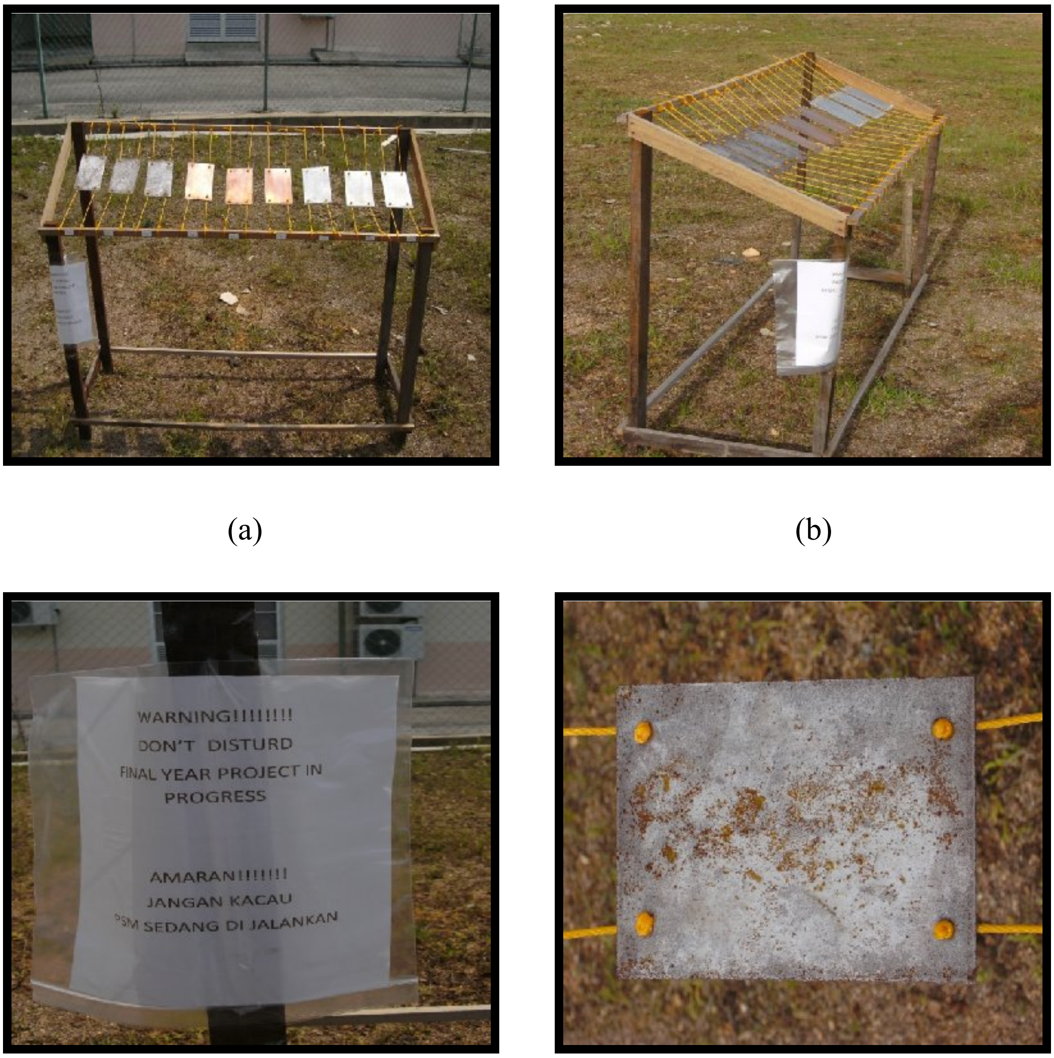
After sample preparation was finish, the clean and dry specimens weighed using weighing balance machine as shown in Figure 3.6 to take the initial weight of the specimens. In this process, specimens must be weighed to at least the nearest 0.001 g before exposure.

Figure 3.6: Weighing Balance Machine

3.5 ENVIRONMENTAL EXPOSURE

3.5.1 Outdoor Testing

For outdoor testing, the specimens are hanged on the rack that was designed earlier and expose to the outdoor atmosphere without any distortions. The specimens for this experiment are placed higher than 760mm from the ground. The base of the rack is fixed to the ground to avoid the rack from falling down. The duration or exposure time is 28 days at UMP football field.



(a)

(b)

(c)

(d)

Figure 3.7: Outdoor exposure (a) Front View (b) Side View (c) Warning (d) Zinc Surface after 28 days

3.5.2 Indoor Testing

For indoor testing, the methods to handle the experiment was adopted from the outdoor testing using same dimension of rack but in this experiment, the specimens are expose to the indoor atmosphere for 28 days. In this research, the specimens were placed in the UMP Manufacturing Laboratory.

(a) (b)

Figure 3.8: Indoor exposure (a) Front View (b) Label in each Specimen

3.6 MACROSCOPIC AND MICROSCOPIC EXAMINATION

Surface visualization has been carried out after the test. Observations on the surface microstructure of the samples to determine the types of corrosion have been observed using Scanning Electron Microscope (SEM) EVO 50 in the UMP Manufacturing Laboratory. The magnification that has been used are 250X and 500X.

Sample Type : C 4
EHT = 0.00 kV
Mag = 500 X
Signal A = TV
WD = 6.5 mm
Date :9 Sep 2009
Time :12:40:50

Figure 3.9: Scanning Electron Microscope (SEM)

The Scanning Electron Microscope (SEM) is a microscope that uses electrons rather than light to form an image. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since SEM only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in research areas today

3.7 CLEANING PROCESS

Corrosion product removal procedures can be divided into three general categories which are chemical, mechanical and electrolytic. Chemical procedures involve the immersion test specimen in the specific solution that is designed to remove the corrosion products with minimal dissolution of any base metal. Mechanical procedures are the methods that often utilized to remove heavily encrusted corrosion products which include scraping, scrubbing, brushing, ultrasonic cleaning, mechanical shocking, and impact blasting. Chemical cleaning procedures and light brushing have been used to clean the specimens in order to minimal the losses of base metal. For the chemical procedures, the solutions that used depend on the type of material. The type of solution was determined by refer to ASTM standard G1-03, Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens. The solution that was used to clean the specimens in this thesis is summarized in Table 3.1.

Figure 3.10: Cleaning Process using Hydrochloric Acid.

Table 3.1: Chemical cleaning procedure for removal of corrosion products

Material	Solution	Time	Temperature
Aluminum Alloy	Nitric acid (HNO_3, sp gr 1.42)	1 to 5 min	20 to 25^{o}C
Copper	500 mL hydrochloric acid (H_2SO_4, sp gr 1.19) Reagent Water to make 1000 mL	1 to 3 min	20 to 25^{o}C
Zinc	85 mL hydrochloric acid (HCL, sp gr 1.19) Reagent water to make 1000 mL	15 s	20 to 25^{o}C

Source: ASTM standard G1-03

3.8 RESULT DOCUMENTATION

After cleaned, the clean and dry specimens are weighed to take the final weight of the specimens. In this process, specimens were weighed to at least the nearest 0.001 g after the cleaning process. The weight lost after the exposures are used to calculate the corrosion rate using Eq (2.10).

CHAPTER 4

RESULT AND DISCUSSION

4.1 INTRODUCTION

In order to understand the variety of atmospheric corrosion effects, the following analyses have been done during the course of this degree study. To provide important basic knowledge on the corrosion types and rate of copper, aluminum and zinc induced by atmospheric corrosion in indoor and outdoor environment in the society. Five different issues are mainly discussed:

(i) Effect of environmental and material types to the surface morphology

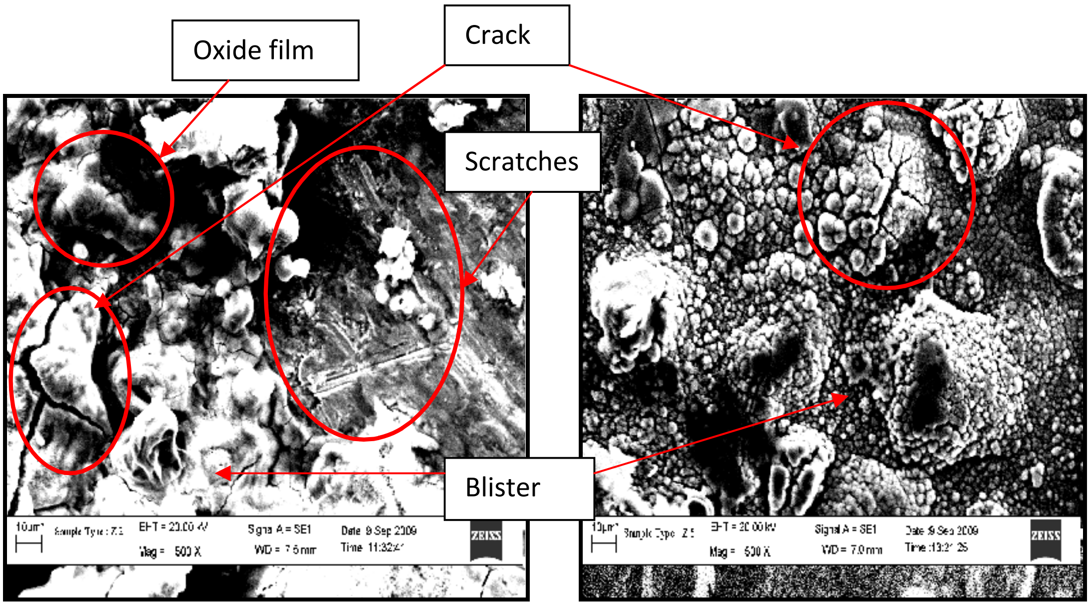
(ii) Comparison in corrosion rates between three types of material which is copper, aluminum, and zinc

(iii) Effect of environmental parameters on the corrosion rates.

(iv) Conclusion

4.2 EFFECT OF ENVIRONMENTAL AND MATERIAL TYPES TO THE SURFACE MORPHOLOGY

Atmospheric air is a mixture of dry air, water vapor and pollutant. Hence, different atmospheric environment commonly have variable types and amount of contaminant that affect the corrosion rate and types. In this study three types of material has been used which is aluminum, copper and zinc. Varies types of material has their own composition that determine their protective behavior. Figure 4.1(a) and Figure 4.1(b) show the comparison between zinc that was exposed to the indoor and outdoor atmosphere.



(a) (b)

Figure 4.1: Zinc surface microstructure exposed to the (a) indoor and (b) outdoor atmosphere

From Figure 4.1(a), the crack, scratches and blister was found on the zinc surface. Scratches that were shown in this figure were the original zinc surface which formed during the cleaning process where the initial corrosion product was removed by using the abrasive paper.

Figure 4.1(b) present the microstructure of zinc specimen that was exposed to the outdoor atmosphere, only the crack and blister are found on the specimen surface. The corrosion product covered whole specimen surface and the original zinc surface cannot be see. Blister formation is the slow corrosion process where the oxygen in the air attacks the zinc base material underneath the protective plated surface, dissipating through tiny little cracks in the surface (K. L. Money, 1987).

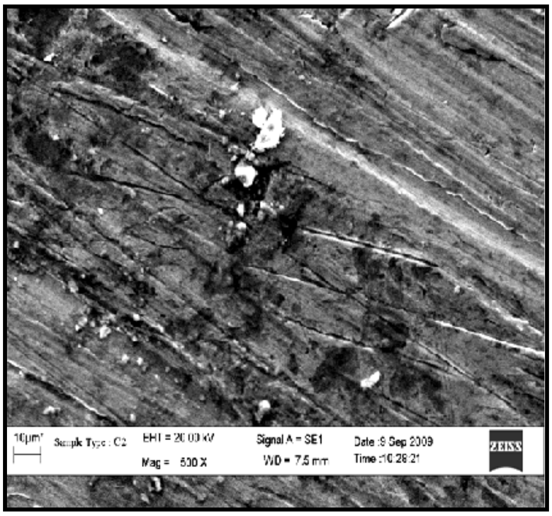
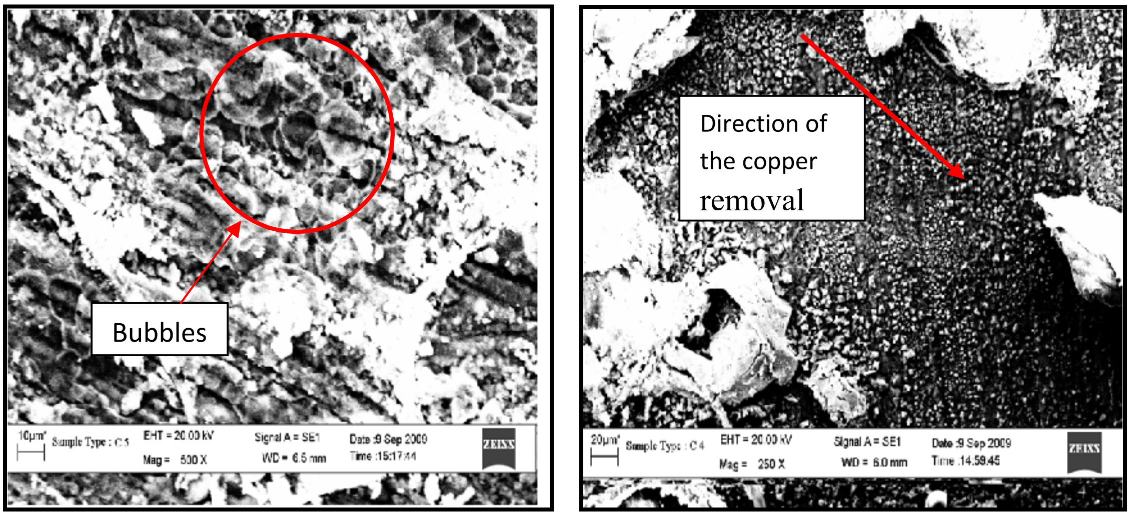


Figure 4.2: Copper surface microstructure exposed to the indoor environment

Figure 4.2 show the surface microstructure of the copper after exposed to the indoor atmosphere. For this specimen, only scratches are found on the surface. The specimen’s surface is roughened due to uniform corrosion that attacks the specimen’s surface. Uniform corrosion occurs when there are local anodic and cathodic sites on the surface of the specimen. Due to polarization effects, these locations shift from time to time and a given area on a metal will be act as both an anode and as a cathode over any extended period of time. The averaging effect of these shifting local action cells results in a rather uniform attack and general loss of material and roughening of the surface. Since the effect of the uniform corrosion unclearly seen, weight loss is the most commonly used method of measuring the corrosion rate of metals when uniform corrosion occurs.



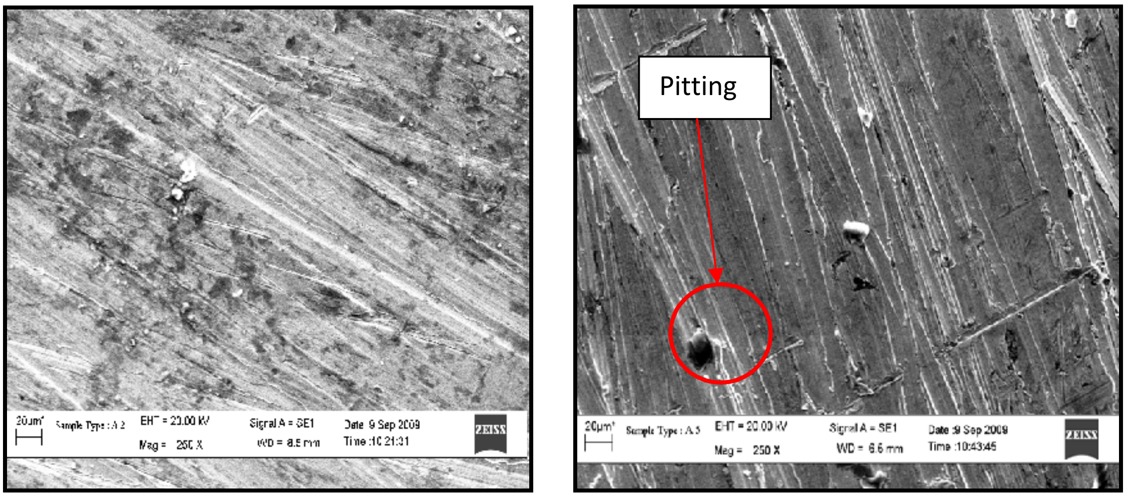
(a) (b)

Figure 4.3: Copper surface microstructure exposed to the outdoor environment.

Figure 4.3 (a) and (b) shows the microstructure of copper exposed to the outdoor atmosphere. Bubbles are found on the specimens surfaces. Air bubbles break the protective oxide on the copper surface causing great mechanical damage. Erosion corrosion also found on the copper surface. Erosion corrosion is caused by removal of the copper surface by action of the copper surface reaction and water flow due to rain. In this study, the direction of the copper removal is clearly showed in the Figure 4.3(b).

Since the specimens exposed to the atmosphere in the angle of 30^o from the horizontal, the direction of the copper removal are followed the rain water flow from the high to lower surface of the specimens.

Figure 4.4 (a) and Figure 4.4 (b) present the aluminum surface microstructure exposed to the indoor and outdoor atmosphere.



(a) (b)

Figure 4.4: Aluminum surface microstructures exposed to (a) indoor environment (b) outdoor environment.

From the Figure 4.4 (a), the scratches and a little uniform corrosion were found on the aluminum surface. Since this specimen exposed to the indoor atmosphere which is low relative humidity, temperature, and contaminant, the aluminum surface in indoor atmosphere are less affected.

From the Figure 4.4 (b), the differences were found on the aluminum surface that has been exposed to the outdoor atmosphere. A deep penetration of the aluminum surface with little uniform corrosion in the surrounding area is found form on this specimen surface. This type of corrosion is call pitting. Pitting is the most common form of corrosion found where there are incomplete chemical protective films and insulating or barrier deposits of dirt, iron oxide, organic, and other foreign substances. In this study, different types of material shows vary types of corrosion depends on the environmental atmosphere.

4.3 CORROSION RATE COMPARISON BETWEEN COPPER, ALUMINUM AND ZINC

Table 4.1: Corrosion Rate in indoor environment

Environment	Specimens		Weight Loss (g)	Corrosion rate(mpy)	Average Weight Loss (g)	Average corrosion rate(mpy)
INDOOR	ALUMINIUM	A1	0.021	0.265	0.021	0.265
		A2	0.017	0.215		
		A3	0.026	0.328		
	COPPER	C1	0.127	0.486	0.150	0.574
		C2	0.192	0.735		
		C3	0.132	0.505		
	ZINC	Z1	0.290	1.392	0.300	1.440
		Z2	0.215	1.032		
		Z3	0.394	1.891		

Table 4.1 shows the result of the corrosion rate for zinc, copper and aluminum specimens exposed to the indoor environment. These results contain the weight loss and corrosion rate for every specimen. Weight losses presented is the subtraction of initial and final specimen weight. Initial weight has been taken before the specimen exposure and the final specimen weight was recorded after the cleaning process. For each specimen, three samples were utilized to get the average weight losses and corrosion rate.

Table 4.2 shows the result of the corrosion rate for zinc, copper and aluminum specimens exposed to the outdoor environment. These results content the weight loss and corrosion rate for every specimen. For each specimen, three samples are utilized to get average weight losses and corrosion rate.

Table 4.2: Corrosion rate in outdoor environment

Environment	Specimens		Weight Loss (g)	Corrosion rate(mpy)	Average Weight Loss (g)	Average corrosion rate(mpy)
OUTDOOR	ALUMINIUM	A4	0.029	0.366	0.033	0.417
		A5	0.037	0.467		
		A6	0.033	0.417		
	COPPER	C4	0.194	0.743	0.214	0.819
		C5	0.211	0.808		
		C6	0.132	0.907		
	ZINC	Z4	0.439	2.107	0.438	2.103
		Z5	0.362	1.738		
		Z6	0.514	2.467		

Corrosion effects for aluminum, copper, and zinc were observed both in indoor and outdoor environments where the weight losses for each specimen after its exposed to the environments were recorded. From the Table 4.1 and Table 4.2, the general results of this research were recorded zinc as the material with the highest mass loses at the same time gave the highest corrosion rate followed by copper and aluminum.

The EMF series, shown in Figure 4.5, arranges metals according to their tendency to corrode. The comparison between the analysis result and this metals arrangements in term of their tendency to corrode have been done to evaluate the result of analysis.

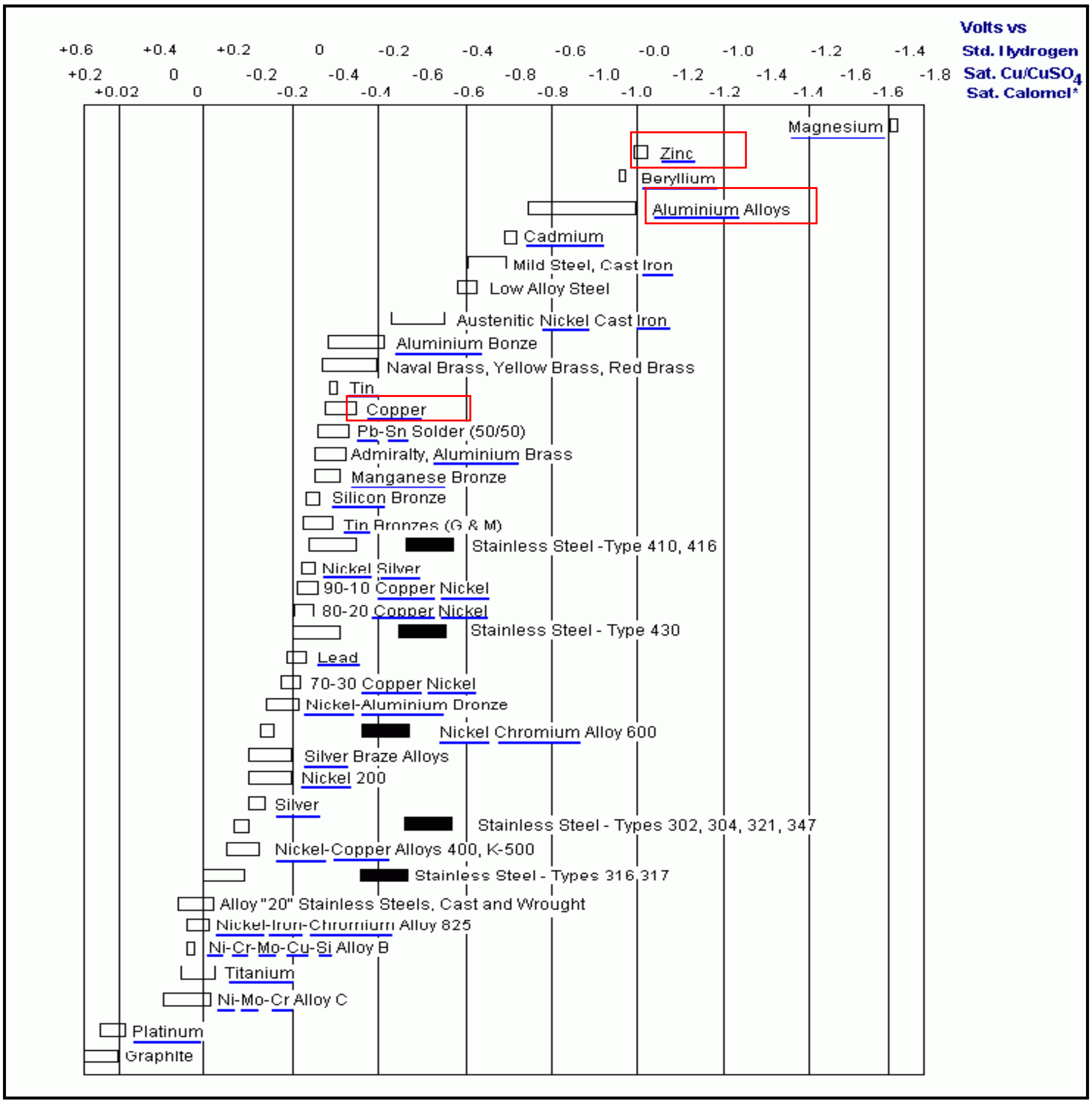


Figure 4.5: EMF series

Source: K. L. Money, (1987)

In this study, the corrosion rate of the specimens does not follow the EMF series. The average corrosion rate of copper which are 0.574mpy in indoor atmosphere and 0.819 in outdoor atmosphere recorded in this research higher than aluminum alloy which are 0.265mpy in indoor atmosphere and 0.417mpy in outdoor atmospheres. Zinc followed the EMF series since the average corrosion rate of this metal are highest which are 1.440mpy in indoor atmosphere and 2.103mpy in outdoor atmospheres. These were due to the several factors that affect the corrosion rate such passivation effect and the environmental factors. Since the metals can set up corrosion cells, this section 4.3 will discuss the corrosion rate comparison between copper, aluminum and zinc, the corrosion mechanism, and the protective manner for each material that was used as the specimens in this study.

Figure 4.6 and Figure 4.7 shows the corrosion rate comparison between these three types of materials in both indoor and outdoor atmosphere.

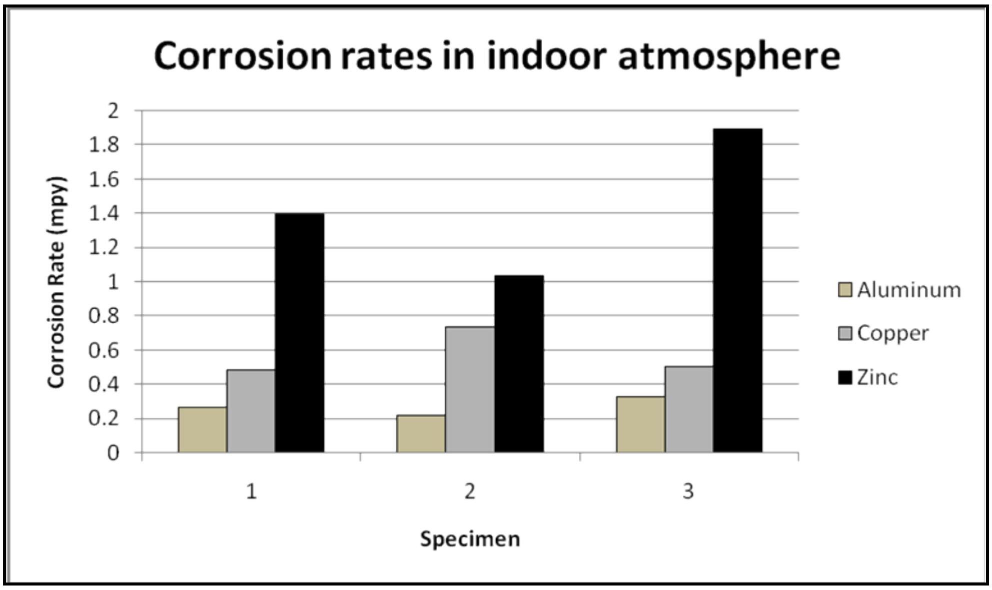


Figure 4.6: Corrosion Rate in Indoor Environment

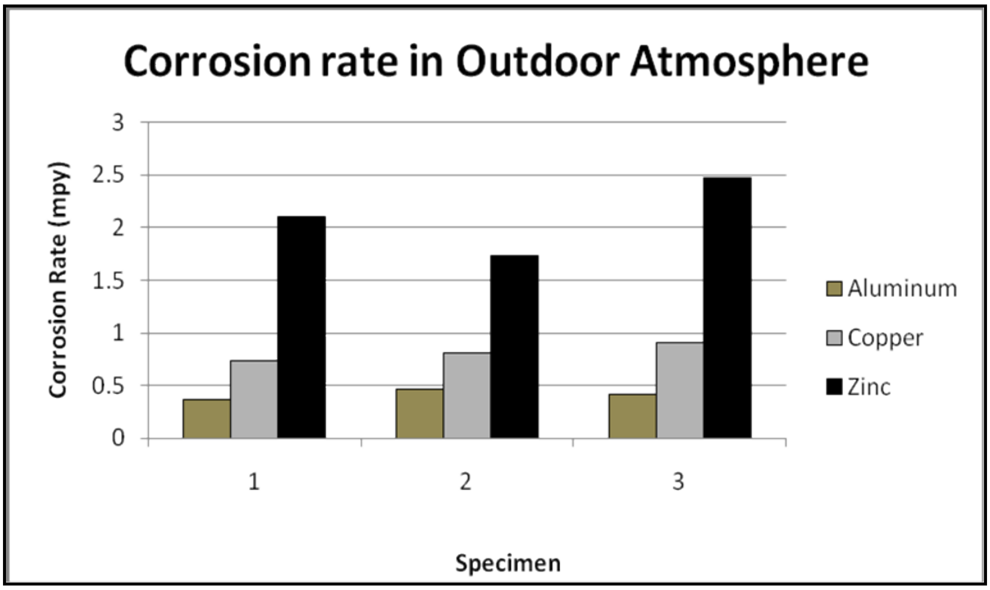


Figure 4.7: Corrosion Rate in Outdoor Environment

As presented in Figure 4.6 and Figure 4.7, zinc achieves the highest corrosion rates compared to the other materials which are 1.440mpy in indoor atmosphere and 2.103mpy in outdoor atmospheres. The highest corrosion rate of the zinc that was recorded in this research is 2.103mpy as the zinc exposed to the outdoor environment. This result also present that the protective film of the zinc was break easily if compare to aluminum and copper

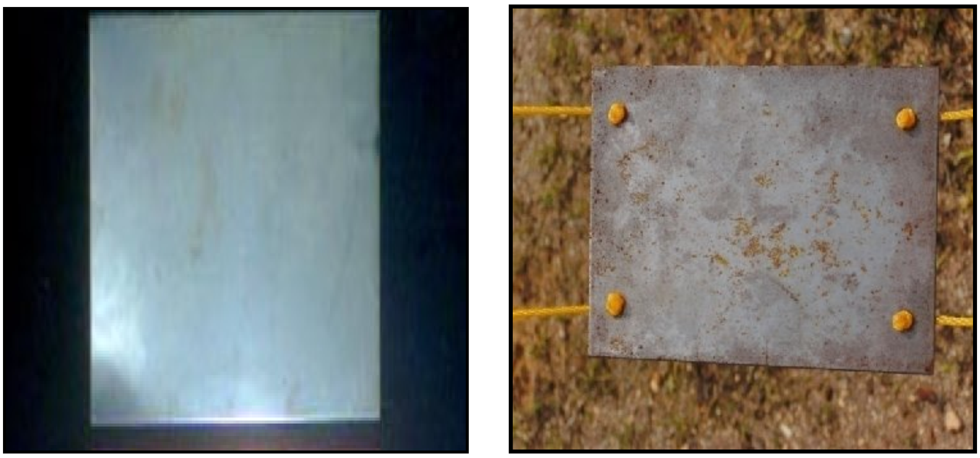
Since corrosion consists of an oxidation reaction and a reduction reaction at the surface of the corroding material. The oxidation reaction generates metal ions and electrons; the electrons are then consumed in the reduction reaction. As is the case with corrosion of metals, the corrosion of proceeds by the reaction (4.1).

$$Zn \rightarrow Zn^{2+} + 2e^{-} \tag{4.1}$$

For environments with water present including moisture in the air, the electrons are consumed by converting oxygen and water to hydroxide ions. In iron and many iron alloys, these hydroxide ions in-turn combined with iron ions to form a hydrated oxide ($Fe(OH)_2$) (Fontana,1986).

In this study, zinc surface reacts very fast, and already after less than a second, the surface will be covered with a layer of zinc oxide (ZnO) with a thickness of a few nanometers. Additionally, in a humid environment a layer of zinc hydroxide ($Zn(OH)_2$) will form as well (Fontana,1986).

After a few hours, zinc hydroxycarbonate ($Zn_5(CO_3)_2(OH)_6$) will commonly form on the surface (Fontana,1986). The red-brown mixture of zinc oxides that found on the zinc surface is rust. Depending on the environment the zinc surface is exposed to, different corrosion rate. As shown in Figure 4.8, zinc was found as the material that mostly affected by the atmospheric corrosion.

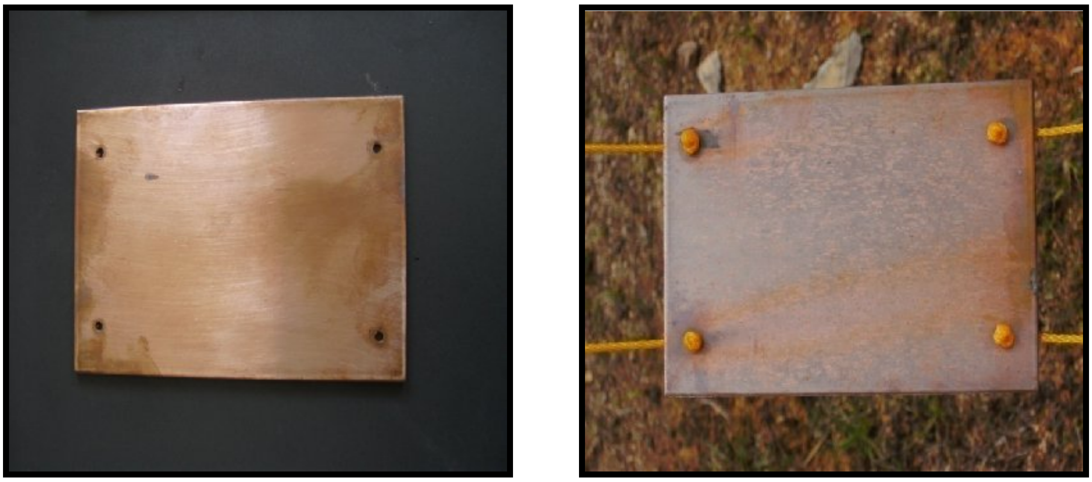


(a) (b)

Figure 4.8: (a) Initial zinc surface (b) zinc surface after 28 days exposed to the outdoor environment

Copper is on one hand, a natural component in most ecosystems and on the other, a metal that always has found many applications in old and modern societies. One of the most important metals in this respect is copper. The average corrosion rate for copper are 0.574mpy in indoor environment and 0.819mpy in outdoor. The highest corrosion rate of copper is 0.907mpy as exposed to the outdoor environment. Table 4.1, Table 4.2, Figure 4.6 and Figure 4.7 present the result for this study which is corrosion rate of copper are higher than aluminum but lower than zinc. Copper show its higher protective behavior if compared to zinc but lower if compared to the aluminum.

Usually, metals like copper form three different region on its surface which are active, passive and transpassive region. Active region having the increases in the oxidation potential that leads to increasing corrosion rates. This region corresponds to the beginning of corrosion. For the passive region, increasing the oxidation potential past the active region reduces the corrosion rate. Transpassive region show same behavior with the active region where increasing the oxidation potential past the passive region, increases corrosion rate.



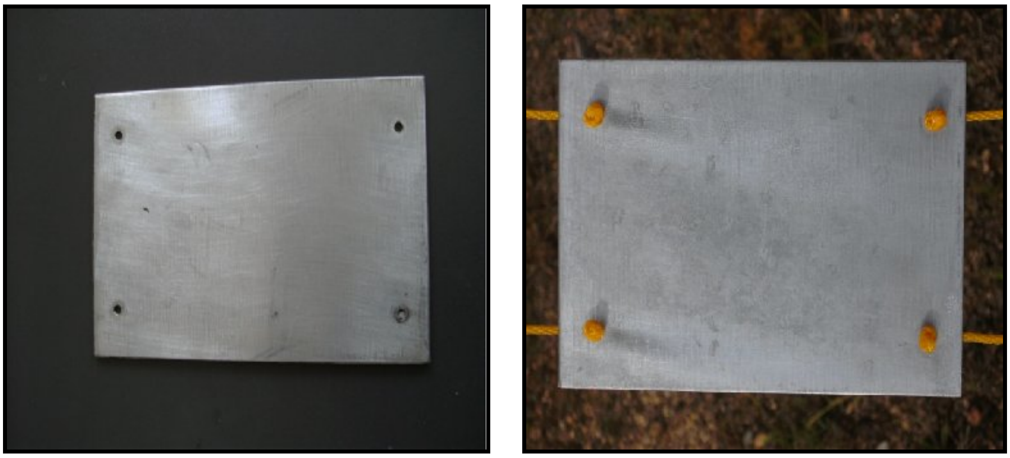
(a) (b)

Figure 4.9: (a) Initial copper surface (b) copper surface after 28 days exposed to the outdoor environment

The general sequence of atmospheric corrosion of copper is well known. Initially oxygen and water react with a fresh copper surface forming a sequential structure consisting of Cu_2O/CuO/[$Cu(OH)_2$ or $CuO.xH_2O$], the main component being Cu_2O, cuprite .This is later followed by reaction with pollutants present as gases (e.g., SO_2, NO_2, O_3, Cl_2, HCl, and H_2S) as ionic constituents of aerosol particles or as ions in rainfall (ASM International, 1987). Eventually a patina of several different compounds forms on top of the initially formed cuprite layer. For atmospheric corrosion to occur, the presence of water on the metal surface is also essential. The amount of water absorbed is dependent on relative humidity and on surface deposits. Figure 4.9 shows the surface a change of the copper metal after 28 days undergoes the exposure process.

Aluminum is one of the most abundant elements in nature. Its low density, high elastic modulus, thermal and electrical conductivity, its corrosion resistance, and its capacity to form alloys with many elements makes it one of the most useful materials of construction.

Compared to other metals, aluminum corrodes rather slowly under atmospheric conditions. The corrosion rate of the aluminum is the lowest which is 0.215mpy in the indoor environments. Aluminum average corrosion rate are 0.265mpy in indoor environment and 0.417mpy in outdoor. The protective manner of the aluminum was caused by the formation of an insulating amorphous oxide film of low solubility in air and aqueous solutions over the pH range from 4 to 8.6.



(a) (b)

Figure 4.10: (a) Initial aluminum surface (b) aluminum surface after 28 days exposed to the outdoor environment

Aluminum and its alloys undergo black to grey staining when exposed to humid atmosphere due to condensation of moisture or rain on the surfaces. The degree of staining does not depend on the composition of water and the staining rate is mainly controlled by the rate of diffusion of oxygen into the thin film of water condensed (K. L. Money, 1987).Of all the aluminum alloys are highly exposed to water staining due to formation of magnesium oxide film. Figure 4.10 shows the changes of the aluminum surface undergoes 28 days exposure process.

Besides a strong humidity dependence it is generally agreed that deposition of SO_2 and chlorides and the pH in rain are major factors that determine the corrosion rate of aluminum. In the presence of SO_2, oxidizing agents such as O_3 and H_2O_2 may also play a role in the atmospheric corrosion of aluminum. Common corrosion products commonly found under these conditions are basic aluminum sulfates and amorphous aluminum sulfate hydrate (Leygraf, 2000).

Indoors, sulfate is the most abundant anion commonly found on aluminum surfaces. The presence of SO_4^{2-} on these surfaces may be due to SO_2 induced corrosion or sulfates associated with particle deposition. The addition of inorganic ionic substances is primarily due to particle deposition. Corrosion rates increased with increasing humidity, temperature and period of exposure.

4.4 EFFECT OF ENVIRONMENTAL PARAMETERS ON THE CORROSION RATES

Figure 4.11 show the average corrosion rate for aluminum, copper and zinc in indoor and outdoor environments.

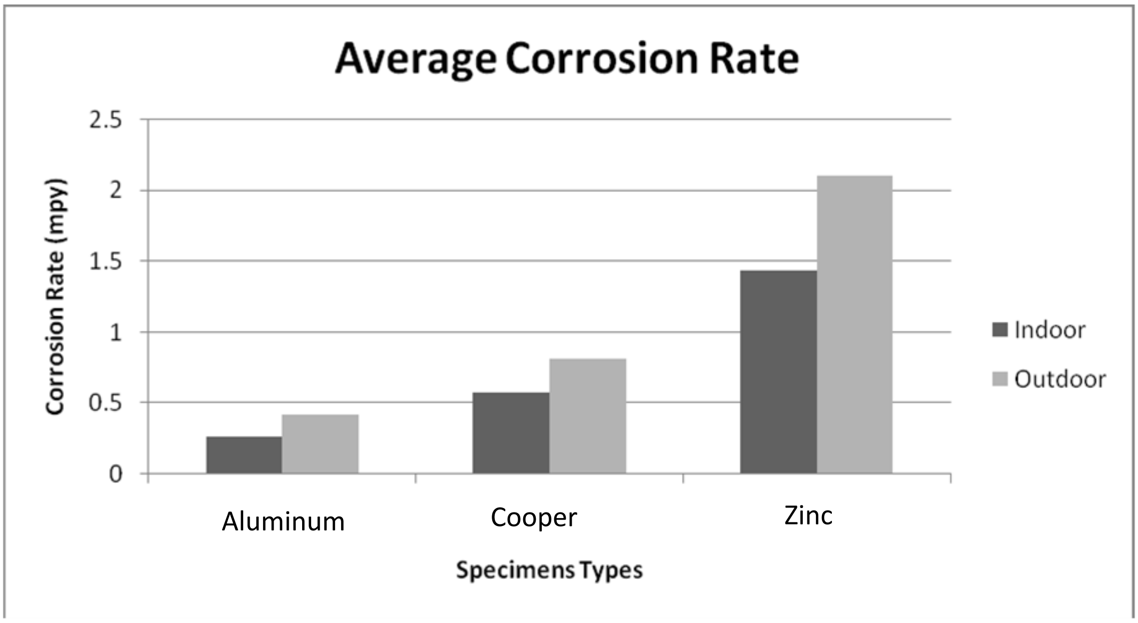


Figure 4.11: Average corrosion rate in indoor and outdoor environments

Here, the same variation have been shown where the corrosion rate of all three types of the specimens that was exposed to the outdoor environment are higher than the same types of material that was exposed to the indoor environment.

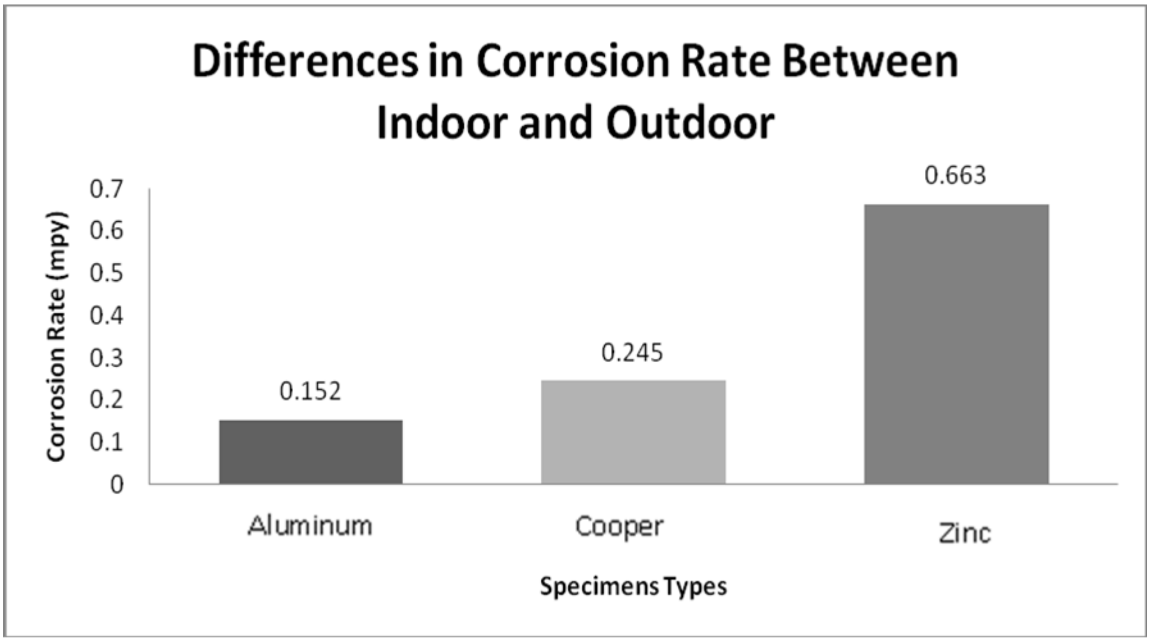
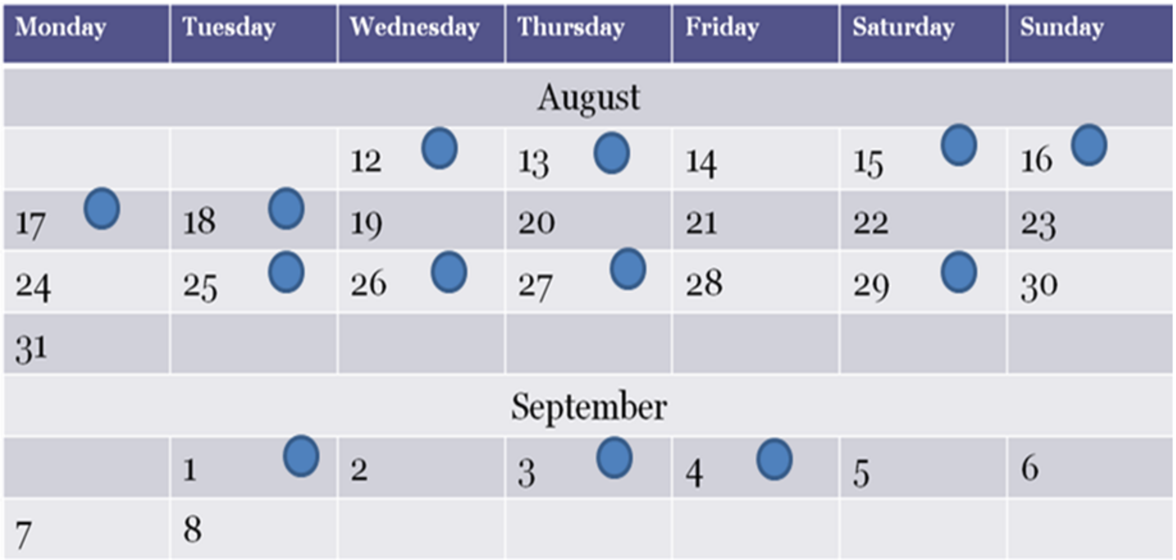


Figure 4.12: Average corrosion rate differences between indoor and outdoor

The corrosion rate differences between the specimens that exposed to the indoor and outdoor can be viewed in the Figure 4.12. Differences for aluminum are 0.152 mpy followed by cooper (0.245mpy) and zinc (0.663mpy). Although the corrosion rate differences vary depends on the material types, same pattern of corrosion acceleration can be seen where the outdoor atmosphere gave higher damage than the indoor atmosphere. There are several parameters that cause the variation of the corrosion rates.

The parameter that mostly affected the corrosion rate at outdoor atmosphere is the relative humidity and times of wetness that is strongly depend to the critical relative humidity. Figure 4.3 show the rain distribution during the exposure period. From the 28 days of the exposure time (August 12, 2009-September 8, 2009), thirteen days are rainy.

Table 4.3: Rain distribution



Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday
August						
		12 ●	13 ●	14	15 ●	16 ●
17 ●	18 ●	19	20	21	22	23
24	25 ●	26 ●	27 ●	28	29 ●	30
31						
September						
	1 ●	2	3 ●	4 ●	5	6
7	8					

Metals exposed in outdoor environment will absorb water from the rain forming a thin water layer on the surfaces. The amount of water adsorbed by the metal surface is very important for the atmospheric corrosion process and most metals rapidly adsorb the first monolayer of water by forming a surface hydroxyl layer. Subsequent water adsorption is similar for many metals and oxides, and the water is absorbed in the molecular form. At 20% RH there will be about one monolayer of water and at 75% RH there will be about five monolayers adsorbed on the metal surface (Callaghan, 1993). The relative humidity (RH) in the atmosphere plays an important role and affects directly the amount of water on the metal surface. The atmospheric corrosion rate of metals increases with the relative humidity during the environmental atmosphere exposure. Figure 4.11 and Figure 4.12 clearly show the effect of this parameter since all the specimens that exposed to the outdoor atmosphere with higher relative humidity due to rain give higher corrosion rate if compared with the specimens that exposed to the indoor atmosphere.

Atmospheric air is a mixture of dry air and water vapor. The air humidity is characterized by the indices relative humidity, absolute humidity, moisture content and specific air humidity. The primary value of the critical relative humidity denotes that humidity below which no corrosion of the metal in question takes place (Leygraf, 2000). For the specimens that placed in the indoor environment, it is covered from the rain. Hence, the relative humidity in the indoor environment is lower if compared to the outdoor atmosphere. The amount of water on the specimen's surface has a direct effect on the corrosion rate. Corrosion rate in indoor atmosphere are lower than in outdoor atmosphere since the relative humidity that accelerate the corrosion do not play an important role in the indoor atmosphere.

Time of wetness is define the as the period of time during which the relative humidity exceeds 80% at a temperature above 0^oC (Leygraf, 2000). Since it's strongly dependent to the relative humidity, the time of wetness in the outdoor atmosphere is higher than indoor atmosphere. Corrosion rate increases quickly with the increasing the time of wetness. 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, adsorbed molecular water layers, and direct moisture precipitation (dew and rain). Rain provide electrolyte for corrosion reactions by washing away harmful corrosive surface species.

Other environment factors that affect the corrosion rate in the outdoor are the dew formation, dust and temperature. Dew is an important cause of the atmospheric corrosion. Dew forms when the metal surface falls below the dew point of the atmosphere. Dew occurred outdoors during the night when the temperature of the metal is lowered as a result of radiant heat transfer between the metal and the sky. Dew also commonly forms during the early morning hours when the air temperature rises faster than the temperature of the metal. The high corrosivity of dew is due to the higher concentration of contaminants in dew than in the rain water, which leads to lower the pH values at the same times accelerate the corrosion rate. As can be viewed in Figure 4.11, all types of the specimens that exposed to the outdoor show the same result which are the corrosion rate outdoor atmosphere gave higher value than the indoor.

Normally, the primary contaminant of air on a weight basis is dust. Dust promotes the corrosion by forming galvanic at the same time form an electrolyte on the surface when it is in contact with metallic surfaces and combined with moisture. An increase in temperature accelerates corrosive attack by increasing the rate of electrochemical and chemical reactions and diffusion process. The highest temperatures recorded during the exposure period are 31°C for indoor environment and 33°C for outdoor environment.

4.5 CONCLUSION

Table 4.4 summarizes the overall results of the study including corrosion rates for the zinc, copper and aluminum that exposed to the indoor and outdoor. This also stated the surface morphology that was found on the specimen surface.

Table 4.4: Summarization of Result

Material / Environment	Zinc	Copper	Aluminum
Indoor	❖ Average corrosion rate = 1.440mpy ❖ Blister and crack covered whole specimens surface	❖ Average corrosion rate = 0.574mpy ❖ General corrosion found on the surface	❖ Average corrosion rate = 0.265mpy ❖ General corrosion found on the surface
Outdoor	❖ Average corrosion rate = 2.103mpy ❖ Scratches still exist on the surface	❖ Average corrosion rate = 0.819mpy ❖ Bubbles and erosion corrosion found	❖ Average corrosion rate = 0.417mpy ❖ Pitting corrosion was observed

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 INTRODUCTION

This chapter will conclude the research and briefly enlightened about the recommendation that can be applied to the research. The conclusion were done according to the appropriate result obtain from previous. From the result, the objective stated were compared and panelized whether it is achieved or not. If the current situation suggest that the objective is fulfilled the recommendation were then optional especially for upcoming project. If circumstances were not, then the recommendation to improve the methodology and troubleshot the situation will be stated within recommendation section. The project was in logical and scientifically manner believed to achieve its objectives. Hence, the recommendations in order to extend and critically improve the product function were stated for future project.

5.2 CONCLUSION

This paper provides information on a study of atmospheric corrosion in indoor and outdoor environment. Varies types of material and environment gave the different results of corrosion rate and types. Generally, aluminum, copper and zinc are attacked by the uniform corrosion both in indoor and outdoor environment. Specifically, zinc surface was attacked by the blister corrosion and little cracks were propagated on the zinc surface. In this study, zinc is the material that mostly affected by the atmospheric corrosion since the corrosion rate of zinc higher than copper and aluminum. Corrosion rate of zinc is higher when exposed to the outdoor environment due to the several factor such as relative humidity, times of wetness and temperature.

Different types of corrosion were found on the copper surface that exposed to the outdoor environment. Air bubbles and the removed copper surface were observed on this specimen. This type of corrosion is called erosion corrosion which happens due to the water flow. Same with aluminum, copper record higher corrosion rate when exposed to the outdoor environment. Here, the corrosion rates of copper are higher than aluminum but lower than zinc in both environments.

Aluminum shows as the material that have higher protective behavior since in this study the corrosion rate of aluminum is the lowest in indoor and outdoor environment compared to copper and zinc. Aluminum surface that exposed to the both environment was attacked by the uniform corrosion but pitting corrosion are found on the specimens that exposed to the outdoor environment.

Outdoor and indoor environment have its own factors that effecting corrosion. Outdoor atmosphere gave more damage to the aluminum, copper and zinc due to the humidity, dew, and temperature. Indoor atmosphere shows the low effect in corrosion acceleration since the specimens are covered from the rain and dew.

5.3 RECOMMENDATION

Atmospheric corrosion is the complex process which varies with the parameters that affecting the corrosion. Hence, in order to improve the researches some addition must be include.

(i) Increase the exposure period
(ii) Analyses the corrosion rate variation depend on exposure time
(iii) Increase the number of specimens to get more accurate average result.
(iv) Analyses the atmospheric corrosion for another types of material such as copper alloy and low alloy steel.

REFERENCES

ASTM Standards, G 1 – 03, Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens.

B. Dobbs and G. Slenski, Mater. Perform.,(1984)

Brown P.W and Masters L.W, Atmospheric Corrosion, Wiley, New York (1982)

B. G. Callaghan, "Atmospheric Corrosion Testing in Southern Africa," Scientia Publishers, CSIR, South Africa, (1993).

B. I. Rickett and J. H. Payer, J. Electrochem. Soc., (1995)

C. Leygraf and T. E. Graedel, Atmospheric Corrosion, The electrochemical society, INC. Pennington, New Jersey,(2000)

Fontana, M.G., Corrosion Engineering, 3rd Edition, McGraw-Hill Book

G. A. King and Duncan J. R., Corros. Mater., (1998).

H. H. Uhlig and R.W. Revie, "Corrosion and Corrosion Control," 3rd ed., Wiley, New York, (1984)

J. H. Payer, W. K. Boyd, D. G. Deppold, and W. H. Fisher, Materials Performance, Vol. 19, (1980)

K. L. Money, "Corrosion Testing in the Atmosphere," Metals Handbook, 9th ed., Vol. 13, ASM International, Metals Park, OH, (1987)

K. Barton, "Protection against Atmospheric Corrosion," Wiley, New York, (1976)

Karlsson A, Moller P. J and Vagn J, Corros. Sciences, (1990)

K. Barton, Schutz gegen atmosphärische Korrosion, Verlag Chemie, Weinheim (1973)

K. L. Money, "Corrosion Testing in the Atmosphere," Metals Handbook, 9th ed.

Leygraf, C., Graedel, T.E. Atmospheric Corrosion; John Wiley & Sons, Inc.: New York,(2000).

L. L. Shreir, R. A. Jarman, and G. T. Burstein (Eds.), "Corrosion, Vol. 1, Metal/Environment Reactions,"Butterworth-Heinemann, Oxford, UK, (1994).

Materials Science and Engineering The University of Edinburgh , Division of Engineering Session (2001-2002).

Metals Handbook Ninth Edition, Vol. 13, ASM International, (1987) Natesan M, PhD Thesis, Anna University, Chennai, India (1995).

Naixin X, Zhao L, Ding C, Zhang C, Li R and Zhong Q, Corros. Sci., (2002).

Norm ISO N. 9223, (1989).

P. B. P. Phipps and D. W. Rice, The role of water in atmospheric corrosion, Corrosion Chemistry (G. R. Brubaber and P. B. P. Phipps Eds.), American Chemical Society Series 89, (1979)

R. Lindström, J. E. Svensson and L. G. Johansson, J. Electrochem. Soc., 147(5), 1751(2000)

S. Lee and R. W. Staehle, Corrosion, (1997)

Speller F.N., Corrosion (Causes and Prevention) McGraw-Hill Book Company Inc., New York, (1951).

Trimgham T.C.E, Causes and Prevention of Corrosion in AIR Craft, SIR ISAAC, Pitman & Sons, Ltd., (1958).

U. R. Evans, C. A. J. Taylor, Corrosion Science 12, (1972).

Vernon, W. H. J. Transactions of the Faraday Society (1923, 1927).

V. Kucera and E. Mattson, "Atmospheric Corrosion," in Corrosion Mechanisms, F. Mansfeld (Ed.), Marcel Dekker, New York, (1987)

W. Ke, Chinese Corrosion Survey Report, First ed, Chemical Industry Press, Beijing, ISBN 7-5025-4792-4/TQx1816, (2003)

Z. Y. Chen, D. Persson and C. Leygraf, In situ Studies of the Effect of SO2 on the Initial NaCl-induced Atmospheric Corrosion of Copper, J. Electrochem. Soc., accept for publication (1993)

APPENDIX A

Table 6.1: Result for Indoor Exposure

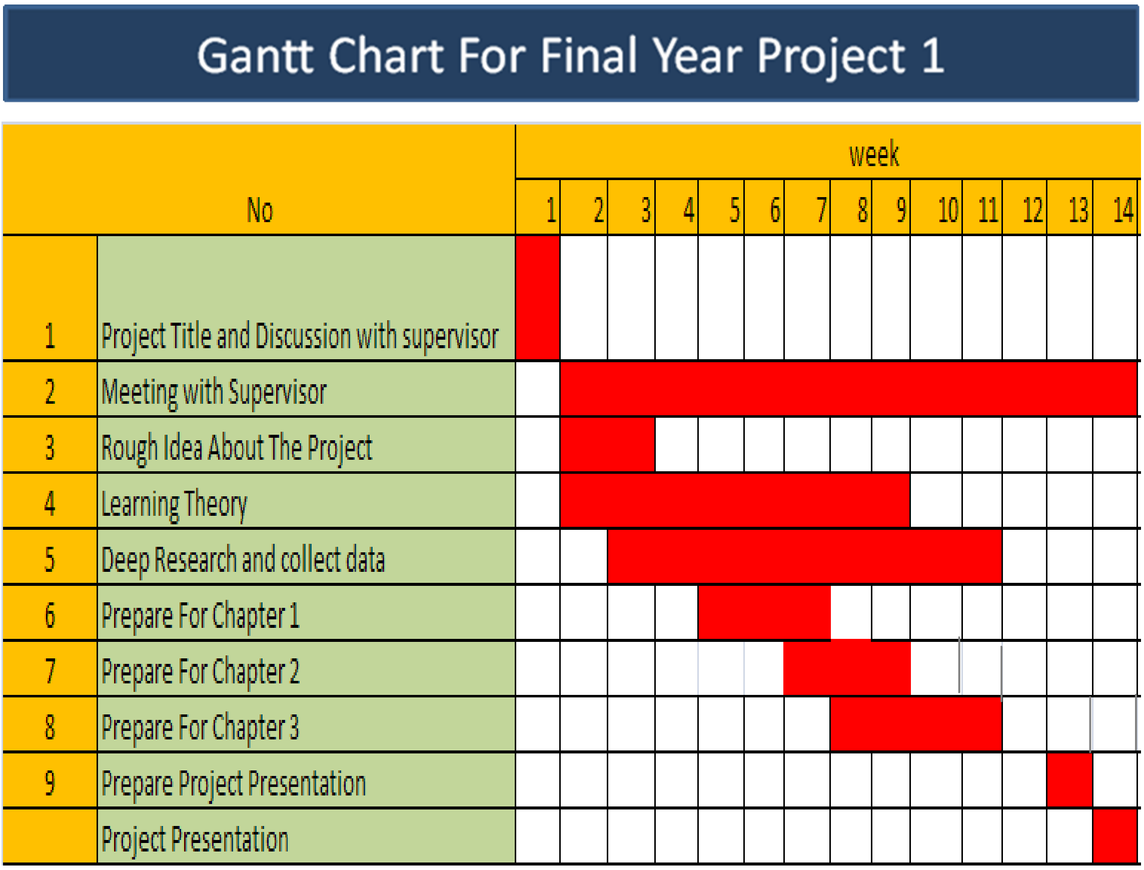
INDOOR									**Environment**
ZINC			COPPER			ALUMINIUM			**Specimens**
Z3	Z2	Z1	C3	C2	C1	A3	A2	A1	
127.515	128.258	127.837	268.251	268.238	267.724	115.136	114.533	113.198	**weight Before Exposure (g)**
127.121	128.043	127.547	268.119	268.046	267.597	115.110	114.516	113.177	**Weight After Cleaning (g)**
0.394	0.215	0.290	0.132	0.192	0.127	0.026	0.017	0.021	**Weight Loss (g)**
1.891	1.032	1.392	0.505	0.735	0.486	0.328	0.215	0.265	**Corrosion rate(mpy)**
0.300			0.150			0.021			**Average Weight Loss (g)**
1.440			0.574			0.265			**Average corrosion rate(mpy)**

APPENDIX B

Table 6.2: Result for Outdoor Exposure

OUTDOOR									**Environment**
ZINC			COPPER			ALUMINIUM			**Specimens**
Z6	Z5	Z4	C6	C5	C4	A6	A5	A4	
128.138	124.219	126.544	267.871	267.299	266.926	115.152	114.337	114.814	**weight Before Exposure (g)**
127.624	123.857	126.105	267.644	267.088	266.732	115.119	114.300	114.785	**Weight After Cleaning (g)**
0.514	0.362	0.439	0.237	0.211	0.194	0.033	0.037	0.029	**Weight Loss (g)**
2.467	1.738	2.107	0.907	0.808	0.743	0.417	0.467	0.366	**Corrosion rate(mpy)**
0.438			0.214			0.033			**Average Weight Loss (g)**
2.103			0.819			0.417			**Average corrosion rate(mpy)**

APPENDIX C

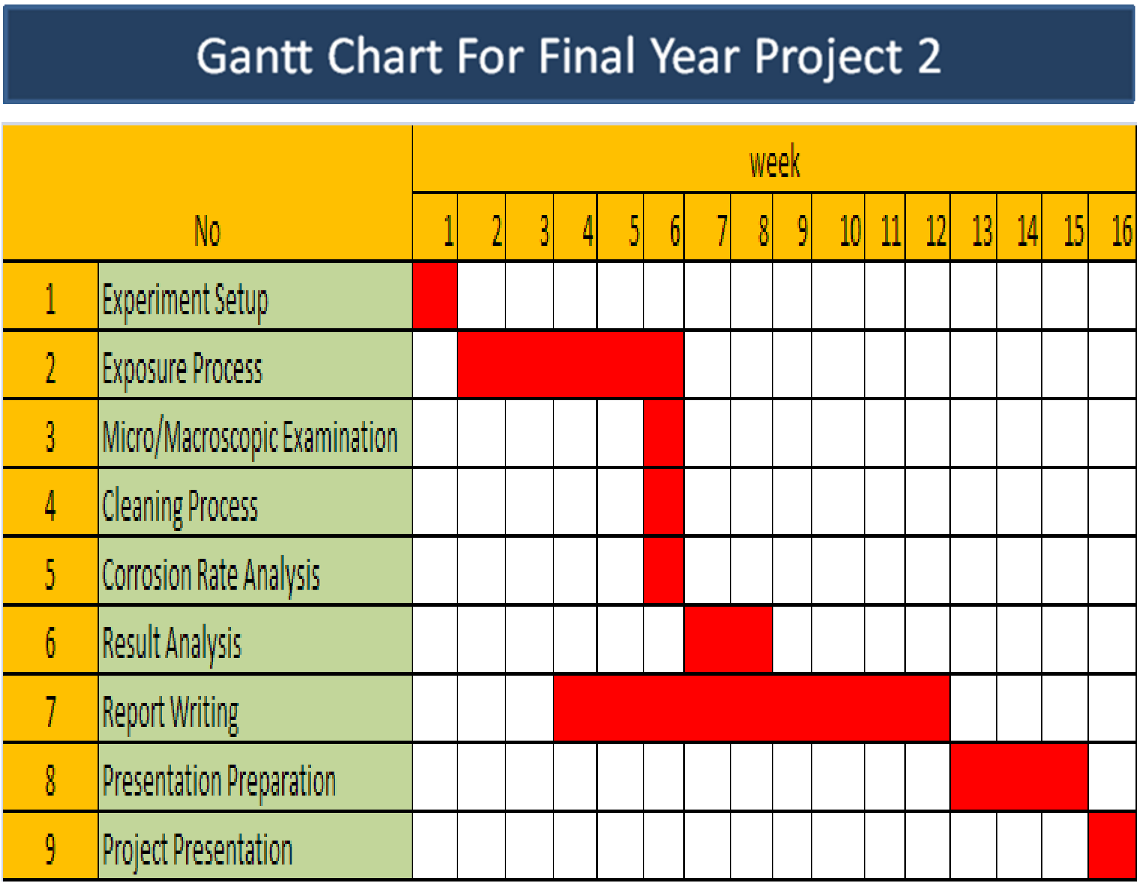


Gantt Chart For Final Year Project 1

No		week													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project Title and Discussion with supervisor	🟥													
2	Meeting with Supervisor		🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥
3	Rough Idea About The Project		🟥	🟥											
4	Learning Theory		🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥					
5	Deep Research and collect data			🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥			
6	Prepare For Chapter 1					🟥	🟥	🟥							
7	Prepare For Chapter 2							🟥	🟥	🟥					
8	Prepare For Chapter 3								🟥	🟥	🟥	🟥			
9	Prepare Project Presentation													🟥	
	Project Presentation														🟥

Figure 6.1: Gantt chart for Final Year Project 1

APPENDIX D



Gantt Chart For Final Year Project 2

No		week															
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	Experiment Setup	🟥															
2	Exposure Process		🟥	🟥	🟥	🟥	🟥										
3	Micro/Macroscopic Examination						🟥										
4	Cleaning Process						🟥										
5	Corrosion Rate Analysis						🟥										
6	Result Analysis							🟥	🟥								
7	Report Writing				🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥				
8	Presentation Preparation													🟥	🟥	🟥	
9	Project Presentation																🟥

Figure 6.1: Gantt chart for Final Year Project 2