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Assoc Prof Dr. Narayanan Sambu Potty

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UNIVERSITI TEKNOLOGI PETRONAS

MARINE CORROSION OF MILD STEEL AT LUMUT, PERAK

by

ONG SHIOU TING

The undersigned certify that they have read, and recommend to the Postgraduate Studies Programme for acceptance this thesis for the fulfilment of the requirements for the degree stated.

Signature:
Main Supervisor: Assoc. Prof. Dr. Narayanan Sambu Potty

Signature:
Co-Supervisor: Assoc. Prof. Ir. Dr. Mohd Shahir Liew

Assoc. Prof. Ir. Dr Mohd Shahir Liew
Head
Civil Engineering Department
Universiti Teknologi PETRONAS
Bandar Seri Iskandar, 31750 Tronoh
Perak Darul Ridzuan, MALAYSIA

Signature:
Head of Department: Assoc. Prof. Ir. Dr. Mohd Shahir Liew

Date: 18 Sept 2012

MARINE CORROSION OF MILD STEEL AT LUMUT, PERAK

by

ONG SHIOU TING

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DECLARATION OF THESIS

Title of thesis: MARINE CORROSION OF MILD STEEL AT LUMUT, PERAK

I ONG SHIOU TING

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Signature of Author

Permanent residence: 7 Jln Pinggiran
Saujana 2/2 ; Tmn Pinggiran Saujana
43000 Kajang, Selangor Darul Ehsan

Date : 17th September 2012 ·

Witnessed by

Signature of Supervisor

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ABSTRACT

The corrosion rate in marine environments affects economic interest since the loss of steel in marine structures has impact on structural safety and performance. With emphasis to maintain existing structures in service, there is increasing interest in predicting corrosion rate at a given location for a given period of exposure. Various corrosion allowances are prescribed for structural members by different standards. There are no studies to determine the appropriate corrosion allowance for offshore steel structures in Malaysia. A field experiment is conducted for estimating the corrosion loss of mild steel under atmospheric, tidal zone and immersion zone corrosion conditions for 2 years in seawater at Boustead Shipyard, Lumut. Parameters such as pH, temperature, salinity, humidity, seawater quality and fouling effect are considered in this experiment to better understand the effects of these parameters jointly on corrosion behaviour. The research objectives are to determine the nature and rate of corrosion and the effect of immersion depth and microalgae on the corrosion rate. Two sets of corrosion coupons of Type 3 mild steel were immersed in seawater. The corrosion rate of the coupon was estimated based on the material weight loss with time. The corrosion rate is controlled by oxidation in short term and bacterial activity in long term. Corrosion rate in the splash zone is observed to be the maximum. The results are also compared with code prescriptions and discussed. A time based corrosion model is developed for sample 1 using EXCEL. The model for splash zone is given by $y = 1.0455t^{1.4165}$ and for immersion zone is $y = 5.8096t^{0.7971}$. Parametric regression model is also developed using SPSS with the parameter pH, temperature, salinity, fouling load and time elapsed. This agreed closely with results from model designed using EXCEL.

ABSTRAK

Pengaratan di kawasan marin memberi kesan terhadap ekonomi negara disebabkan pengaratan struktur-struktur marin memberi kesan terhadap keselamatan dan prestasi strukturnya. Dengan penekanan untuk mengekalkan struktur supaya berfungsi dengan baik, terdapat banyak kajian untuk meramal kadar pengaratan pada satu-satu tempat dalam satu tempoh masa yang tertentu. Terdapat pelbagai kadar pengaratan yang dibenarkan dalam piawaian-piawaian berbeza. Walau bagaimanapun, tiada kajian untuk menentukan kadar pengaratan yang sesuai untuk struktur keluli di laut Malaysia. Satu eksperimen dijalankan untuk menganggar kadar pengaratan keluli pada keadaan atmosfera, zon pasang surut dan rendaman berterusan selama 2 tahun di dalam air laut di Boustead Shipyard, Lumut. Parameter seperti suhu pH, kemasinan, kelembapan, kualiti air laut dan kesan plankton dan benthos dipertimbangkan dalam eksperimen ini supaya dapat memahami dengan lebih mendalam tentang kesan parameter ini terhadap sistem pengaratan. Objektif kajian ini adalah untuk menentukan sifat semulajadi dan kadar pengaratan serta kesan kedalaman rendaman yang berbeza dan mikro alga (plankton dan benthos) terhadap kesan pengaratan. Dua set kupon keluli Jenis 3 direndam di dalam air laut. Kadar pengaratan kupon keluli ditentukan dengan mengira kehilangan berat dalam satu tempoh masa. Kadar pengaratan dikawal oleh pengoksidaan dalam jangka pendek dan aktiviti bakteria dalam jangka masa panjang. Kadar pengaratan di zon pasang surut adalah maxima. Kadar pengaratan juga telah dibandingkan dengan preskripsi kod yang sedia ada dan dibincangkan. Satu pengaratan model yang berasaskan masa dibentuk untuk sampel 1 dengan menggunakan EXCEL. Model untuk zon pasang surut ialah $y=1.0455t^{1.4165}$ dan model untuk zon rendam ialah $y= 5.8096t^{0.7971}$. Di samping itu, kadar pengaratan model regresi juga dibentuk melalui SPSS dan parameter seperti pH parameter kemasinan, suhu, berat mikro alga dan masa diambil kira. Ini bersetuju rapat dengan keputusan daripada model yang direka bentuk menggunakan EXCEL.

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LIST OF ABBREVIATIONS

Al	Aluminium
ANOVA	Analysis of Variance
ASTM	American Society for Testing and Materials
BS	British Standard
CPS	Coating Protective Systems
CR	Corrosion Rate
Cu	Copper
D	pipeline diameter (mm)
DF	Durability Factor
df	degree of freedom
DNV	Det Norske Veritas
E	a vector of environment and material parameters.
EC	Electrical Conductivity
FAC	Flow Accelerated Corrosion
FL	Fouling Load
HT	High Tide
K	number of predictors in the model
LPR	Linear Polarization Resistance
LT	Low Tide
MIC	Microbiologically Influenced Corrosion
MLR	Multiple Linear Regression
Mn	Manganese
MS	Mean Square term
MSE	Residual Mean Square
MST	Total Mean Square
MT	Median
Ni	Nickel
MWQCS	Marine Water Quality Criteria and Standards.

P	Phosphorus
PAH	Polycyclic Aromatic Hydrocarbon
PTS	Petronas Technical Standard
RH	Relative Humidity
S	Sulphur
SEE	Standard error of the estimate
SPSS	Statistical Package of Social Science
SRB	Sulphate Reducing Bacteria
SS	Sum of square term
SSE	Sum of Squares, error
SST	Sum of Squares, total
SSR	Sum of square, regression
T	pipeline radius (mm)
TDS	Total Dissolved Salts
U	liquid flow velocity (m/s)
ZRA	Zero Resistance Ammetry

LIST OF SYMBOLS

D_h	hydraulic diameter of the pipe. (D-2t) (mm)
nCO_2	fraction of CO_2 in the gas phase
pCO_2	partial pressure of CO_2 (bar)
P_{opr}	operating pressure (MPa)
T_{mp}	temperature (^{0}C)
V_{cr}	corrosion rate (mm/year)
V_m	flow dependent contribution to the mass transfer rate.
V_r	flow independent contribution to the reaction rate
c_x	concrete cover (cm)
i_{corr}	corrosion rate ($\mu A/cm^2$)
w/c_e	water cement ratio
dT1	corrosion loss volume in year T1
dT2	corrosion loss volume in year T2
T1	year of inspection T1
T2	year of inspection T2
c(t,E)	corrosion loss of material
fn(t,E)	mean valued function
b(t,E)	bias function
ϵ(t,E)	zero mean error function
b_k	Coefficient on the kth predictor
y_i or y	Corrosion rate
e_i	Error term
s_e^2	Error variance

CHAPTER 1

INTRODUCTION

1.1 Background

Many of the world's marine structures and offshore structures (in particular) are reaching the end of its design life. With the increasing emphasis on attempting to maintain existing structure in service for longer periods of time and hence to defer replacement costs, there is increasing interest in predicting corrosion rate at a given location for a given period of exposure once the protective cover is lost.

Allowance must be made for structural deterioration since protective measures such as paint coatings, galvanizing or cathodic protection may be ineffective. Moreover for already corroding structures, the present and future expected rates of corrosion (metal loss, pit depth) are important for predicting the remaining safe life of the structure.

Corrosion allowances are prescribed for structural members by different standards such as BS 5950[1], EC3 [2], Norsok-M001 [3], API RP2A WSD [4], and DNV [5]. There were many empirical field investigations on the corrosion of steel in marine environment. Field trials are recommended to assess the likely corrosion rates at the site of interest. Laboratory tests cannot replicate the corrosion that occurs under actual field conditions since the corrosion process is nonlinear in time. It cannot generate the marine bacteriological process involved in corrosion in real seawaters.

The weather environment can be classified as severe (eg. The North Sea), moderate (Gulf of Mexico) or mild (eg.Malaysia) with additional cost for corrosion allowance being 9%, 6% and 4% of the total platform cost inclusive of the piling [6].

The reduction in corrosion allowance can signify large savings. Alternatively, structures may still be safe at the end of the design life.

When evaluating corrosion of steel structures in marine environment, it is necessary to examine the zone of marine environment to which the structure is exposed. These zones are: atmospheric zone, splash zone and continuously submerged zone. The corrosion rate in each of the zones can vary considerably.

Corrosion coupons is a preferred tool for monitoring corrosion since they provide accurate results at a reasonable cost, are easy to use and can provide general information that is quantitative and visual. Though different types of coupons have been used (strip coupons, disc coupons, rod coupons, coupons with applied stress etc.), the strip coupons produce the most accurate results and have been used in this work.

In the 1940-1950s, a complete scale experimental field investigation along the US Atlantic seaboard was conducted using both single electrically isolated coupons and vertical continuous steel strips. The corrosion mass loss profile was published by Humble, LaQue and Larrabee [7]-[9] and these studies have been widely quoted in literature. The studies show that the splash zones, the region above the mean tide level encountered the most severe corrosion and a very similar profile patterns were produced for both the short term (151 days) and longer term (5 years) of exposure. A five year test program was undertaken to assess the relative corrosiveness of seawater at 14 test sites world-wide in 1983 [10]. The studies indicate that factors such as temperature, dissolved oxygen, flow, and degree of fouling, bacterial activity and pollution affect the corrosion though the parameter in terms of chloride content and pH are similar in seawater [11]. In 1995, Melchers [12] published a concept for a corrosion prediction model that explains the marine corrosion in multiple phases. The model shows the progression of corrosion versus time. A separate research initiative have been carried out in Australia on marine immersion corrosion by developing the probabilistic models for structural reliability assessment [13], [14] and effect of water pollution on immersion corrosion [15].

Ratnam et al. studied marine corrosion and bio fouling on different materials under immersed conditions off Chennai coast in India [16]. Shifler discussed the factors leading to accelerated degradation of materials exposed to various marine environments and the use of modelling to assess and predict the corrosion behaviour [17]. In Malaysia, studies on structural corrosion are very few. Wan Nik et al. investigated corrosion behaviour of mild steel in seawater at Kuala Terrengganu coastal area but only concentrating on corrosion in fully submerged zone [18]. Noor et al studied the effect of extreme corrosion defect on pipeline remaining life time [19]. Noor, Yahaya and Mohd Nor studied corrosion in oil pipelines and vessel ballast tanks using statistical and probabilistic methods [20]. Yahaya et al. (2011) studied metal loss caused by soil corrosion [21]. Ong analysed the condition and degree of deterioration of offshore structures based on inspection reports of various platforms. The inspections utilized the method of cathodic potential and the percent wastage of anode [22].

The corrosion process of steel in marine environments depends on numerous parameters. These parameters can be classified into endogenous parameters related to the steel material, exogenous parameters related to the environment and a dynamic component related to the time of exposure. A model for marine corrosion can incorporate at least some of these parameters in order to better match the environmental conditions that are likely to be encountered or else can be simply related to time.

The review studies reveal that there is a lack of studies on marine and offshore corrosion on structural steel and determination of appropriate corrosion rates and corrosion allowances for Malaysian conditions. An experiment which involves fabrication of corrosion coupon of type 3 steel and immersing the same using steel frames in different seawater zones at the BOUSTEAD Shipyard Sdn. Bhd. at Lumut in Malaysia was undertaken.

1.2 Problem Statement

Corrosion is a major problem in marine structures, which inflict huge financial losses and sometimes it may cause collapse of the structure. The article published in Offshore Technology in 2012 stated that the total annual cost of corrosion in the oil and gas production industry alone is estimated to be $1.3 billion, including $589m in surface pipeline and facility costs, $463m in down-hole tubing expenses and $320m in capital expenditure related to corrosion [23]. According to international corrosion society NACE, if oil and gas production firms manage corrosion effectively, they can improve compliance with safety, health and environmental policies, increase plant availability and reduce the amount of leaks, deferment costs and the amount of unplanned maintenance [23].

The historical accidents due to structural failure are less than 10% of the total failures based on worldwide data in the 1990s [24]. However, these statistics are according to the population where very few structures have experienced corrosion failure. Thus, historical data of failures due to corrosion may be excluded in these statistics. Moreover, many of the marine structures are aging rapidly and the corrosion protection may be not available.

Degradation of the marine structure due to corrosion may decrease the ability of structures to withstand overload due to wave and current loading. Decreasing safety margin is the worst hazard for many of the marine structures. Evaluation of corrosion is very difficult since underwater inspection is involved. No studies on the development of time based corrosion model as well as parametric corrosion rate model for steel structures under marine exposure by using experimental field data in Malaysia has been carried out.

The major task in this thesis is to develop a time based as well as parametric based corrosion model and to extract other important information related to corrosion behaviour.

1.3 Objectives of study

Based on the background presented in the previous sections, the main objectives of the research work is to develop time based and multiple parameter based corrosion model for steel structures under marine exposure by using experimental field data and to extract others important information related to corrosion behaviour. The following are the sub objectives of the work:

1. To compare the qualitative nature of corrosion in different zones (atmospheric, splash and immersion) in marine structure.
2. To compare the rates of corrosion in different zones and with the limits in the codes of practice.
3. To determine the effect of differences in chemical composition of steel on the corrosion rate of the steels.
4. To analyse how fouling production at marine environment affects the steel's corrosion rate.
5. To develop time based corrosion rate model and multi parameter corrosion rate model using regression analysis.

1.4 Scope of Work

Many studies have been done by researches in different parts of the world on corrosion involving extensive laboratory experimentation to study the correlation between weight loss of the corrosion coupons and parameters that influence metal loss such as pH, temperature, operational pressure and penetration rate of chemical substances. This thesis concentrates on the analysis of corrosion data collected from experiment conducted by immersion of corrosion coupons of type 3 steel in real marine environment at Lumut, Perak, Malaysia. The location is selected because its hinterland is an industrial area and proximity of the naval shipyard. Though PTS 20.073 recommends four steel types (high strength steels type 1 and 2) and Mild steels (type 3 and 4), only type 3 has been considered in this study mainly because of availability [25]. Two samples of type 3 mild steel obtained from different sources (from China and Japan) are considered. They have been named as sample 1 and sample 2. Other types of marine structural steels are not included.

The first part of work is the evaluation of the corrosion rate using corrosion coupons by weight lost method and the study of the effect of different zones on corrosion rate. The second part investigates the effect of fouling organisms and composition of steel on corrosion rates in different zones. The development of the corrosion allowance is based on the physical evidence from weight loss method. The effects of material properties and environmental parameters upon corrosion growth are considered in developing the generic assessment approach of corrosion rate. The variation of corrosion parameters is analysed statistically. The overall results will be compiled, analysed and compared with the recommended values in the current code.

1.5 Research Significance and Contribution of the Study

In a study of corrosion cost conducted jointly by C.C Technologies Inc., USA, Federal Highway Agencies, USA and National Association of Corrosion Engineers in 2001, the direct corrosion cost is a staggering $276 billion- approximately 3.1% of the nation's gross domestic product(GDP) [26]-[28]. In Japan, the cost of corrosion is estimated to be 5258 trillions; the average corrosion cost is 3.5-4.5% of the GDP. Unlike weather related disaster, corrosion can be controlled, but at a cost. The aging steel structure is one of the most serious problems faced by the society today and in Malaysia, many of the 200 offshore steel jacket platforms have reached the end of their designed lifetime. The petroleum, chemical, petrochemical, construction, manufacturing, pulp and paper and transportation industries are the largest contributors to corrosion expenditure.

Lumut consists of mix industrial development inclusive of port, light, medium, heavy and terrace factory shop lot. Industries currently operating in the Lumut Port Industrial Park include processors for minerals, non- minerals, feed meal, and vegetable oils as well as metal work, metal fabrication, biodiesel, grain import and re-export preparation and shipbuilding. Offshore fabrication company which is involved fabrication of offshore structure and mobile offshore production unit is also located at Lumut. Thus, the studies on corrosion behaviour at Lumut are very important.

Materials are resources of a country and it is dwindling fast. Metal crisis will happen in the future. It is important to preserve these valuable resources thus it is important to understand how these resources are destroyed by corrosion and how they must be preserved by applying corrosion knowledge and what are the chemical additives that prolong the steel life span. The knowledge from the research gives material science researchers and maintenance engineers the ability to study the environmental effects on corrosion for mild steel at marine environment. Better understanding of environmental condition reduces modelling variability and improves predictability.

This research has the potential to extend mild steel structural performance and optimize maintenance costs for marine structure in the maritime shipping (commercial and naval) and offshore oil industries as well as benefit shipyards (commercial and naval), ports, and harbours.

1.6 Thesis Organization

This thesis is organized as shown in Figure 1.1 into five chapters. Chapter 1 provides a general background of the problem of structural corrosion and discusses the different areas of study on corrosion in general, structural corrosion and models used to study corrosion. The chapter contains the problem statement, the main objectives and sub objectives of the work, the scope of study, the research significance and contribution from the study.

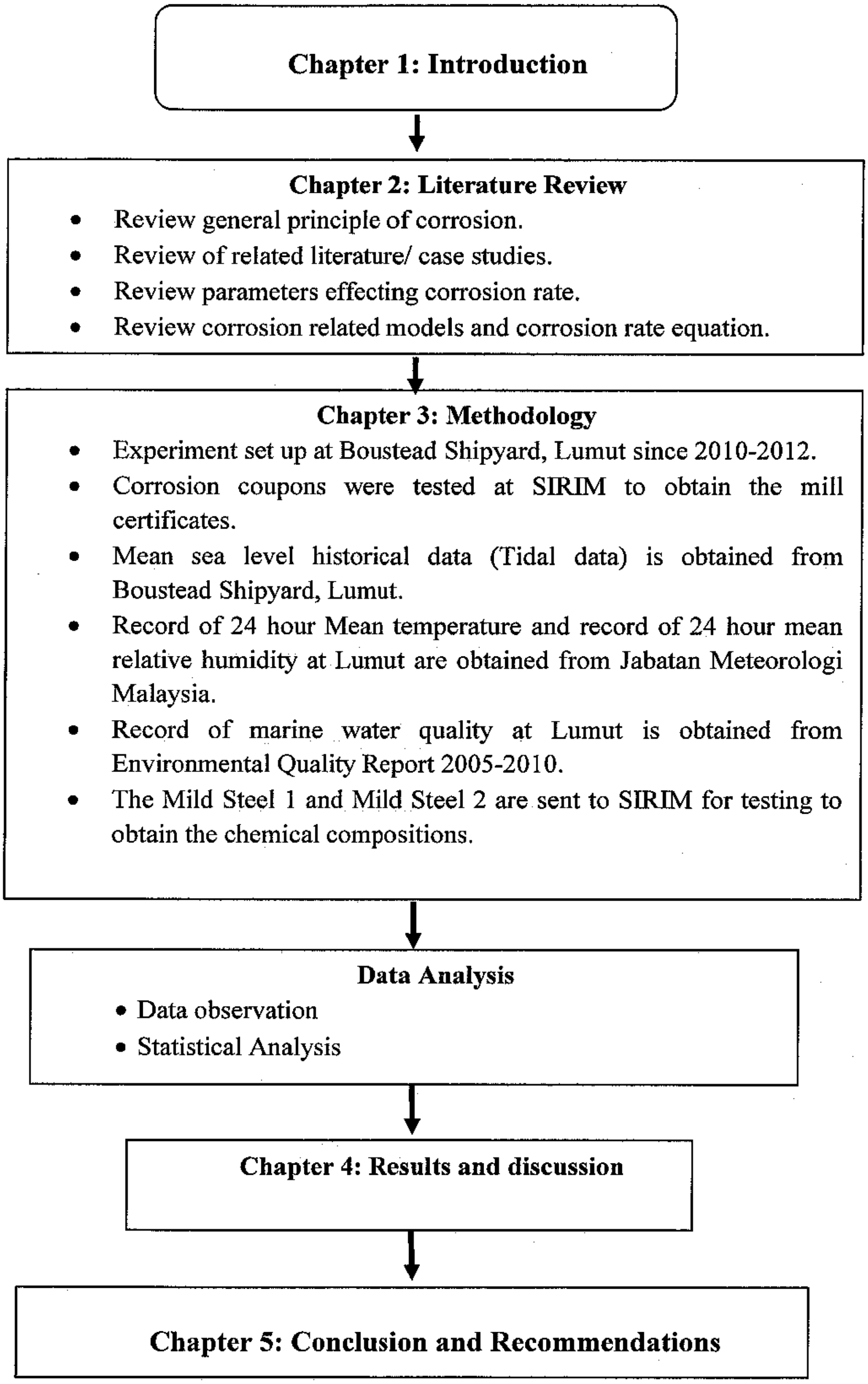
In Chapter 2, the literature related to the areas of study is presented. The areas reviewed include general principle of corrosion, types of corrosion, the parameters affecting corrosion rate, corrosion studies done in different parts of the world, and corrosion related models (corrosion time based and parametric corrosion model) and corrosion rate equation.

The detailed methodology of the research is presented in Chapter 3. Methodology consists of the following:-

- Details of the Experimental set up at Boustead Shipyard, Lumut to study the nature and rate of corrosion during the period 2010 – till present.
- Testing of the Corrosion coupons at SIRIM to determine the material composition of the steels used for the corrosion studies.
- Collection of the Mean sea level historical data (Tidal data) from Boustead Shipyard, Lumut.
- Collection of Average Monthly 24 hour Mean temperature and average monthly 24 hour mean relative humidity at Lumut from Jabatan Meteorologi Malaysia in Kuala Lumpur.
- Description of the procedure adopted for analysis and interpretation of the data

Chapter 4 consists of the results and discussion. It includes the details of the data collected, the results of the data analysis and discussion of the results.

Chapter 5 concludes the thesis report with the research findings and recommendations for future research. Appendix A provides supporting information on the processed data and detailed background on the experimental set up. Appendix B illustrates the step-by-step flow chart of the fabrication and set up of the experiment for determination of marine corrosion rates of type 3 steel at Lumut.



Chapter 1: Introduction

Chapter 2: Literature Review

- Review general principle of corrosion.
- Review of related literature/ case studies.
- Review parameters effecting corrosion rate.
- Review corrosion related models and corrosion rate equation.

Chapter 3: Methodology

- Experiment set up at Boustead Shipyard, Lumut since 2010-2012.
- Corrosion coupons were tested at SIRIM to obtain the mill certificates.
- Mean sea level historical data (Tidal data) is obtained from Boustead Shipyard, Lumut.
- Record of 24 hour Mean temperature and record of 24 hour mean relative humidity at Lumut are obtained from Jabatan Meteorologi Malaysia.
- Record of marine water quality at Lumut is obtained from Environmental Quality Report 2005-2010.
- The Mild Steel 1 and Mild Steel 2 are sent to SIRIM for testing to obtain the chemical compositions.

Data Analysis

- Data observation
- Statistical Analysis

Chapter 4: Results and discussion

Chapter 5: Conclusion and Recommendations

Figure 1. 1 Organisation of the thesis

1.7 Limitations

This thesis evaluates the coupons obtained from field experiment thus this implies a loss of a certain degree of control over the experimental conditions and hence a loss of accuracy. However, there appear to be no other options since controlled laboratory experiments have to date been unable to replicate field conditions. The laboratory observations are incomparable to field test; by using artificial seawater biotic marine conditions are difficult to replicate in the laboratory. Thus, the results are obtained under field conditions only.

The corrosion rates of the coupons are derived based on the weight loss method. Other methodologies of measuring the corrosion rate are not evaluated. The study was conducted using exposed (uncoated) steel test coupons and did not consider "at-sea" conditions such as coating protection systems (CPS), cathodic protection or any special operational conditions. Also, parameter such as dissolved oxygen in the seawater, deposition rate of SO_2 and Cl, flow effect (velocity) are outside of the scope of this thesis.

The study evaluated corrosion rate of only type 3 steel. Further these studies were done at coastal area. The conditions at offshore platform location are likely to be different. Also studies were evaluated only at Lumut. The study determined the parametric linear corrosion rate using 5 variables, pH, salinity, temperature, fouling load and time period (in months). The numbers of samples were only 7 due to the limited nature of the experiment. Malaysia has a long coastline and comparative studies at different locations can be carried out.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This research carried out a study of the corrosion on corrosion coupons made of type 3 steel at Lumut, Perak to simulate the corrosion of marine structures in tropical environment. In this chapter, corrosion issues will be reviewed and general principle of corrosion, which includes corrosion problems suffered by engineering structures or systems and the corrosion behaviour, will be discussed. Several studies were carried out to gain understanding of the corrosion behaviour and to determine the effect of various parameters on the corrosion and the average lifetime of the structure were reviewed. The corrosion related models have been discussed briefly with the purpose of demonstrating the model complexity due to its dependency on various environmental parameters. It is vital to take into consideration the combination of material and environment when analyzing corrosion.

For a clearer overview, the literature review carried out is organized as follows:

2.2 Types of Corrosion

2.3 Forms of Corrosion

2.4 Mechanism of Corrosion

2.5 Effects of Corrosion on Various Types of Environment

2.6 Methodologies of Measuring the Corrosion Rate

2.7 Corrosion Rate Models

2.2 Types of Corrosion.

The common types of corrosion are explained below.

2.2.1 General or Uniform Corrosion

General corrosion is defined as corrosive attack dominated by uniform thinning. The destructive result of chemical reaction between a metal or metal alloy and its environment causes corrosion. The metal atoms are present in chemical compounds. During the chemical reactions, the same amounts of energy are needed to extract metals from their minerals as that is required to returns the metal to its combined state in chemical compounds that are similar or even identical to the minerals from which the metals were extracted.

Although high-temperature attack in gaseous environments, liquid metals, and molten salts may manifest itself as various forms of corrosion, such as stress-corrosion cracking and de-alloying, high-temperature attack has been incorporated under the term "General Corrosion" because it is often dominated by uniform thinning.

The most commonly encountered corrosion is uniform or general corrosion. The corrosive environment must have the same access to all parts of the metal surface, and the metal itself must be metallurgically and compositionally uniform. It is responsible for the greatest wastage of metal on a tonnage basis yet rarely leads to an unexpected failure if regular inspections are carried out. Most of the structural steelwork on the site will suffer this form of corrosion; however, the application of a good paint system during original construction followed by the implementation of a planned maintenance painting programme will keep deterioration under control [29].

2.2.2 Galvanic Corrosion

Galvanic corrosion and the related inter-granular corrosion can produce highly localised anodic attack and significant loss of section with little or no corrosion being visible. Such corrosion can take place where two dissimilar metals are located next to each other without suitable precautions being taken [30]. Common examples of locations where such corrosion occurs are aluminium roof and wall cladding fixed to carbon steel structures without insulating washers, supporting of pipes and equipment on structures [29].

2.2.3 Crevice and Pitting Corrosion

Crevice and pitting corrosion are insidious forms of deterioration that produce considerable loss of section at small, localised anode sites which can lead to sudden and unexpected failure. The driving power for pitting corrosion is the lack of oxygen around a small area. This area becomes anodic while the area with excess of oxygen becomes cathodic; leading to very localized galvanic corrosion. The presence of chlorides, example in seawater, significantly aggravates the conditions for formation and growth of the pits through an autocatalytic process [29].

2.2.4 Stress Corrosion

Stress corrosion and the related corrosion fatigue, require the presence of both stress and a corrosive environment and are characterised by the highly local attack they produce [30]. Such environments are more associated with particular structural locations in nitrate fertilizer factories [29].

2.2.5 Erosion Corrosion and Fretting

Erosion corrosion and fretting are specialized forms of metallic deterioration that do not require the presence of an electrolyte common in all other forms. The combination of a corrosive fluid and high flow velocity results in erosion corrosion [30]. The same stagnant or slow flowing fluid will cause a low or modest corrosion rate but rapid movement of the corrosion fluid physically erodes and removes the protective corrosion product film and exposes the reactive alloy beneath and accelerates corrosion. Despite this, they too can result in local loss of metal section and subsequent sudden failure [29].

2.3 Forms of Corrosion

Over the years, corrosion scientists and engineers have recognized that corrosion manifests itself in forms that have certain similarities and therefore can be categorised into specific groups. However, many of these forms are not unique but involve mechanisms that have over lapping characteristics that may influence or control initiation or propagation of a specific type of corrosion [31].

The most familiar and often used categorization of corrosion is: uniform attack, crevice corrosion, pitting, inter-granular corrosion, selective leaching, erosion corrosion, stress corrosion, and hydrogen damage [31]. This classification of corrosion is based on visual characteristics of the morphology of attack.

Forms of corrosion are:

1. **General corrosion**
    - Atmospheric corrosion
    - Galvanic corrosion
    - Stray-current corrosion
    - General biological corrosion
    - Molten salt corrosion
    - Corrosion in liquid metals
2. **High-temperature corrosion**
    - Oxidation
    - Sulfidation
    - Carburization
3. **Localized corrosion**
    - Filiform corrosion
    - Crevice corrosion
    - Pitting corrosion
    - Localized biological corrosion
4. **Metallurgically influenced corrosion**
    - Inter-granular corrosion
    - De-alloying corrosion
5. **Mechanically assisted degradation**
    - Erosion corrosion
    - Fretting corrosion
    - Cavitation and water drop impingement
    - Corrosion fatigue
6. **Environmentally induced cracking**
    - Stress-corrosion cracking
    - Hydrogen damage
    - Liquid metal embrittlement
    - Solid metal induced embrittlement

Descriptions of the above forms of corrosion are available in [31].

2.4 Mechanism of Corrosion

Small physical and/or chemical differences present in metals such as minor impurities or local composition variations or environment for example changes in amount of dissolved oxygen varying with the depth of immersion, non-uniform salt concentrations due to pollution, etc will cause corrosion to occur [31].

There are two types of corrosion, which are categorized: dry and aqueous. The former may be described as the metal directly oxidizing, thereby returning to a lower chemical energy level. This type of corrosion is slow and relatively uniform. Temperature and diffusion of oxygen through the oxide determine the rate of corrosion. Thus, the thickness and physical stability of the rust layer are significant. The seawater which contains dissolved salts greatly increase the water conductivity and hence its corrosiveness. There must be a complete electrical circuit in both the structure and the aquatic medium. The process of corrosion of metal immersed into seawater is shown in Figure 2.1. A current can flow only in the existence of a potential difference any source of potential difference, for example, electrical; bimetallic [due to contact between different metal (Figure 2.2)]; physical, such as surface defects or stress concentration; chemical; or temperature difference, may also cause corrosion.

To initiate the corrosion process, the negatively charged ion in the electrolyte flow from where they are produced at the cathode toward the anode. The ions flow from the anode to the cathode unless an opposing voltage is applied with the aim of suppressing this current in the structure itself. The presence of these negative ions near the anode encourages positively charged metallic ions to dissolve into the electrolyte when they combine with any available negative ions to form a corrosion product. If the corrosion product forms a barrier to the ionic movement, the corrosion product can be discontinues [31]. This so called "passive" coating reforms and heal spontaneously provided oxygen is available but rapid corrosion can occur in crevices or under marine growth [32].

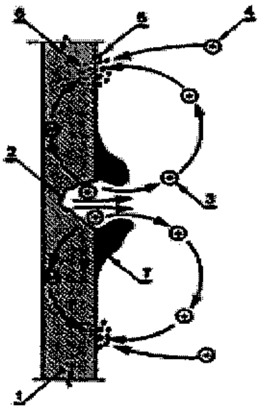


Figure 2. 1 Corrosion of steel immersed in water [32]

1-Steel, 2-Pit, 3-Iron ion, 4-Hydrogen Ion, 5-Hydrogen film, 6-Impurity, 7-Product of Corrosion Fe $(OH)_2$.

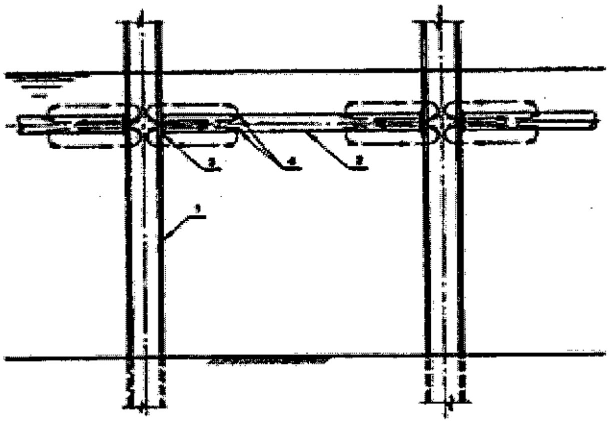


Figure 2. 2 Example of Galvanic corrosion

Couples (dissimilar-Electrode Cells). 1-A242 H pile, low alloy steel (cathode), 2-mild steel pipe brace node, 3-weld, 4-pit. Note: Pitting occur current leaves the anode to enter the electrolyte.[32]

The chemical reactions that take place on iron corroding in seawater are as follows.

At the anode iron goes into solution

$$Fe \rightarrow Fe^{2+2} + 2e \qquad (2.1)$$

The electron flows to the cathode through the metallic circuit. At the cathode oxygen converts hydrogen atoms into water.

$$2H^{+} + \frac{1}{2} O + 2e \rightarrow H_2O \qquad (2.2)$$

Or converts water to hydroxyl ions.

$$H_2O + \frac{1}{2} O_2 + 2e \rightarrow 2OH^{-} \qquad (2.3)$$

Adding the Eqn (2.1) and (2.3)

$$Fe + H_2O + 1/2O_2 \rightarrow Fe(OH)_2 \qquad (2.4)$$

Iron is converted to ferrous hydroxide. Other reactions can occur such as conversion of ferrous hydroxide ($Fe(OH)_2$) to ferric hydroxide ($Fe(OH)_3$) by further reaction with oxygen [33].

2.5 Effects of Various Types of Environment on Corrosion.

The environments are classified as rural, urban, industrial, marine or combinations of these. These types of environment are described as follows:

Rural: This environment usually has less aggressive agents (deposition rate of SO_2 and NaCL lower than 15 mg m^{-2} day^{-1}). Their principal corrosives consist of moisture, relatively small amounts of sulphur oxides (SO_2) and carbon dioxide (CO_2) from various combustion products [34]. Rural environment is the least corrosive and normally does not contain chemical pollutants but does contain organic and inorganic particulates [35].

Industrial: Sulphur oxides (SO_2) and nitrogen oxides produced by burning of automotive fuel and fossil fuels in power stations are the main reasons for corrosion [35]. The deposition of the pollutant on the metal surface causes the critical relative humidity, above which metals corrode to drop to about 60%. Other chemicals such as chlorides, phosphates, hydrogen sulphate, ammonia and its salts are present in the industrial environment. Thus the corrosion rate will be affected by these pollutants [34].

Marine: The topography of the shores, wave action at the surf line, prevailing winds and relative humidity affects the corrosion rate. The corrosiveness increases actively with decreasing distance from the shore [35]. The salt spray can be carried by severe storms inland as much as 15km. Marine fog and windblown spray droplets (deposition rate of NaCl higher than 15 mg m^{-2} day^{-1}) can carry salt and deposit on steel surfaces. These pollutants expedite corrosion at relative humidity more than 55%. The corrosion rates in marine atmospheres are usually high due to the presence of chloride (Cl^-) ion derived from sodium chloride [34].

2.5.1 Different Zones in Marine Environment.

Seawater is one of the most corrosive and most abundant naturally occurring electrolyte. Seawater and its surrounding environment attack the structural metals and alloys. There are five zones at the seawater environment, which include the subsoil, continuously submerged, tidal, splash zone above high tidal and atmospheric zone [8]. In deep water locations, the zones are mud, deep ocean, tidal submerged, splash spray and marine atmospheric zones. Figure 2.3 shows the different marine zones around metallic pile of harbour structure.

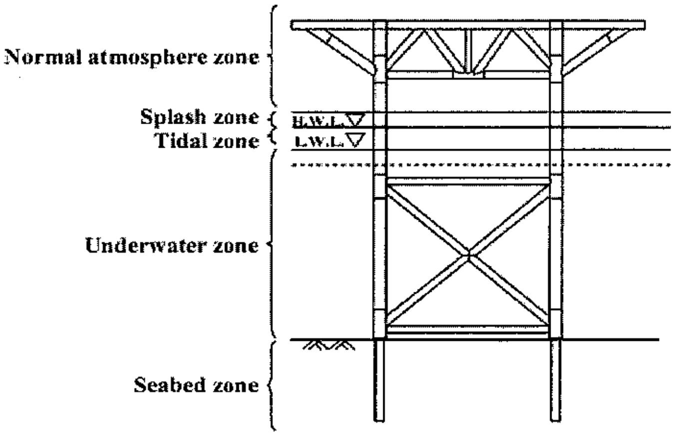


Figure 2.3 Different Marine Zones on Marine Structure [8]

Each zone gives different results. Oxygen, biological activities, pollution, temperature, salinity and velocity are the major factors, which affected the corrosion behaviour of materials in the submerged zone. Each of the zones is described below-

Atmospheric- The elements that affect the atmospheric corrosion in a marine environment are the time of wetness, temperature, material, atmospheric contaminants and pollutants, composition of corrosion products and biological species [36]. Atmospheric corrosion rate will tend to increase with winds directly from the ocean to the site. The direction and velocity of the wind can affect the accumulation of entrained seawater related particles on specimen surfaces. Magnesium and calcium chlorides are hydroscopic and tend to keep surfaces wet or moist [37]. Sulphur oxide lowers the critical humidity required to activate corrosion and increases the aggressiveness of the marine atmospheric.

Splash Zone- Above the tidal zone are the splash and marine atmospheric zones, the former being subject to wave action and salt spray and the latter mainly to airborne chlorides and is less aggressive. This zone can be distinguished as an aerated seawater environment where exposed metals are almost continually wet and biofouling organisms do not attach [38].

Tidal Zone- The tidal zone is an environment where the metal is alternatively submerged in seawater and exposed to the splash zone as the tide fluctuates. This zone lies between the low-water neap tides and high-water spring tides. Metals are exposed to well aerated seawater and biofouling does occur in the submerged condition. The biofouling either can protect the metal surface from attack or can accelerate localized corrosion [38].

Submerged/ Shallow Ocean Zone- The submerged environmental zone is characterized by well-aerated water combined with marine biofouling organisms of both the plant and animal variety. In the shallow ocean, the corrosion rate of metals varies and the resistivity of steel is dependent on the existence of oxygen at cathodic sites on the steel surfaces [38].

Deep Ocean Zone-The deep ocean environment varies from the ocean surface, as oxygen, temperature and salinity vary with depth. The temperature and salinity levels are similar in both the Atlantic and Pacific Oceans [38]. The oxygen concentration decrease at both sites as the depth is increased to an intermediate level; however, the reduction in oxygen is much greater in the Pacific Ocean than in the Atlantic. Dissolved oxygen increases at both locations as the depth is further increased.

Mud Zone- In mud zones, anaerobic sediments present contain bacteria which develop gases such as NH_3, H_2S and CH_4. Sulphides present can attack metals such as steel and copper alloys. The corrosion rate of low carbon steel in this environment is usually lower than that in the seawater environments described above because of the reduction supply of oxygen available for the cathodic reaction [38].

2.6 Methods of Measuring Corrosion Rate

A general overview of the methods to measure corrosion rate is provided below:-

2.6.1 Corrosion Coupon Method

A weighed sample (coupon) of the metal is introduced into the process and later removed after a specific exposure time. The coupon is cleaned of all corrosion products and is reweighed.

The weight loss is converted to an average corrosion rate. There are a few standards to comply when using coupons to derive the corrosion rate which include ASTM G1 "Preparing, Cleaning and Evaluating Corrosion Test Specimens," and American Society for Testing and Materials (ASTM), ASTM G31 "Laboratory Immersion Corrosion Testing of Metals." This method is simple and inexpensive. It provides a physical example of corrosion when it is removed from a system and allows an analysis of corrosion products. This method is not suitable for short term exposure because the result obtained is not accurate [39].

2.6.2 Polarization Methods

This method determines the corrosion current density under steady- state conditions. It consists of two electrochemical techniques which include Tafel Extrapolation (for lab measurement) and Electrochemical Linear Polarization Resistance (LPR) [39], [40].

Tafel deals with corrosion current density estimation from full polarization sweeps. Corrosion current is the current between the anodic and cathodic sites. The polarization curves are not reversible and sensitive to many experimental as well as environmental variables which introduce high variability in the Tafel constants. The anodic curves may not show linear behaviour near E_{corr}.

LPR technique is based on complex- chemical theory. In fundamental terms, a small voltage is applied to an electrode in solution. The current used to sustain a specific voltage shift (typically 10mV) is directly related to the corrosion on the surface of the electrode in the solution. The corrosion rate can be obtained by measuring the current.

The advantage of the LPR is that the corrosion rate is determined instantaneously and the disadvantage is that it can only be used in relatively clean aqueous electrolytic environments. It will not work in gases or water/emulsion where fouling of the electrodes prevents measurements being made [39].

2.6.3 Galvanic Monitoring

It is an electrochemical measuring technique with ZRA probes, two electrodes of dissimilar metals exposed to the process fluid. A natural voltage (potential) difference exits between the electrodes when immersed in solution and the current is formed because of the potential difference. The rate of the corrosion is determined by the most active of the electrode couple. It is usually applied in water injection systems where the dissolved oxygen concentrations are the main concern [39].

2.6.4 Electrical Resistance Monitoring

The probe consists of an element which is placed in-situ and permanently exposed to the process stream. It measures the change in Ohmic resistance of a corroding metal element and the action of corrosion on the surface of the element produces a decrease in its cross-sectional area with a corresponding increase in its electrical resistance. The increase in resistance relates to metal loss and the metal loss as a function of time thus the corrosion rate is obtained [39].

2.6.5 Hydrogen Penetration Monitoring

Hydrogen is a by-product of the corrosion reaction in acidic condition. The steel can absorb the hydrogen produced in acidic condition especially when traces of sulphide or cyanide are present. This may lead to hydrogen induced failure by one or more of several mechanisms. The probes basically detect the quantity of hydrogen permeating through the steel by mechanical or electrochemical measurement and to use this as a qualitative indication of corrosion rate [39].

2.7 Corrosion Rate Models

There are theoretical and empirical models to estimate the rate of corrosion. Generally, empirical models are developed based on a defined relationship between material and environmental properties to estimate the corrosion rate.

A theoretical model such as linear estimation is simpler and practical and to estimates the average growth rate based on metal loss evidence regardless of the effect of the material and environment properties.

2.7.1 Linear Model

The corrosion growth rate can be calculated using the linear corrosion growth model. This theoretical model is used on metal volume loss data or corrosion depth by comparing two corresponding defect dimensions at different time [21]. The linear equation can be expressed as:

$$CR = \frac{dT2-dT1}{T2-T1} \tag{2.5}$$

where:

CR: corrosion growth rate

dT1: corrosion loss volume in year T1

dT2: corrosion loss volume in year T2

T1: year of inspection T1

T2: year of inspection T2

2.7.2 The deWaard & Milliams Model

The averaged corrosion growth rate in oil and gas pipeline due to CO_{2}- induced corrosion can be estimated using deWaard & Milliam empirical model [40].

The reaction of carbon dioxide was controlled by the charge transfer and water with steel and was symbolized algorithmically in the form of CO_2 partial pressure and exponential temperature function in this empirical model. One of the ultimate benefits of the deWaard-Milliam model is that it is competent enough to deduce corrosion rates by ignoring the absolute corresponding dimension of corrosion defect in later inspection such as in the linear model method.

The rates of corrosion are deduced by:

$$V_{cr} = \frac{1}{\frac{1}{Vr}+\frac{1}{Vm}} \tag{2.6}$$

where:

$$\log (V_r) = 4.93 - \frac{1119}{T_{mp}+273} + 0.58 \log (pCO_2) \tag{2.7}$$

and

$$pCO_2 = nCO_2 P_{opr} \tag{2.8}$$

$$V_m = 2.45 \frac{U^{0.8}}{D_h^{0.8}} p_{opr} \tag{2.9}$$

where:

D = pipeline diameter (mm)

D_h = hydraulic diameter of the pipe. (D-2t) (mm)

nCO_2 = fraction of CO_2 in the gas phase

pCO_2 = partial pressure of CO_2 (bar)

P_{opr} = operating pressure (MPa)

t = pipeline radius (mm)

T_{mp} = temperature (^{0}C)

U = liquid flow velocity (m/s)

V_{cr} = corrosion rate (mm/year)

V_m = flow dependent contribution to the mass transfer rate

V_r = flow independent contribution to the reaction rate.

2.7.3 Corrosion Model of Concrete Reinforcement Bar

This model was presented by Vu and Stewart [41] to estimate the development of corrosion of reinforcement bar in concrete structure. This model is best used when the corrosion rate is controlled by the existence of water and oxygen at the steel structure, and concrete cover. This model stated that corrosion rate would increase very quickly with time amid the first few years after commencement but then slower as it drawing near to uniform state.

$$I_{corr} = \frac{37.8\left(1-\frac{w}{c_e}\right)^{-1.64}}{cx}(\mu A/cm^2) \tag{2.10}$$

where:

c_x = concrete cover (cm)

i_{corr} = corrosion rate ($\mu A/cm^2$)

w/c_e = water cement ratio

The equation 2.10 can be rewritten as below when the effect of corrosion commencement time is taken into account.

$$i_{corr-t} = i_{corr} . 0.85 t_p^{-0.29} (\mu A/cm^2) \tag{2.11}$$

where:

t_p = time since corrosion initiation in year.

2.7.4 Probabilistic Model of Immersion Corrosion

Melchers [11] has developed a probabilistic model for steel corrosion loss. There is considerable variability in corrosion losses depending on the environmental factors and material parameters. This includes physical parameters such as water temperature, water velocity, water depth and chemical parameters such as pH, water hardness and biological aspects such as marine growth, bacteria content and nutrient levels.

The material aspects such as the precise steel composition, including carbon were taken into account for corrosion loss. It is appropriate to consider these quantities as random variables with parameters that change with time. Thus the generic form of the proposed model has material loss due to corrosion as a function of time is given below:

$$c(t,E) = b(t,E)fn(t,E) + \epsilon(t,E) \qquad (2.12)$$

where:

$c(t,E)$: corrosion loss of material

$fn(t,E)$: mean valued function

$b(t,E)$: bias function

$\epsilon(t,E)$: zero mean error function

E: a vector of environment and material parameters.

In 1995, Melchers published a concept for a corrosion prediction model that describes marine corrosion in multiple phases. Figure 2.4 shows the essential features of the corrosion loss- exposure time model [12].

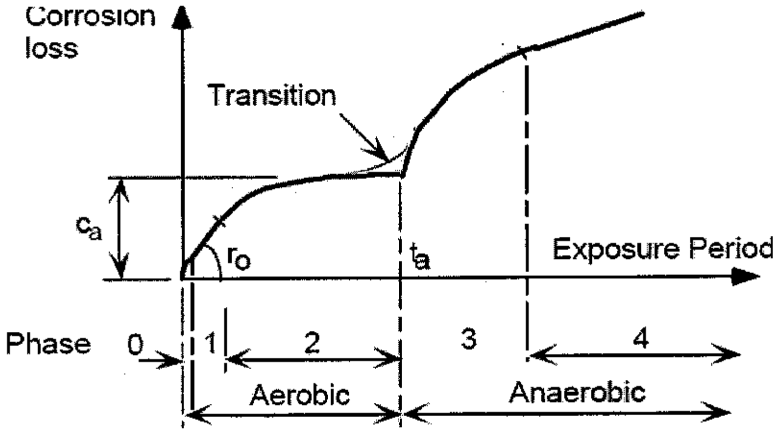


Figure 2. 4:Essential Features of the Corrosion Loss – Exposure Time Model [12]

The steel surface is intruded by a complex mix of bacterial, nutrient and various environmental influences at the beginning of the exposure. It will take some time for the corrosion process to become fully established and can then be considered to be under 'activation' control, i.e., it is governed by the rate at which local chemical reactions can occur unhindered by external diffusion or transportation limitations. It does not contribution much to corrosion loss because it only last for a short time (days). In Figure 2.4, it is labeled 'Phase 0'.

The corrosion rate is controlled by the rate of arrival of oxygen at the corroding surface and very soon an equilibrium situation develops. This is limited mainly by the rate of oxygen diffusion possible from the water adjacent to the corroding surface; hence, the term 'oxygen concentration' controlled [42]. Theoretically, a slightly non-linear function of time, the process may be modeled as a linear function. This part is categorized 'Phase 1'.

The rate of oxygen diffusion will control the rate of corrosion and as corrosion continues, there is a build-up of corrosion products (rust) on the corroding surface. The build-up of corrosion products (rust) tends to reduce the rate of oxygen supply to the corroding surface. It is categorized as 'Phase 2' in the model to be described at Figure 2.4. It becomes increasingly difficult for oxygen to reach the corroding surface as the rust layers build-up. This leads to the development of anaerobic conditions, more or less uniform over the corroding surface. This provides conditions under which sulphate-reducing bacteria (SRB) can flourish under the right nutrient conditions. In brief, SRB attack the steel through their waste products (metabolites), principally H_2S, producing FeS in the process. As a result, the rate of corrosion now depends on the rate of metabolism which in turn depends on the rate of supply of nutrients [15]. This constitutes 'Phase 3'. Eventually, a near-steady-state situation develops over the corroding surface with the rate of corrosion dependent on the rate of supply of nutrients and the loss of rust layer through erosion and wear [43]. This is known as 'Phase 4'.

2.8 Corrosion Rate Calculation and Standard Corrosion Rates.

The rate of corrosion is defined in various forms. The easiest in dimensionless units is the percentage change in weight of a coupon in an exposed time interval to obtain the percentage change per year [44]. The corrosion rate depends on Faraday's Law.

The electrochemical reaction involved oxidation of 96486.7 Coulombs (equal to one Faraday) of charge transfer or reduction of one gram equivalent weight of the material according to the Faraday's law. The number of coulombs is developed by Faraday by dividing Avogadro's number (6.032×10^{23}) which equals the number of atoms of any specific atom whose weight equals its gram atomic weight by the number of electrons in one coulomb (a coulomb is that amount of electrical charge equal to the charge carried by 6.24×10^{18}electrons)[45].

Corrosion Rate Calculation in Metric Units:

Micrometers per annum:

$$\mu\text{mpa}=\left[\frac{\textit{weight loss of coupon (g)}}{\textit{total exposed area of coupon}(cm)^2}\right] \text{x} \left[\frac{3.65 \times 10^6}{[\textit{exposure time in days}]\times[\textit{density of metal} \left(\frac{g}{cm^3}\right)}\right] \tag{2.13}$$

Mils per year:

$$\text{mpy}=\left[\frac{\textit{weight loss of coupon (g)}}{\textit{total exposed area of coupon}(in)^2}\right] \text{x} \left[\frac{2.23 \times 10^4}{[\textit{exposure time in days}]\times[\textit{density of metal} \left(\frac{g}{cm^3}\right)}\right] \tag{2.14}$$

2.9 Corrosion Rate Expressions

Gravimetric method or electrochemical methods are the available methods to measure the rate of corrosion.

Gravimetric Method:

Corrosion rate (mmpy)

$$= [87.6 \text{ x Weight loss (mg)}] \div [\text{Area } (cm^2) \times \text{time (hrs)} \times \text{Density}] \tag{2.15}$$

Electrochemical method:

Corrosion rate (mmpy)

$$= 3.2 \text{ x } 1_{corr}\ (mA/cm^2) \text{ x Eq.wt/ Density} \tag{2.16}$$

Sometimes the corrosion rate is also given:-

$$= \text{mmd x } 1.144/\text{Density} = \text{mpy} \qquad (2.17)$$

where mdd is mg per square decimetre per day, mpy is mils per year. Also the formula for calculating the corrosion rate given as

$$\text{Mpy} = 534\text{W}/\ \text{DAT} \qquad (2.18)$$

where W: weight in gram

D: Density

A: Area in cm^2

T: Time of Exposure in hours

Weight of metal dissolving (g) = K x I x t

$$K = \frac{\text{Atomic Weight of Metal } (\frac{g}{mol})}{\text{No.of Electrons Transferred x } 96{,}500\ (\frac{Amp}{Sec})} \qquad (2.19)$$

where: I = current (amps)

t = time (sec)

There are many different units used to calculate the corrosion rate, R. The corrosion rate can be obtained in a variety of units with appropriate value of K. Table 2.1 gives the constant K value to calculate the corrosion rate unit desired.

Table 2-1 Relationships between Corrosion Rate and Constant (K) [31]

Corrosion rate units desired (mpy)	**Constant (K) in corrosion rate**
Mils per year (mpy)	3.45×10^6
Inches per year (in/yr)	3.45×10^3
Inches per month (ipm)	2.87×10^2
Milimeters per year (mm/yr)	8.76×10^4
Micrometers per year (μm/yr)	8.76×10^7
Picometers per second (pm.s)	2.78×10^6
Grams per square decimetre per day (g/m2/h)	$1.00 \times 10^4 \times d(a)$
Miligrams per square decimetre per day (mdd)	$2.40 \times 10^6 \times d(a)$
Micrograms per square meter per second (μg/m2/s)	2.78×10^6 x d(a)

Note: Density, (a) is not required to obtain the corrosion rate in these units. The density in the constant K cancels out the density in the corrosion rate equation. Relationships among some units commonly used for corrosion rates are shown in Table 2.2.

Table 2-2 Relationships among Units for Corrosion Rates [31]

	Factor for conversion to					
Unit	mdd	g/m2/d	μm/yr	mm/yr	mils/yr	In/yr
Miligrams per square decimetre per day (mdd)	1	0.1	36.5/d	0.0365/d	1.144/d	0.00144/d
Grams per square meter per day (g/m2/d)	10	1	365/d	0.365/d	14.4/d	0.0144/d
Microns per year (μm/yr)	0.0274d	0.00274d	1	0.001	0.0394	0.0000394
Milimeters per year (mm.yr)	27.4d	2.74ed	1000	1	39.4	0.0394
Mils per year (mils/yr)	0.696d	0.0696d	25.4	0.0254	1	0.001
Inches per year (in/yr)	696d	69.6d	25400	25.4	1000	1
d is metal density in grams per cubic centimetre (g/cm^3)						

The corrosion rates of carbon steel for one year of exposure on test sites situated in temperate, sub tropical and tropical marine sites with general chloride deposition rates (> 100 mg/m^2 day) is shown in Table 2.3 [46].

Table 2-3 Corrosion Rates for Carbon Steel for One Year of Exposure in Different Climate Regions [46]

Climate	Corrosion rate		Extreme (μm/year)
	(μm/year)	(mm/year)	
Temperate	30 – 70	0.03 – 0.07	Approx. 100
Sub tropical	40 – 170	0.04 – 0.17	Approx. 250
Wet Tropical	80- 700	0.08 – 0.70	Approx. 1000

ISO has placed the atmospheric zone in high corrosion category with corrosion rate of unprotected steel in the range of 80 - 200μm (3 – 8 mils) per year and mass loss of 650 – 1500 g/m^2 [46]. The corrosion rates are even higher in the splash zone at 200 – 500 μm (8 – 20 mils) per year. The corrosion rate for unprotected steel in the immersion zone is in the range of 100 -200 μm (4 – 8 mils) per year [47].

EN 12500 has quantitatively classified the corrosivity of an environment on the basis of mass loss of standard flat specimens (rectangular shape 50 x 100m) based on one year of exposure as shown in Table 2.4[48].

Table 2-4 Mass loss (g/m^2) for One Year Field Test Exposure in Five Corrosivity Classes.

Corrosiveness category	C1	C2	C3	C4	C5
Description	Very low	Low	Medium	High	Very high
Carbon Steel	≤10	10-200	200-400	400-650	650-1500

BS 6349-1-2000 Code of Practice for Maritime Structures classifies exposure of an area of steel in marine environment into vertical zones [49]. The notional average and upper limit values of corrosion for exposed, unprotected structural steels in temperate steels in temperate climates in mm/side/year is given in Table 2.5.

Table 2-5 Notional average and upper limits for corrosion rates in (mm/side/year) for different zones in temperate climate (BS 6349-1-2000) [49]

Zone	Average	Upper Limit
Atmospheric (in the dry)	0.04	0.10
Splash zone (above MHWS)	0.08	0.17
Tidal Zone (MLWS and MHWS)	0.04	0.10
Intertidal low water zone	0.08	0.17
Continuous immersion zone	0.04	0.13

Corrosion rates are also classified as low, moderate, severe and very severe as shown in Table 2.6 [50].

Table 2-6 Classification of corrosion rates (in mils per year or mpy) [50]

Classification	Low	Moderate	Severe	Very Severe
Corrosion rate (mpy)	<1.0	1.0 – 4.9	5.0 – 10.0	>10.0

The rates of corrosion of metals mostly are expressed as mpy or mmpy. The relative scale for corrosion of metal is given in Table 2.7- 2.8 [44], [51].

Table 2-7 The Relative Scale for Corrosion of Metal [51]

	Corrosion Rate	
	mpy	μmpa
Low	<1.0	<25
Moderate	1.0-4.9	25-126
Severe	5.0-10.0	127-254
Very Severe	>10.0	>254

Table 2-8 The Relative Scale for Corrosion of Metal [44]

	Corrosion Rate	
	mpy	mmpy
Safe	<5	0.125
Moderate	5-50	0.125-1.25
Severe	>50	1.25

There is another term to name the corrosion rates, which is penetration rate as shown in Table 2.9 [31]. It lists some general guidelines, which can be used to determine maximum corrosion rates for cases of general (uniform) corrosion.

Table 2-9 Penetration Rate and Characteristic of Corrosion [31]

Penetration rate, mpy	Characteristics
1 max	Corrosion is very low
10 max	Low corrosion
20 max	Fairly low corrosion
50 max	High corrosion
>50	Excessive corrosion

2.10 Parameters Affecting the Corrosion in Marine Environment.

The interpretation and evaluation of the natural phenomena to which the maritime structure is exposed is vital during design stage. Information related to these phenomena might exist from current available sources, even though such data can always be circumscribed in scope and utilization, and more exploration that is comprehensive might be needed to allow the selections of design parameters. The parameters that affect corrosion in marine environment are the presence of microbes, dissolved oxygen, flow effect, tides, salinity, pH effects, meteorological and climatologically factors and steel composition.

Environments are difficult to define and their broad and uncertain variability reduces the predictability to which the materials are exposed. The presented research has been confined mainly to corrosion in relatively shallow seawaters at Lumut, Perak. The depth by itself would not give huge impact on corrosion loss according to available evidence and microbiological parameter is likely to be important. Different environmental parameters in seawater, which affect corrosion, are dissolved oxygen and the flow effect. In the following sections, the effects of all the above parameters are explained.

2.10.1 Presence of Microbes

Microbes are present everywhere in soils, freshwater, seawater and air. The microbes of sulphate reducing bacteria is one of the wide spread types of bacteria that causes severe corrosion which leads to structural failure. A corrosion problem is not indicated merely by detection of microorganisms in an environment. The number of microorganisms of the specifically corrosive types will determine the corrosion problem [52].

Microbiologically influenced corrosion (MIC) is responsible for the degradation of a wide range of materials. Figure 2.6 shows a useful representation of materials degradation by microbes in the form of pipe cross section [53]. Microorganisms can attack most metals and their alloys, (e.g. stainless steels, aluminium and copper alloys, polymers, ceramic materials, and concrete).

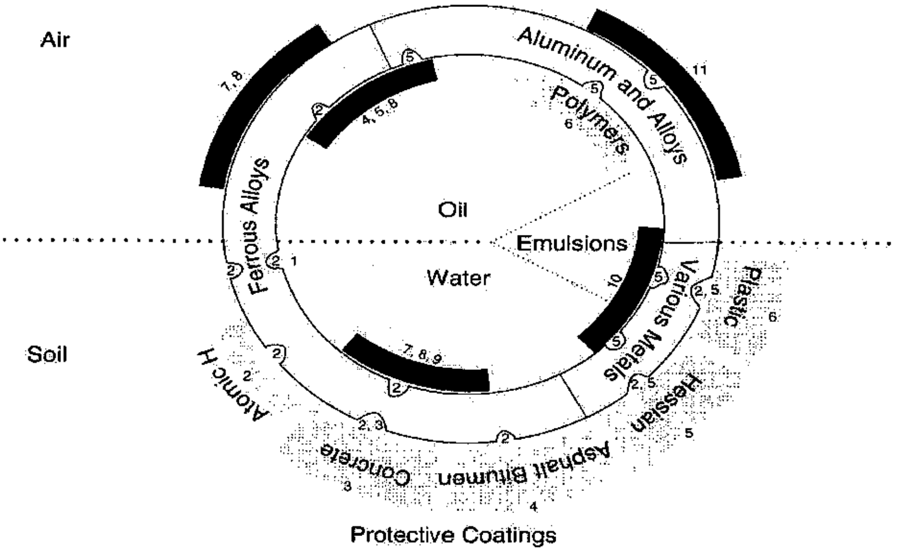


Figure 2.5:Schematic illustration of the principle methods of microbial degradation of metallic alloys and protective coatings [53].

In Figure 2.5, the principle methods of microbial degradation have been marked as 1-11. This numbering is described below.

1. Tubercle leading to differential aeration corrosion cell and providing environment for “2”.
2. Anaerobic sulphate reducing bacteria (SRB).
3. Sulphur oxidizing bacteria, providing sulphates and sulphuric acid.
4. Hydrocarbon utilizers, breaking down aliphatic and bitumen coatings and allowing access of “2” to underlying metallic structure.
5. Various microbes producing organic acids as end products of growth, attacking mainly non-ferrous metals alloys and coatings.
6. Bacteria and molds breaking down polymers.
7. Algae forming slimes above the ground damp surfaces.
8. Slime forming molds and bacteria (which may produce organic acids or utilize hydrocarbons) providing differential aeration cells and growth conditions for “2”.

9. Mud on river bottoms and so on providing matrix for heavy growth of microbes (including anaerobic condition for "2")

10. Sludge (inorganic debris, scale, corrosion products, etc.) providing matrix for heavy growth and differential aeration cells, and organic debris providing nutrients for growth.

11. Debris (mainly organic) on metal above ground, providing growth conditions for organic acid-producing microbes.

There are many types of marine fouling organism in submerged zone. Marine growths are classified into three main categories, namely hard growth, soft growth and long and flapping weed. Hard growth includes mussels, oysters, barnacles and tubeworms. Soft growth includes seaweeds, soft corals, sponges, anemones, hydroids, sea squirts and algae. Long flapping weed is kelp that could also come under soft growth but it is singled out because of its much bigger size. The fouling organisms attached to the structures will obstruct underwater inspection as well as create load to the structures thus it is called fouling load. They will result additional loading due to increased area to current loading.

The general fouling organisms along the Lumut coast are plankton, benthos, algae, bryozoans, barnacles and mussels. An environmental experiment was conducted at Lumut coast on September 2010 by Tenaga National Berhad Research Sdn Bhd in collaboration with Universiti Teknologi Malaysia [54]. There were 36 species of phytoplankton found during high tide whereas 42 species during low tide. The most common phytoplankton species were Thalassiosira sp.and Ceratium furca. A total of nine groups of zooplankton comprised of Phylum Cnidaria, Phylum Ctenophora, Phylum Chaetognatha, Phylum Mollusca, Phylum Annelida, Phylum Athropoda, Phylum Echinodermata, Phylum Chordata and Phylum Ectoprocta were found in the course of this study. In terms of benthos, a total of 6 phylum, 4 family and an approximately about 118 genus have been sorted out and identified. Six phylum identified include Annelida, Crustacea, Mollusca, Echinodermata, Sipuncula and Vertebrata. Generally there is not much difference of species compared to the list recorded in previous ECMP (2007) study [54].

2.10.2 Dissolved Oxygen

Oxygen is the main element reactant affected in the cathodic reaction and is involved in the passivation reactions that occur for most metals and alloys in seawater. Solubility is a measure of the quantity of an ion or gas in a solution [31]. Photosynthesis by marine plants and wave action can cause increase oxygen solubility in surface seawater to make it supersaturated by as much as 200% of its equilibrium concentration [55]. However, the dissolved oxygen concentration can reduce and become under-saturated due to oxygen consumption created by the decomposition of organic matter. The corrosion rate of iron increases with increasing oxygen concentration at any given temperature [31]. The solubility of oxygen decreases as the temperature increases from 0°C through 100°C [31]. The reaction kinetics increases following temperature increment thus the corrosion rate drops very fast at the boiling point due to the continuous drop in oxygen concentration.

2.10.3 Salinity

There are two main ways of determining the salt content of water namely (1) Determination of Total Dissolved Salts (or Solids) and (2) Electrical Conductivity Method. Total Dissolved Salts (TDS) is measured by evaporating a known volume of water to dryness, then weighing the solid residue remaining. Electrical conductivity (EC) is measured by passing an electric current between two metal plates (electrodes) in the water sample and measuring how readily current flows (ie conducted) between the plates. The more dissolved salt in the water, the stronger the current flow and the higher the EC. Measurements of EC can be used to give an estimation of TDS [56]. The differences in salinity of seawater are very little between the major oceans with an average salinity level typically in the range 30-35parts per thousand [56].

Water salinity has relatively little direct effect on corrosion rate, at least in the short term, a result first demonstrated in classical laboratory experiments conducted by Heyn and Bauer in 1910 and confirmed by Mercer and Lumbard in 1995 in very carefully conducted experiments [57], [58]. According to DNV-RP-B401, the major seawater parameter affecting cathodic protection in situ includes salinity [59].

2.10.4 pH Effects

The pH in the range of 4-10 has little effect on the early rate of corrosion including in seawater. It may have a modest effect on the rate of metabolism of the bacterial and marine growth (fouling) that commences, typically immediately on immersion of steel in seawater. The rate of metabolism is the principal corrosion action of bacteria. Therefore the rate of corrosion tends to reduce with higher pH values at the corroding surface.

In the acid range of pH (approximately <4) and probably also in the extreme alkaline range (>13.5) where impurities play a role in the hydrogen evolution reaction, differences in manufacture affect the corrosion rate. An iron or steel high in residual elements such as carbon, nitrogen, sulphur and phosphorus corrodes faster in acids compared to a relatively pure iron [31].

Calcium and magnesium carbonates present in seawater and in hard fresh waters are known to form deposits within the corrosion rust layers. The reduction in rate of supply oxygen to the corroding surface will reduce the corrosion rate. The ability of the carbonates to deposit increases with increasing pH of the water. The pH in seawater normally varies only very little (usually between 8.0 and 8.3 due to the buffering capacity of seawater). Therefore the calcium carbonate balance of the water as controlled by the pH of the water plays an important role in determining the rate of corrosion for longer exposure [60]. The pH in seawater and carbonate content affect the formation of calcareous layer associated with cathodic protection and thus the current needed to achieve and maintain cathodic protection of bare metal surfaces [61].

It is not feasible to give an exact relation between the seawater environmental parameters such as pH and salinity and cathodic current demands to achieve and to maintain cathodic protection. This is due the variation of geographical location, depth and season.

2.10.5 Meteorology and Climatology

Authoritative meteorological and climatologically data are gathered from the meteorology office covering the Lumut, Perak area. The information gathered includes the estimates of averages monthly and annual values of rainfall, temperatures and humidity. The Department of Environment, Ipoh, Perak can also provide information such as seawater quality, dissolved oxygen, total suspended solid, the percentage of oil and grease, Escherichia coli, arsenic, cadmium, chromium, copper, lead and mercury present in the Lumut seawater. The Malaysia Marine Water Quality Criteria and Standards requirement is provided in Table 2.10.

Table 2-10 Malaysia Marine Water Quality Criteria and Standards [62]

Malaysia Marine Water Quality Criteria and Standards (MMWQCS)	
Parameter	Class 3
Beneficial Uses	Ports, Oil & Gas
Temperature (°C)	≤2 °C increase over maximum ambient
Dissolved Oxygen (mg/L)	3
Total Suspended Solid (mg/L)	100 mg/L or ≤10% increase in seasonal average, whichever is lower
Oil and Grease	5
Mercury *(µg/L)	50
Cadmium* (µg/L)	10
Chromium (VI)(µg/L)	48
Copper (µg/L)	10
Arsenic (III)* (µg/L)	50
Lead (µg/L)	50
Zinc (µg/L)	100
Cyanide (µg/L)	20
Ammonia (unionized)(µg/L)	320
Nitrite (NO2) (µg/L)	1000
Nitrate (NO3) (µg/L)	1000
Phosphate (µg/L)	670

Table 2.10 (Continued) Malaysia Marine Water Quality Criteria and Standards [62]

Phenol (µg/L)	100
Tributyltin (TBT) (µg/L)	0.05
Faecal Coliform (Human health protection for seafood consumption) - (MPN)	200 Faecal coliform/ 100ml 200 E.coli/100ml
Polycyclic Aromatic Hydrocarbon (PAHs) mg/g	1000

2.10.5.1 Temperature Factor

The service temperature close to or above the stability limit will greatly affect the metal. Temperature affects reaction rates, surface temperature, heat flux and associated surface concentrations in aqueous and temperature gradient chemical transfer in aqueous environments. An increase in temperature is accompanied by an increase in reaction rate in most chemical reactions. The reaction rate doubles for each 10° Celsius (°C) rise in temperature. This is suggested by a rough rule of thumb. It is vital to take into consideration the influence of temperature when analyzing why materials fail and in designing to prevent corrosion although there are numerous exceptions to the rule [63].

2.10.5.2 Relative Humidity

Relative humidity is the ratio of the quantity of water vapour contained in the atmosphere to the saturation quantity at a given temperature, expressed as %. The air humidity is characterized by the indices RH, absolute humidity, moisture content and specific air humidity. Gases such as SO_2, Cl_2, H_2S, particulates of NaCl and other salts are present in industrial and sea shore places [64]. The fundamental concept for atmospheric corrosion processes is the existence of a thin film electrolyte that can form on metallic surfaces when exposed to a critical level of humidity. The corrosive contaminants it contains are known to reach relatively high concentrations, especially under conditions of alternate wetting and drying while this film is almost invisible. The nature of the corroding material, the tendency of corrosion products, surface deposits to absorb moisture, and the presence of atmospheric pollutants affects the critical humidity level. It has been shown that for example, this critical humidity level is 60% for iron if the environment is free of pollutants [65]. There is a sharp rise in corrosion rate probably because of the capillary condensation of moisture within the rust at 75%- 80% RH. There is a further increase in rusting at 90% due to the vapour pressure of saturated ferrous sulphate solution, ferrous sulphate being identifiable in rust as crystalline agglomerates [66]. Atmospheric corrosion proceeds by balanced anodic and cathodic reaction in the presence of thin film electrolytes.

The relative humidity at marine environment usually is high, as well as salt rich aerosols. The thickness of the adsorbed layer of water on zinc surface increases with relative humidity percentage and that corrosion rates increase with the thickness of the adsorbed layer according to the studies done by the researchers [65].

2.10.6 Flow Effect

Exposure of the metallic surface to high flow rates can accelerate the corrosion damage due to the destruction of protective film. For example carbon steel pipe carrying water is usually protected by a film of rust that slows down the rate of mass transfer of dissolved oxygen to the pipe wall. The corrosion rates are typically < 1mm per year. The removal of the film by flowing sand slurry has been shown to increase the corrosion rate 10-fold to ~10mm per year.

Figure 2.6 illustrates the various states of an oxide surface film behaviour as liquid velocity or surface shear stresses are increased [67]. The summary of change in the corrosion and erosion mechanisms associated with flow accelerated corrosion (FAC) is shown in Figure 2.6 and Figure 2.8.

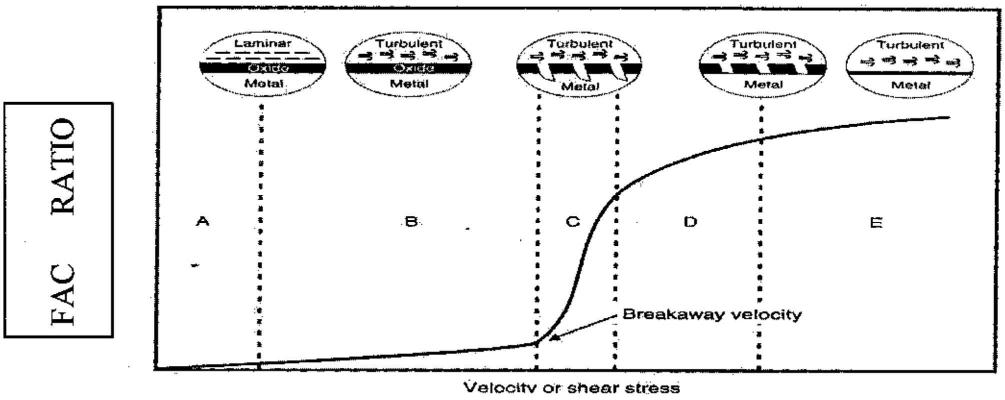


Figure 2.6: Changes in the corrosion and erosion mechanisms as a function of liquid velocity [67].

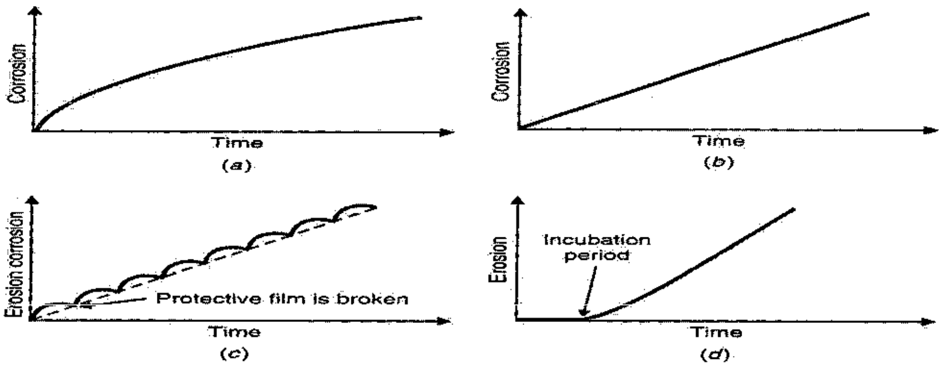


Figure 2.7: Various Time Dependent Corrosion-Erosion Behaviours and Processes [67]

The various time dependent corrosion-erosion behaviours and processes are explained in the following

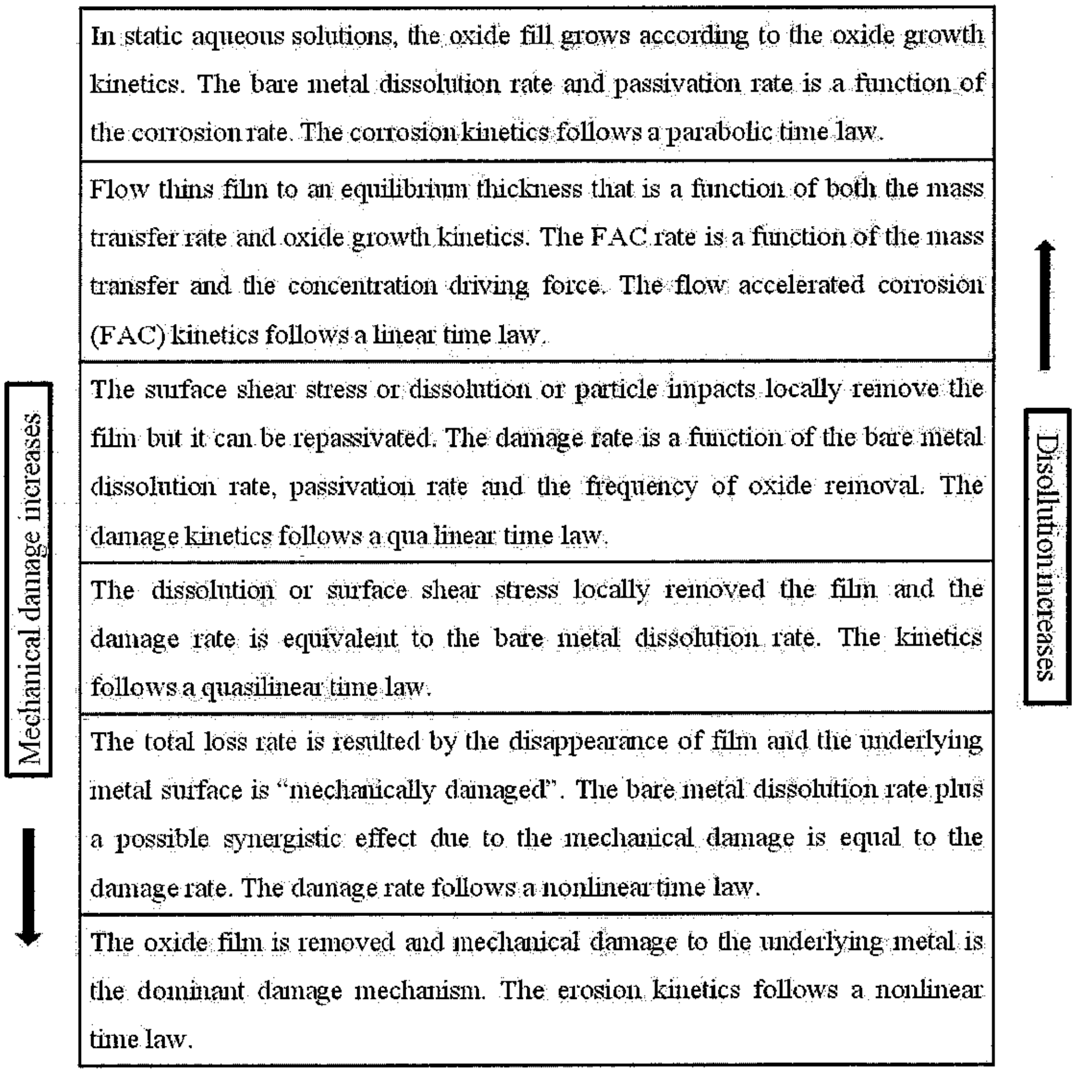
(a) Corrosion follows a parabolic time law,

(b) Flow Accelerated Corrosion follows a linear time law,

(c) Erosion and corrosion follows aqua-linear time law with repeated breaks in the protective surface film,

(d) After an initial incubation period, the erosion linear time dependency starts.

The corrosion rate is low and decreases parabolically with time due to the formation and growth of a corrosion protective film at the surface (curve a in Figure 2.7) in stagnant water. Corrosion streams from a flow conditions coexist at low flow velocities at which laminar and turbulent flow conditions coexist (Parts A and B of Fig. 2.6). The flowing water will dissolve the protective film that forms on the surface by corrosion. The phenomenon is generally accepted as a steady state process. Linear corrosion kinetics (curve b in Figure 2.7) is exhibited and a new layer of protective film with the same thickness will replace the water interface. The various time dependent corrosion-erosion behaviours and processes are shown in Figure 2.8.



In static aqueous solutions, the oxide fill grows according to the oxide growth kinetics. The bare metal dissolution rate and passivation rate is a function of the corrosion rate. The corrosion kinetics follows a parabolic time law.

Flow thins film to an equilibrium thickness that is a function of both the mass transfer rate and oxide growth kinetics. The FAC rate is a function of the mass transfer and the concentration driving force. The flow accelerated corrosion (FAC) kinetics follows a linear time law.

The surface shear stress or dissolution or particle impacts locally remove the film but it can be repassivated. The damage rate is a function of the bare metal dissolution rate, passivation rate and the frequency of oxide removal. The damage kinetics follows a qua linear time law.

The dissolution or surface shear stress locally removed the film and the damage rate is equivalent to the bare metal dissolution rate. The kinetics follows a quasilinear time law.

The total loss rate is resulted by the disappearance of film and the underlying metal surface is "mechanically damaged". The bare metal dissolution rate plus a possible synergistic effect due to the mechanical damage is equal to the damage rate. The damage rate follows a nonlinear time law.

The oxide film is removed and mechanical damage to the underlying metal is the dominant damage mechanism. The erosion kinetics follows a nonlinear time law.

Figure 2.8: Summary of damage mechanisms experienced with FAC.[67].

2.10.7 Tides

The astronomical tides generated by the cyclic variations in gravitational attraction of the moon and the sun on the water masses of the earth affects the water level under long period fluctuations [68].

There are three types of tide namely diurnal tides, semi- diurnal tides, and mixed tides. Tides have one high, one low water per tidal day is called diurnal tides, and area like northern Gulf of Mexico and Southeast Asia encountered this type of tides. Semi-diurnal will have two high and two low waters per tidal day. It is common on the Atlantic Coasts of the United States and Europe while in mixed tides, will have a higher water and lower high water as well as high low water and lower low water. The tides around west coast of Canada and the United States are of this type. [69]

2.10.8 Steel Compositions

The effects of alloying elements are summarized as follows [70]: carbon increases the steel's strength and hardness but tends to decrease its ductility and toughness. Structural steels usually have carbon content between 0.15 to 0.30% [71]. Manganese increases strength and hardness in similar manner except that it also increases the toughness. The percentage of manganese in the structural steel ranges from about 0.50 to 1.70. Chromium, copper, nickel and silicon all serve to increase the corrosion resistance of the steel; manganese likewise has a beneficial effect on the corrosion resistance. Copper and nickel is highly resistant to corrosion in sweater because its electrode potential is adjusted to be neutral with regard to seawater [72]. Silicon may also be present as deoxidizers. Phosphorus and sulphur are considered to be impurities and should be minimized if possible because it reduces the ductility of the material. Sulphur triggers internal segregation in the steel matrix. Thus in all steel grade specification, the amount of P and S that are allowed should be less than 0.04 to 0.05%.

The relationship between anti-corrosion properties of steel in marine environment and alloy elements was considerably different with variation of marine environment [73]. The similar alloy element's effect on the marine structure (such as oil platform, steel pile whaft, etc) in the sea mud zone, submerged zone, tidal zone, splash zone and marine atmospheric zone were entirely different [74]. There are researches done and proved that a certain kind of alloy element can improve the corrosion resistance of steel in the splash zone but not in the fully immersed zone. In fact, it would increase the corrosion rate of the steel at the fully immersed zone [75].

Corrosion science theory states that small changes (say <0.5%) in alloys used in steel composition should have zero or negligible effect on the degree of corrosion that occurs while oxygen diffusion controls the corrosion process [76]. The reason for this lies in fundamental corrosion principles. These provide that when the rate of corrosion is governed by the rate of oxygen diffusion to the corroding surface, as is the case in Phases 1 and 2, the composition of the steel is of little impact, since the diffusion is controlled respectively by the rate of oxygen diffusion out of the water (Phase 1) or by the permeability of the increasing thickness of the rust layers (Phase 2) [13].

The condition does not change fundamentally with greater levels of alloying except that oxygen diffusion through the rust layers prone to become more difficult in Phase 2. It is for this reason that the corrosion loss tends to decrease with various alloys [76] but their effect depends on how much they can influence the permeability of the rust layers. For Phases 3 and 4 of the model, the effect of alloying tends to be quite different from that in the earlier phases [76]. The reason for this is simply that the corrosion process is now controlled by the rate of anaerobic bacterial activity and this depends (i) on the rate of nutrient supply to the bacteria and (ii) on the resistance of the steel to the metabolic products of bacterial activity. It is generally accepted that the principal metabolite is H_2S. The ability of alloys to enhance resistance of the steel to H_2S attack is therefore the central issue, a matter not previously noted in the corrosion literature, which tends to be concerned with short term rather than long-term corrosion resistance. It immediately 'explains' why, for example, Cr as an alloy is not particularly useful for longer-term immersion resistance, since it is not resistant to H_2S attack.

The corrosion is appreciably reduced when a steel is alloyed in the proportions of a stainless steel (>12% Cr) or high silicon iron or high nickel iron alloy for which oxygen diffusion no longer controls the rate. The addition of certain elements in small amounts (e.g 0.1-1% Cr, Cu or Ni) has marked effect on the protective quality of naturally formed rust films for atmospheric exposures.

In fresh water, the carbon content of a steel has no effect on the corrosion rate but a slight increase in rate (maximum 20%) has been observed in seawater as the carbon content is raised from 0.1 to 0.8%. This reason for this increase is probably related to greater importance of the hydrogen evolution reaction in chloride solution (with complexing of Fe^2+ by Cl-) supplementary to oxygen depolarization as the cathodic surface of cementite (Fe^3C) increases.

More specialized steel with larger alloy compositions will have a lower initial rate of corrosion particularly for alloying elements such as chromium, molybdenum and aluminium and to a lesser extent for nickel, silicon, titanium and vanadium. Carbon content has essentially no effect on initial rate of corrosion [77].

2.11 Offshore Corrosion Rate and Corrosion Protection Provision

The extra wall thickness required for the service life of a steel structure can be obtained by knowing the expected general corrosion rate.

The offshore corrosion rate as steel thickness loss per year is given in Table 2.11 Localized higher rates of corrosion can occur due to several mechanisms. These conditions, applicable corrosion rates and preventive measures are discussed:

Table 2-11 Offshore Corrosion Rate Measured as Steel Thickness Loss Per Year [78]

Area	**Corrosion rate (steel loss per year)**
Atmospheric zone	80-200μm (3-8mils)
Splash zone	200-500μm (8-20mils)
Immersion	100-200 μm (4-8mils)

At atmospheric zone, the corrosion rate of unprotected steel is typically in range of 80-200 μm (3-8mils) per year. For comparison, most steel structures placed inland are situated in zones classified C3 where the corrosion rate is only 25-50 μm(1-2mils) per year.

The extended periods of wetness and high concentration of chlorides that accelerate corrosion causes high corrosion rates. The UV-light from the sun is also another factor that causes degradation. At splash zone highest stresses-corrosion rates of 200-500 μm (8-20mils) per year have been measured. Erosion due to water and possible debris may also contributes to this corrosion. At immersion area which is at the lowest tide, fouling could leads to corrosion [46], [47].

Different authorities such as Det Norske Veritas, The Norwegian Petroleum Directorate and Norsok developed codes of practice to regulate the requirements for materials selection and corrosion protection for offshore structure. The splash zone corrosion protection provision for steel structure is shown in Table 2.12.

Table 2-12 Splash Zone Corrosion Protection Provision for Steel Structures by Different Authorities [59],[79]-[80].

Det Norske Veritas	In 1977: Special corrosion protection system (not defined) and minimum 12 mm corrosion allowance.
The Norwegian Petroleum Directorate	Prior to 1992: Minimum 10mm corrosion allowance. In 1992: Coating and corrosion allowance. For thin film coating (thickness <1mm); Corrosion allowance = (design life-5 years) x 0.4mm/year; minimum 5mm Reduction if: 1. Structure is inspected in dry dock or sheltered water at least every 5 years, and/or 2. Coating with thickness more than 1mm (rubber) or sheathing is used. No quantitative reduction guides given. 1999: Same as Norsok
Norsok	1994: Corrosion allowance and coating. For thin film coating:corrosion allowance minimum 5mm. For design lives >17.5years, Corrosion Allowance =(design life- X years) x 0.4mm/year, where X=5 for thin film coating and X = 10 for thick film coating.

2.12 Review of Worldwide Research on Corrosion

Currently there are many countries preparing the corrosivity maps confined to the region of their interest independently. It is important to prepare the corrosion maps on a global level with the on-going liberalization and globalization of the industries. Thus, different organizations which are involved are gathered together. The data prepared are brought together and compiled in a data bank. The data gathered are presented and discussed in the light of the global data. The collection of corrosivity data at atmosphere in different locations had been going on in various countries [81]. Few important studies are summarized below:-

USA: Laque center is the first institute involved in carrying out atmospheric corrosion studies. The mass loss technique was used to determine the corrosivity at few sites located in Canada as well as USA. The data had proved that short term mass loss data can produce huge differences due to unpredictable environmental factors in natural atmospheric environments and seasonal effects. Therefore longer exposure (eg. 1-2 years) is intended to average out the influence of huge fluctuations in short term (eg. 1 month) environmental variables [81].

New Zealand: New Zealand is located in the southwest Pacific with prevailing westerly winds depositing huge amounts of sea salt far inland creating a critical atmospheric corrosion hazard. The atmospheric corrosivity survey conducted in New Zealand selected 168 sites located throughout New Zealand with carbon steel, aluminium and galvanized steel exposed for a year. The corrosion rates ranged between 18-4800 gm^{-2}per year for carbon steel and 0.7-1417gm^{-2}per year for galvanized steel. Aluminium showed critical results with maximum corrosion rate of 2.6 gm^{-2} per year. Corrosion rates for aluminium were greater than zero at a number of severe marine sites. At one industrial site a rate of 1.3 gm^{-2}per year was recorded. The correlation between atmospheric corrosion rate and proximity to the coast is evident in these results. The levels of chloride deposition affect the corrosion rate [82].

Spain: Corrosion studies on aluminium have been done at three clearly differentiated meteorological areas in Spain; namely the central, north western and sourthern areas. The study was conducted by the researchers from the Centro Nacional de Investigaciones Metalurgicas, Ciudad Universitaria, Madrid. The corrosion thickness loss (μm) and their respective durability factors (DF) are shown in Table 2.13. Durability by definition is the ability of the steel to resist weathering action, chemical attack and abrasion while maintaining its desired engineering properties [83]. Based on the data, it is seen that the durability factor for aluminium varies greatly ranges from 34 – 144 (Table 2.13). Apart from that, the durability factor varies from station to station; different stations at the same location has different durability factor.

Table 2-13 Corrosion (μm) and Durability Factors (DF) of Aluminium.

Area	**Station**	**Period 1982-83**		**Period 1983-84**	
		μm	**DF**	**μm**	**DF**
South	1	0.37	51	0.24	-
	2	0.41	39	0.32	43
	3	0.33	34	0.29	41
	4	0.10	144	0.12	93
North west	1	0.81	45	0.63	52
	2	0.49	76	0.5	77
	3	0.31	75	0.17	125
	4	0.33	79	0.19	134
Central	1	-	-	0.18	66
	2	-	-	0.11	98
	3	-	-	0.13	82
	4	-	-	0.18	53

Germany: Atmospheric corrosive experiments were done in the former German Democratic Republic in the period from 1979 to 1989 without any significant changes observed. However, when the result is compared to the data obtained in the same location in the period of 1989 – 1994; significant decrease of corrositivity of metallic materials is observed. This decline was caused by the lower deposition rate of corrosion pollutant such as Hydrogen Sulphide [83]. With the establishment of the Federal Republic of Germany in 1989, active measures on environment protection have been introduced and hence lead to the positive improvement of the air quality at the location of study.

In 1993, a study of outdoor corrosion resistance of zinc-electroplated steel (15 μm thickness) was reported by Julve and Gustems [84]. The study was conducted over a period of four years at 11 outdoor sites in the metropolitan area of Barcelona. Mass loss method and ASTM 'rating number' method were used to determine the corrosion rate. The ASTM rating numbers corresponds to the percentage of corroded area. The influence of relative humidity, chlorides, sulphur dioxide and particles in suspension were taken into consideration and discussed. Based on the study, it was identified that the corrosion rate of zinc-electroplated steel increased in the marine environment. Table 2.14 shows the corrosion rate of zinc-electroplated steel.

Table 2-14 Corrosion Rate (kg m^{-2} y^{-1}) of Zinc - Electroplated Steel [84]

Outdoor exposure site	Type of atmosphere	Zinc-electroplated
Molina	Urban	0.0055
Poble Noy	Urban-industrial	0.0089
Hospitalet	Urban	0.0059
Sant Adria	Urban-industrial	0.0088
Badalona	Urban-industrial	0.0092
Montcada	Urban-industrial	0.0071
Sant Vicenc	Rural-industrial	0.0056
Viladecans	Rural	0.0052
Comella	Urban	0.0049
Prat	Rural-industrial	0.0056
Port	Marine	0.0300

An experiment of atmospheric corrosion of low carbon steel and copper is reported in Espadaz, et al. [85]. Corrosion specimens are placed at twenty four sites along the Galicia Coast (North-Western of Spain). The experiment sites are located at different altitudes and distances from the shore. The equations to predict the corrosion rate is developed through the statistical analysis of the data obtained. Based on the result, a correlation coefficient of 0.967 for low-carbon steel and 0.905 for copper is formulated. The correlation coefficient is a quantity that gives the quality of a least squares fitting to the original data [85].

India: For the past 32 years, there has been a dramatic change in the environment quality in India [86]. This is due to the rapid development in the country which directly related to the industrialization, population growth and the ever expanding vehicle population. Based on the past research data, it is clear that non ferrous material such as galvanized steel and aluminium have better durability factor. In most cases, aluminium proves to be the more cost effective solution when compared to galvanized steel. The typical durability factor based on relative corrosion rates (one year data) for galvanized steel and aluminium are shown in Table 2.15.

In 2002, based on the studies reported by Vashi, et al. [87] conducted on the corrosion rate of aluminium at industrial area at Ankleswar, South Gujarat; the monthly corrosion rate of aluminium is around 4 -30 (1 to 5 μm/y) mg/sq.dm., while the yearly corrosion rate is around 65 – 126 (1 to 15 μm/y) mg/sq.dm. As compared to mild steel and zinc, aluminium or aluminium coated materials are more corrosion resistant.

Table 2-15 Typical Durability Factor based on Relative Corrosion Rates for Galvanized Steel and Aluminium (one year data) [82]

Location	Galvanized	Aluminium
SVRECT, Surat	10.75	6.85
MPT, Mormugoa	2.46	41.26
NIO, Goa	13.27	120.96
NMPT, Mangalore	16.16	21.25
IOC, Mumbai	18.89	27.2
INS Naval Base,	24.29	180
Kayamkulam	-	84
CECRI Unit,	3.43	3.09
Mandapam Camp	8.69	155.79
Nagapattinam	89.75	Very High
Cuddalore	12.21	44.15
INS Naval Chennai	44.94	60.93
Near Nellore	-	551.72
CECRI Unit Kochi	31.64	502.78
Mettupalayam	-	33.33
MPL, Manali	25.22	81.56
Tirupur	-	6
LPSC Mahendragiri	3.86	2.52
Coimbatore	-	4
Portblair	1.4	9.5

In 2000, another corrosion study on galvanized steel and aluminium was reported by Indira, et al. [88]. This experiment was done in a period of one year (from August 1998 – July 1999) at a marine environment at Kochi, India. Mass loss method was used to determine the monthly corrosion rate. The atmospheric pollutants such as chloride and sulphur were estimated periodically and correlated with the corrosion rate values.

The atmospheric corrosion rate of galvanized steel is between 0.0025 – 0.0314 mpy while the corrosion rate of aluminium is between 0 – 0.0014 mpy. The results of the study clearly show that aluminium has better durability as compared to galvanized steel.

In 1996, a study on the corrosion rates of various metals such as aluminium, copper and stainless steel 304 was conducted by Mohan et al. [89] in order to design proper corrosion preventive methods. The experiment was conducted at the eastern (Site 1,2,3) and western coast (Site 4 and 5) of southern India for a period of 12 months. Table 2.16 shows the corrosion rate of the various metals throughout the period of the experiment.

Table 2-16 Corrosion rate of metals at various locations [89]

			Corrosion rate in mm/yr		
Location		**Period**	**Aluminium**	**Copper**	**Stainless Steel**
East Coast	Site	3	0.0007	0.03000	0.00150
		6	0.007	0.02000	0.00500
		9	0.0026	0.01800	0.00550
		12	0.0029	0.01500	0.00500
	Site	3	-	-	-
		6	-	-	-
		9	-	-	-
		12	-	-	-
	Site	3	0.0110	0.25500	0.00060
		6	0.0092	0.01460	0.00060
		9	0.0017	0.00512	0.00027
		12	0.0020	0.00870	0.00040
West Coast	Site	3	-	-	-
		6	0.0001	-	-
		9	0.0004	-	-
		12	0.0005	-	-
	Site	3	0.0002	-	-
		6	0.0001	-	-
		9	0.0004	-	-
		12	0.0014	-	-

Based on the experiment result, it was concluded that the corrosion rate at the eastern coast (site 1, 2 and 3) is higher than the western coast (site 4 and 5). Prolonged exposure of copper shows a decreasing corrosion rate; on the other hand, aluminium and stainless steel 304 indicates slow initial corrosion rate but increase rapidly with time.

In 2011, an extensive study on the seasonal dependencies of copper corrosion rates and runoff rates is reported by Odnevall et al.[90] The two year experiment was conducted at both rural and urban area at the beginning of four different seasons. The location of the experiment is about 8 km south of Stockholm. At the rural location, seasonal differences in the corrosion rate can be observed throughout the experiment. This is mainly due to the differences in relative humidity. As of the samples at the urban location, no seasonal effect was observed. Based on the study, it is recorded that the yearly runoff rates are independent of time while the rate of corrosion decrease with time. Depending on the season, the yearly runoff rates ranges from 1.1 – 1.7 gm^2 y^1 at the urban area, and from 0.6 – 1.0 gm^2 y^1 at the rural area. The quantity of precipitation and environmental characteristics are the two main contributions to the seasonal variations. The adhering copper patina ensures that the runoff rates are significantly lower than the corrosion rate.

In 1986, a study on the corrosion rates of aluminium and brass in the tropical marine atmosphere is reported by Ananth, et al. [91]. The two years exposure was done at Mandapam Camp on east coast, India and the corrosion rate is determined by the weight loss method. The corrosion rate of brass is collected monthly while the result for aluminium is collected quarterly. The formation of corrosion products prevents further corrosion on the metals and hence causes a decrease of corrosion rates with time. Copper based metal are more resistant to chlorides as compared to the aluminium based metals. The corrosion rate of the metals for 2 years exposure in comparison with a few other studies is summarized in Table 2.17.

Table 2-17 Corrosion rate, $g/m^2/day$ [91]

Metal	**Present study 2 years**	**India 2 years**	**Sweden 2 years**	**Panama 1 year**
Copper	-	0.127	0.00245	0.10130
Brass	0.050	0.0585	0.00200	0.03014
Aluminium	-	0.00698	-	0.00274

According to the report by Sundaram, et al. [92] the presence of moisture is necessary in order for corrosion to occur. The corrosion results of various types of metals at one of the test site are presented in Table 2.18.

Table 2-18 Corrosion rate of metals at site No. 2 [92]

Period of exposure	**Corrosion rate (mdd)**		
	Aluminium	**Copper**	**Stainless steel 304**
Quarterly			
Jan-Mar	0.0234	2.331	0.0265
Apr-Jun	0.0685	4.700	0.0494
Jul-Sep	0.0697	5.352	0.0873
Oct-Dec	0.0278	1.097	0.0431
Half-yearly			
Jan-Jun	0.053	2.986	0.0545
Jul-Dec	0.057	3.027	0.0492
Nine months			
Jul-Mar	0.047	2.183	0.033
Yearly			
Jan-Dec	0.0403	2.187	0.033
Jul-Jun	0.0425	1.874	0.0926

The combination of high humidity, high temperature and intense solar radiation whether it is natural or man-made will greatly increase the rate of metal corrosion. An experiment was done at the Mandapam Camp, a tropical marine location at the south-east of India which fits these few corrosion enhancing criterias. Copper based material gave the highest corrosion rate ranged from 1.097 – 5.352 mdd The corrosion rate of stainless steel 304 ranged from 0.0265- 0.0926 mdd) and aluminium ranged from 0.0278-0.0697 mdd.

Cuba: Antonio, et al. [93] reports the experiment done on the influence of environmental parameters and main pollutants such as sulphur dioxide and chlorides on the corrosion of copper and aluminium (Table 2.19).

The experiment was setup at three test sites under different exposure conditions which are the coastal, urban industrial and rural areas for a period of 18 months. Apart from that, the specimens were exposed to both indoor and outdoor conditions at the test sites. The most significant variables observed during the experiment is the interaction between chlorides deposition rate of rainfall (outdoors) and wetness at temperature between 5 – 25 ^{0}C (indoors). Depending on the nature of the metal, other variables also play an important role in the corrosion process. ISO 9223 was used to classify the atmospheric corrosion aggressiveness based on the environmental data and corrosion rate results. However, the prognostic of ISO 9223 is not always in agreement with the result obtained in Cuba. The average corrosion values for copper and aluminium is presented in Table 2.19.

Table 2-19 Copper and aluminium corrosion rates (g/m^2 a ± standard deviation) [93]

Exposed Time (months)	Rural				Coastal			Urban - industrial	
Copper	**Outdoor**	**Sheltered**	**Ventilated Shed**	**Closed space**	**Outdoor**	**Sheltered**	**Ventilated shed**	**Outdoor**	**Sheltered**
6	27.4 ± 1.6	9.8 ± 0.8	3.5 ± 0.2	0.2 ± 0.04	5.3 ± 0.7	44.5 ± 0.5	19.8 ± 4.5	23.9 ± 1.8	6.8± 1.5
12	19.4 ± 0.4	11.5 ± 0.5	1.9 ± 0.3	0.2 ± 0.02	34.6 ± 0.04	54.1 ± 2.6	47.2 ± 3.7	19.8 ± 0.04	8.5 ± 0.4
18	4.3 ± 0.6	8.6 ± 0.7	1.9 ± 0.3	2.0 ± 1.2	30.3 ± 2.0	72.4 ± 3.5	33.1 ± 0.5	15.0 ± 0.5	7.5 ± 0.7
Aluminium									
6	0.3 ± 0.04	1.1 ± 0.14	0.2 ± 0.03	0.4 ± 0.08	4.3 ± 0.2	4.8 ± 0.1	2.2 ± 0.1	0.7 ± 0.05	1.1 ± 0.04
12	0.3 ± 0.02	1.2 ± 0.14	0.3 ± 0.01	0.3 ± 0.10	3.2 ± 0.03	4.0 ± 0.4	1.6 ± 0.3	0.6 ± 0.05	1.7 ± 0.13
18	0.2 ± 0.01	0.8 ± 0.11	0.2 ± 0.00	0.3 ± 0.04	2.2 ± 0.4	3.6 ± 0.2	1.4 ± 0.1	0.4 ± 0.00	1.8 ± 0.1

Taiwan: A corrosion exposure test reported by Horng et al [94] concentrated on the 3 classes of galvanized steel which are the Class A, Class B and Class C [95]. The Class are differentiated according to zinc coating. The galvanized steel wire strands are placed at rural, marine and industrial areas around Taiwan in 1984 for a period of 24 months.

The specimens' rate of corrosion is determined using the weight loss method and the results are tabulated in Table 2.20. The results of the experiment are then compared to laboratory results derived from salt spray test to determine the role of salinity and other weathering parameters which affect the corrosion.

Table 2-20 Weight loss after 1 and 2 years, exposure and salt spray test [94]

		Exposure Wt. Loss (g/m^2)		
Exposure Site	**Exposure Period (years)**	**Class A**	**Class B**	**Class C**
Penghu	1	83.5	33.5	42.3
	2	294	-	-
Keelung	1	4.7	0	0
	2	66.8	-	-
Peitou	1	4.7	0	0
	2	20.5	-	-
Kaoshiung	1	9.5	0	0
	2	98.4	-	-
Pingtung	1	4.3	0	0
	2	85.1	-	-
Taitung	1	0.9	0	0
	2	98.4	-	-
Salt Spray	0.25	225	8.2	7.6
	1.3	-	41.1	36.2
	2	855	-	-

Based on the experiment, the Class A galvanized steel wire strand started to rust after 3 months of exposure indicating high salinity and corrosivity at the Penghu area. X-ray diffraction and SEM-EDS methods are used to examine the corrosion product to determine the possible mechanisms of atmospheric corrosion. As shown in the result, the Class A galvanized steel at Penghu area recorded an exceptionally high corrosion rate (3 – 14 times greater) as compared to other areas. The corrosion rate of Class A galvanized steel at Penghu is also higher than Class B and Class C after 1 year of exposure.

Ibero-American: Another corrosion project named MICAT was done on carbon steel specimens exposed for 1 – 4 years in 22 rural and urban atmospheres. Almeida, et al. [96] summarizes the results of the experiment which takes into consideration the test site characterization, chemical and morphological determination of the steel corrosion product layers (SCPLs) in order to understand the corrosion phenomena.

The project reported the effect of climatology to the steel corrosion rates and SCPL properties. The atmospheres of the test sites were classified into a few different ISO groups but the steel corrosion rates did not differ much. No further study has yet to be done to identify the reason why corrosion rates are not affected by atmospheres. However, it is observed that the SCPLs protection layers increased with time at all the different atmosphere test sites.

China: Corrosion of insulated coupons at several different levels relative to mean sea level was measured over a period of 3 years at the transport wharf for the Shengli oil field, located in the offshore oil exploitation area in the Chengdao Sea [73]. The data, reported as corrosion rates, have been converted to total corrosion losses and are plotted in Figure 2.9 for the immersed, mid-tide and splash zones. Subjective trend lines have been added using Figure 2.4 as a guide.

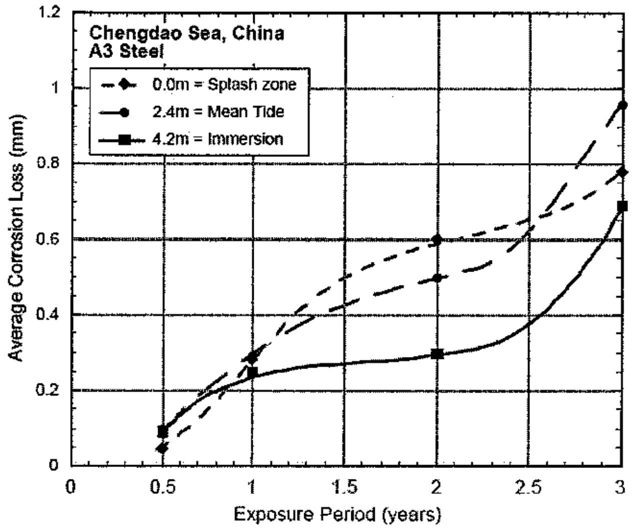


Figure 2.9 Interpreted trend lines at mean high tide (HT), median (MT) and low tide (LT) levels for field data for marine corrosion losses of A3 steel as functions of exposure period. Data points derived from corrosion rates.[73].

Argentina: The atmospheric corrosion experiment of aluminium in Argentina with known ambient parameters is reported by Vilche, et al. [34].The samples are exposed at six different test sites and the corrosion is determined by weight loss method. In order to characterize the protective properties of the surface layers generated on the metal, electrochemical techniques are performed on the exposed metal surface in 0.1 M Sodium Sulphide solution. A few important aspects such as the total affected area, surface facing the sky and the ground, sample density and exposure time are taken into consideration when calculating the corrosion. The corrosion rates of the aluminium samples are presented in Table 2.21.

Table 2-21 Corrosion Rate of Aluminium from Weight Loss Measurements [34]

Test station	Period (years)	(µm / year)	Test station	(µm / year)
San Juan	1	0.015	Iguazu	0.03
		0.057		0.08
		0.015		0.10
	2	0.012		0.06
	3	0.005		0.03
	4	0.0015		0.03
Camet	1	0.14	Villa Martelli	0.05
		0.21		0.03
		0.29		0.06
	2	0.13		0.02
	3	0.08		0.03
	4	0.15		0.04
Jubany	1	1.54	La Plata	0.05
		1.07		0.08
		1.38		0.06
	2	1.19		0.05
	3	0.43		0.02
	4	0.67		-

Singapore: There are many petrochemical plants on Jurong Island, Singapore thus it has a relatively high pollution level compared to other locations around the island. The corrosion behaviour of seven materials (Al-brass, cupro-nickel, titanium, the austenitic-super stainless steel UNS S31254 (SMO), the duplex-super stainless steels S32900 (329) and S32750 (2507) and type 316L austenitic stainless steel) has been assessed both in laboratory experiments for 28 days and in a mock up test system for 26 months[97]. Table 2.22 and Table 2.23 show the results obtained from the laboratory experiments and mock up test system.

It was found that the seawater around Singapore's Jurong Island appears to be quite aggressive with respect to pitting corrosion, despite having a chloride content on only about 13,000 ppm. This is to be due to its total organic carbon content, which rises from a mixture of biological and pollution sources.

Table 2-22 Comparison between corrosion in artificial seawater and Singapore stagnant seawaters[97].

	Artificial seawater			Singapore seawater		
Specimen	Weight loss (g)	Corrosion rate (g/m^2hr)	Pitting potential (mV)	Weight Loss(g)	Corrosion rate (g/m^2hr)	Pitting potential (mV)
ALB	0.0038	0.0050	-20 (DZ)+	0.0004	0.0005	-30 (DZ)+
CUP	0.0163*	0.0213*	145	0.0005	0.0006	225
Ti	0.0003	0.0004	N.A	<0.0001	<0.0001	N.A
SMO	0.0001	0.0001	N.A	0.0001	0.0001	N.A
329	0.0001	0.0001	N.A	<0.0001	<0.0001	N.A
2507	0.0005	0.0006	N.A	0.0003	0.0004	N.A
316L	0.0006	0.0008	670	0.0001	0.0001	553

*crevice corrosion, +dezincification

Table 2-23 Effect of temperature on corrosion rate in Singapore stagnant seawater [97].

Material	Corrosion rate(g/m^2hr)		
	40°C	60°C	80°C
ALB	0.0005	0.0124	0.0034
CUP	0.0006	0.0007	0.0034
Ti	<0.0001	<0.0001	<0.0001
SMO	0.0001	<0.0001	<0.0001
329	<0.0001	<0.0001	<0.0001
2507	0.0004	<0.0001	<0.0001
316L	0.0001	<0.0001	<0.0001

The 316L showed the highest corrosion rate ($0.029g/m^2hr$). The copper-based alloys showed significantly higher corrosion rates than their stainless steel counter parts and of all materials test. However, at 80°C, a thick tarnish layer developed on the cupronickel alloy that allows it to resist pitting corrosion better than type 316L stainless steel. Weight loss coupons revealed that the corrosion rates of all grades of stainless steel were not sensitive to temperature It was found that crevice corrosion represents the most serious threat to heat exchangers operating with Singapore seawater; none of the high grade stainless steels or the two copper based alloys were immune to this form of attack. In conclusion, titanium gives the optimum results even at a temperature of 80°C [97].

Malaysia: In 2010, analysis on the condition and degree of corrosion deterioration of offshore structures based on inspection reports of various offshore jacket platforms was done by S.T. Ong [22]. The method of Cathodic potential, the percent wastage of anode and ultrasonic wall thickness measurements are used for the purpose.

The inspection history of Offshore Platform A showed that most of the anodes are approaching their designed working life of 70% wastage. Few anodes that exceeded 70% wastage have been replaced. Few anodes were reported missing in earlier inspections was seen in subsequent inspections. The data for ultrasonic wall thickness for Offshore Platform A is scattered and missing no comparison can be done. Simultaneously, an experiment which involves fabricating of samples of different types of mild steel and immersing the same in different seawater zones at the BOUSTEAD Shipyard Sdn Bhd at Lumut are conducted to enhance the research. This formed the basis of the current post graduate work.

In 2011, a study on corrosion behaviour of mild steel in seawater at two different sites of Kuala Terengganu coastal area was conducted for a 60 days by Wan Nik et al. [18]. Only immersion zone is considered in this study. The composition of the steel is shown in Table 2.24.

Table 2-24 Composition of Mild Steel for corrosion study at Kuala Terengganu [18]

Element	**Percentage (%)**
Copper	0.14
Manganese	0.35
Silicon	0.17
Sulphur	0.025
Phosphorus	0.03
Iron	Remainder

The salinity at site 1 ranges from 30.5-33.3 ppm and at site 2 is 30-32 ppm. At site 1, the temperature for seawater ranges 27.36-27.7 °C and at site 2 the temperature for seawater ranges 27.3-27.5 °C. Weight loss analysis and polarization study was used and the result showed that the corrosion rate increases with respect to immersion period. The weight loss analysis shows that the highest percentage weight loss is about 4.3% (25 days) at site 1 and 4% (25 days of exposure) at site 2. The highest corrosion rate at site 1 is 6500mm/year at 30 days of exposure and the peak of corrosion rate at site 2 is 5000mm/year at 25 days of exposure. All the plots (30days data) recorded shows similar pattern. The two sites have only small differences in seawater parameters thus it did not give any impact towards the corrosion behaviour of mild steel.

2.12.1 Period of Field Experiment Conducted by Worldwide Research.

Various field experiments were conducted worldwide by researchers and Table 2.25 shows the durations of the field experiments. Table 2.25 indicates that the period of corrosion studies are generally between 0.15 to 4 years. The corrosion studies cover various types of metals.

Table 2-25 Period of Field Experiment Conducted by Worldwide Research.

Source	Duration(years)	Nature of Study
Larrabee (1945)[98]	1.5	Trans. Electrochem. Soc
Larrabee(1953)[99]	1-1.5	Corrosion Resistance of High Strength Low Alloy Steels as Influenced by Composition and Environment
Researchers from the Centro National Investigation Metallurgical, Ciudad University, Madrid (1982)[83]	3	Corrosion and Durability Factor of Aluminium
Julve et al., (1993)[84]	4	Corrosion Resistance of Zinc-Electroplated Steel
Vashi et al. (2002)[87]	1	Corrosion Rate on Aluminium
Indira et al.(1998)[88]	1	Corrosion Study on Galvnized Steel and Aluminium
Mohan et.al(1996)[90]	1	Corrosion Study on Aluminium, Copper and Stainless Steel
Ananth et al., (1986)[91]	2	Corrosion on Brass and Aluminium
Odnevall et al.(2011)[89]	2	Copper Corrosion

Table 2-25 (Continued) Period of Field Experiment Conducted by Worldwide Research.

Almeida et al.(2000)[96]	4	Carbon Steel at Urban and Rural Atmosphere
Antonio et al.(2000)[93]	1.5	Influence of Environment Parameters and Main Pollutants on Corrosion
Horn et al.(1984)[94]	2	Corrosion on Galvanised Steel
Li Y Hou et al.(2004)[73]	3	Corrosion on Insulated Coupons at several different levels at transport whart.
Koshelev and Rozenfeld (1960)[100]	4.5-4.6	Surface Roughness Effect on Marine Immersion corrosion of Mild Steel.
Blekkenhorst et al. (1986)[101]	3-3.5	Development of High Strength Low Alloy Steels for Marine
Southwell et al.(1979)[102]	0.8	Atmospheric Corrosion Testing in the Tropics
Jeffrey and Melchers(2009)[103]	1.0	Corrosion of Vertical Mild Steel Strips in Seawater.
Wan Nik et al.(2011)[18]	0.15	Corrosion Behaviour of Mild Steel in seawater from 2 different sites at Kuala Terengganu.
S.T Ong (2010)[22]	2	Marine Corrosion of Mild Steel in Lumut

2.13 Regression Corrosion Models

2.13.1 General

In statistics, linear regression is an approach to modelling the relationship between a scalar dependent variable y and one or more explanatory variables denoted X. The case of one explanatory variable is called simple regression. More than one explanatory variable is multiple regression [104]. Linear regression was the first type of regression analysis to be studied rigorously, and to be used extensively in practical applications. This is because models which depend linearly on their unknown parameters are easier to fit than models which are non-linearly related to their parameters and because the statistical properties of the resulting estimators are easier to determine [104].

One of the aims of this research is to develop statistical model for better understanding the effect of parameters such as pH, salinity, fouling organisms, months and temperature on the corrosion rate. In this work, multiple linear regression has been evaluated as means to generating equations for the corrosion rate. Statistical models are based on semi- empirical statistical relations among available data and measurements. They do not necessarily reveal any relation between cause and effect. It attempts to determine the underlying relationship between sets of input data (predictors) and targets (predictands). Examples of statistical models are regression analysis [105], [106]. Correlation between two variables does not automatically imply that one causes the other (though correlation is necessary for linear causation in the absence of any third and countervailing causative variable, and can indicate possible causes or areas for further investigation; in other words, correlation is a hint).[107], [108]

Most of the predictive models used are regression models that fit the data such that the root mean square error is minimized. The relation between the quantity of corrosion and the causes, and the predicting equation is obtained by multiple linear regression. Generally, multiple regression analysis modelling is effective to identify areas of risk, i.e., correlating among the corrosive factors in an environment and the resultant corrosion and finally obtaining a regression equation for the prediction of corrosion risk [107], [108]. The effect of inputs on the output can be studied using regression coefficients, standard errors of regression coefficients and the level of significance of the regression coefficients [109].

An overview of multiple linear regression analysis can be found in Andrade et al. and Clear (1989), Otsuki (2008), Dawn et al.(2007) and Richard (2010)[110]-[114].

Andrade et al. [110] and Clear [111] has conducted study to estimate the remaining service life of reinforced concrete in which corrosion is the limiting degradation process. Both models assume the linear change of corrosion rate with time. However, the measured corrosion rates are changing with time depending on the variations of the temperature and humidity. A linear change of corrosion rate with time is not expected and this should be taken into account when attempting service life estimates. Thus, Andrade and Clear calculates an average corrosion rate over a year. Another method to solve this problem is by using empirical extrapolation [110].

Atmospheric corrosion phenomena have been studied and statistical models based on regression analysis have been developed by many researchers [115]-[120]. Abdul Wahab et al. used regression analysis to predict corrosion rates of various metals at specific location in Oman [121]. The atmospheric corrosion of common metals was studied at five locations. The study was designed to be conducted for three years. Multiple linear regression models were fitted to the data to further determine the relationships between corrosion, the locations and the times of exposure of the metals. The regression equations for predicting the corrosion rate by the type of metal are shown in Table 2.26.

Table 2-19 The multiple linear regression equations for the corrosion rate (mg/cm^2) by type of metal [121].

No.	Metal type	Model	R^2
1	Aluminum	-0.62 + 2.09 (Sohar) + 1.23 (month14) + 1.19 (month58)	0.572
2	Brass	0.92 + 8.10 (Sohar) + 1.81 (month14)	0.443
3	Copper	-1.22 + 8.95 (Sohar) + 5.62 (month14)	0.611
4	Epoxy	1.18 – 2.52 (Al-Fahl) – 4.032 (Al-Khod) + 2.93 (Sohar) + 1.15 (momth14)	0.535
5	Galvanized	4.29 + 9.56 (Al-Khod) + 6.59 (Al-Rusail) + 13.31 (Sohar) + 1.817 (month14)	0.427
6	Mild steel	26.59 – 8.58 (Airport) + 2.87 (month58)	0.277
7	Stainless steel	2.23 + 3.70 (Sohar)	0.283

For most metals, it was found that the rates of corrosion tended to increase monthly for the first four months and then remained unchanged thereafter. The rate of corrosion increased by 1.23 mg/cm^2 per month in the first four months, then dropped to 1.19 mg/cm^2 per month during the fifth to the eighth month with respect to time.

Sohar area also recorded very high corrosion for copper (8.95 mg/cm^2) and brass (8.10 mg/cm^2). During the first four months, the corrosion rates for the two metals increased at the rates of 5.62 mg/cm^2 and 1.18 mg/cm^2 per month, respectively, indicating the very fast build-up in corrosion rate in copper during these months, compared to the other metals.

No further corrosion appeared to take place in either brass or copper after the fourth month of exposure, at all locations. The coefficients of regression “R^2” for the regression equations ranged from as low as 0.28 for mild and stainless steel to 0.61 for copper, indicating much of the variations in the data are due to some variables not included in the analysis [121].

Otsuki performed multiple regression analysis with data collected from 95 piers and concluded that the major factors of deterioration can be age, weight of the vehicles, the frequency of strong wind and waves, in spite of the poor coefficient of regression [112]. The factors were years from the construction (X1), the weights of the vehicle on the pier (X2), the effect of the wind (X3), and the effect of the wave (X4). The results of the regression analysis are shown in Table 2.27.

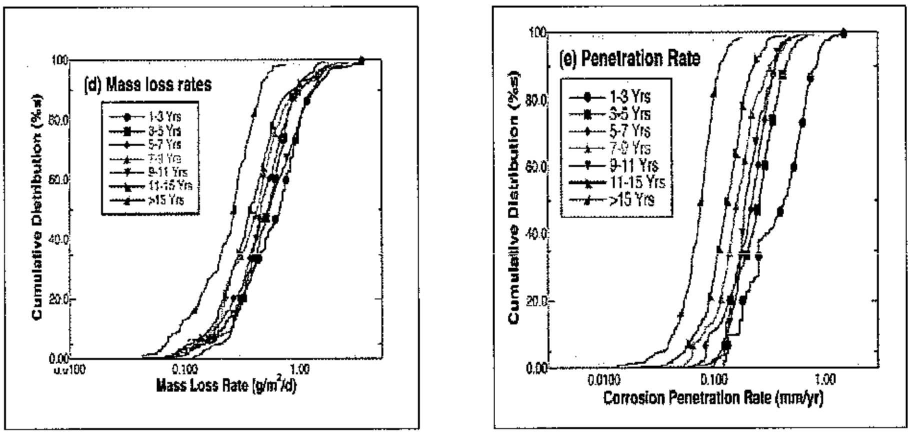
Table 2-20 The results of regression analysis (normalized)[112]

Dependent variables	Linear Regression	Coefficient of regression
Rank of deterioration	Y=0.581X1+0.317X2-0.173X3-0.090X4	0.376
Amount of cracks per unit length of the facility	Y=0.113X1+0.494X2+0.264X3_0.139X4	0.437
Amount of deterioration per unit length of the facility	Y= 0.142X1+0.494X2+0.260X3+0.091X4	0.411
where: X1: the age, X2: the weight of vehicles (by weight), X3: the frequency of strong wind (more than 10m/s), X4: the influence of waves		

Dawn et al. conducted a research which involved the formulation, calibration, and validation of models that show the effects of the environment on corrosion for four materials (carbon steel, zinc, copper, and aluminum) and two types of specimens (flat and helix)[113].

The models were formulated with a structure that yields rational effects for four environmental variables: time-of-wetness, sulfur dioxide, salinity, and temperature. The prediction accuracy of the models was assessed using goodness-of-fit statistics. Both calibration and validation suggest that the environmental components of the models can be used with other time-dependent corrosion models to assess the effects of variation in environmental conditions.

Richard conducted the analysis of pipeline steel corrosion data from NBS (NIST) between 1922- 1940 and relevance to pipeline management [114]. The data from the original NBS studies were analyzed using a variety of commercially available software packages for statistical analysis. The emphasis was on identifying trends in the data that could be exploited in the development of an empirical model for predicting the range of expected corrosion behavior for any given set of soil chemistry and conditions. The cumulative distribution functions examining the effects of alloy composition and exposure time on the measurement is shown in Figure 2.10.



(a)Mass Loss for different Retrieval Periods

(b) Corrosion Penetration Rates for different retrieval Periods

Figure 2.10 Cumulative distribution functions examining the effects of alloy composition and exposure time on the measurement [114]:

It can be seen that the corrosion penetration rate tends to slow to a much greater extent with exposure time than the mass loss rate as shown in Figure 2.9.

This indicates that the corrosion penetration rate is being limited by the mass transport of cathodic reactants or anodic products through the corrosion products building up at the pit while the rate limiting processes governing the mass lost are not facing the same restrictions.

It is concluded that equations for the estimation of corrosion damage distributions and rates can be developed from these data but these models will always have relatively large uncertainties resulting from the scatter in the measurements due to annual, seasonal and sample position dependent variation at the burial sites [114].

2.13.2 Theory of Multiple Linear Regression

Multiple linear regression (MLR) is a method to model the linear relationship between a dependent variable and one or more independent variables.

The Model equation expresses the value of the predictant variable as a linear function of one or more predictor variables and an error term and is of the form [115]-[119]

$$y_i = b_0 + b_i x_{i,1} + b_2 x_{i,2} + \ldots + b_K x_{i,K} + e_i \tag{2.20}$$

where

$x_{i,K}$ = value of kth predictor in year i; b_0 = regression constant; b_K = coefficient on the kth predictor; y_i = predictand in year I; e_i = error term.

The above model is estimated by using least squares, which yields parameter estimates such that the sum of squares is minimised.

The error term is unknown because the model is unknown. When the model has been estimated, the regression residuals are defined as

$$\hat{e}_i = y_i - \hat{y}_i \tag{2.21}$$

where the y terms are observed value of the predictant in year I and predicted value of the predictant in year *i* respectively. The residuals measure the closeness of fit of the predicted values and actual predictant in the calibration period. An algorithm for estimating the regression equation ensures that the residuals have a mean of zero for the calibration period. The variance of the residuals measures the “size” of the error, and is small if the model fits the data well.

MLR is based on least squares. The model is fit such that the sum of squares of differences of the observed and predicted values is minimised. The model creates a connection in the form of a straight line that best approximates all the individual data points. The dependent variable and the independent variable are called the predictant and predictors respectively. The regression estimators are optimal in the sense that they are unbiased, efficient and consistent. Unbiased means that the expected value of the estimator is equal to the true value of the parameter [120]. Efficient means that the estimator has a smaller variance than any other estimator [120]. Consistent means that the bias and variance of the estimator approach zero as the sample size approaches infinity [120]. A multiple linear regression model is based on several assumptions [120].

a. Linearity: the relationship between the predictand and the predictors is linear. If the relationships are non linear, there are two recourses namely (1) Transform the data to make the relationships linear or (2) Use an alternative statistical model (e.g., neutral networks, binary classification trees). Scatter plots should be checked as an exploratory step in regression to obtain possible departures from linearity.
b. Non stochastic: the errors are uncorrelated with the individual predictors which can be checked using scatter plots of the residuals against individual predictors.
c. Zero mean. The expected value of the residuals is zero which is guaranteed by the least squares method of estimating regression equations.
d. Constant variance: The variance of the residuals should be constant. A violation of this occurs when the scatter (variance) increases over time or when the error variance changes with the size of the predicted values.
e. Nonautoregression in which it is assumed that the residuals are random or uncorrelated in time.
f. Normality in which the error term is assumed to be normally distributed.

Like the case of simple linear regression and correlation, MLR does not allow us to make causal inferences, but it does allow us to investigate how a set of explanatory variables is associated with a dependent variable of interest. The coefficient relating the explanatory (x) variable to the dependent (y) variable is 0 when there is no relationship between the explanatory variable and the dependent variable. Alternately the coefficient relating the x variable to the y variable is not equal to zero when there is some kind of relationship between x and y[121].

2.13.2.1 Sum of squares terms.

Several regression statistics are computed as functions of the sum of squares terms: There are normally observed in a regression output from EXCEL or SPSS. SSE is the residual (or error) sum of squares.

$$\text{SSE}=\sum_{i=1}^{n}\hat{e}_i^2 \text{ sum of squares, error} \tag{2.22}$$

$$=\sum_j^n (r_j - r_{avg})^2 \tag{2.23}$$

$$=\sum_j (r_j)^2 \tag{2.24}$$

Since the expected value of residual r_{avg} is assumed to be zero, SST is the sum of squares of deviation of the experimental values of dependent variance y_i from its average value or SST is the sum of the deviation from its average which different is a constant.

$$\text{SST}=\sum_{i=1}^{n}(y_i - \bar{y})^2 \text{sum of squares, total} \tag{2.25}$$

SSR is the sum of square of deviation of the SST of y_i predicted by regression model values of the dependent variable y from the average experimental value $y_{i\,avg}$.

$$SSR = \sum_{i=1}^{n}(\hat{y}_i - \bar{y})^2 \text{ sum of squares, regression} \tag{2.26}$$

n= sample size (number of observations in calibration period)

2.13.2.2 Coefficient of determination

The explanatory power of the regression is summarized by its "R-square" value, computed from the sums of squares terms as:

$$R^2 = \frac{SSR}{SST} = 1 - \frac{SSE}{SST} \qquad (2.27)$$

R^2 also called the coefficient of determination is often described as the proportion of variance described by regression [122]. The relative sizes of the sum of squares terms indicate how good the regression is in terms of fitting the calibration data. If the regression is a total failure, the sum of squares of residuals equals the total sum of squares, no variance is accounted for by regression, and R^2 is zero [123].

The sum of squares terms and related statistics are summarized in Table 2.28 (Analysis of Variance (ANOVA)):

Table 2-28 ANOVA table [123]

Source	df	SS	MS
Total	n-1	SST	MST= SST/ (n-1)
Regression	K	SSR	MSR = SSR/K
Residual	n-K-1	SSE	MSE=SSE/(n-K-1)

where:

n= sample size; K-= number of predictors in the model; Source = source of variation; SS= sum of squares term; df= degree of freedom for SS term; MS= mean squared terms; SSE = sum of squares, error; SST = sum of squares, total; SSR= sum of squares, regression; MST=Total mean square; MSR= Regression mean square; MSE= Residual mean square

It should be noted that SST = SSE + SSR.

The letters in Table 2.26 are described below. MST is the total mean square or total variance given by $\frac{SST}{n-1}$ where the (n-1) is the degree of freedom. SST has only one constant (parameter b_o in equation below). n is the number of observation.

The regression mean square (MSR) or regression variance is given by:

$$MSR = \frac{SSR}{k} = \frac{SSR}{p+1} \tag{2.28}$$

which had k= p+1 parameters (one per each variable out of p variable total plus intercept).The number of degree of freedom in this case is the. difference between the total number of degree of freedom (df_t) and number of degree of freedom for residual (df_e).

$$df_R = df_F - df_E = (n-1) - (n-k) \tag{2.29}$$

$$= k-1 = p \tag{2.30}$$

MSE is Residual (error) mean square or error variance. SSE is with the random error variance. SSE is associated with the random error the regression model which has k=p+1 parameters. It means that there are k constants and number of degree of freedom is

$$df_E = n-k \tag{2.31}$$

The mean squared terms are the sums of squares terms divided by degrees of freedom [120]. The residual mean square (MSE) is the sample estimate of the variance of the regression residuals [120], [123].

The population value of the error term is also written as δ_e^2 while the sample estimate is given by

$$s_e^2 = MSE \tag{2.32}$$

2.13.2.3 Testing of the significance.

F ratio estimates the statistical significance of the regression equation. F- Ratio takes into account the degrees of freedom, which depend on the sample size and the number of predictors in the model [120][123]. A model can have a high R^2 and not statistically significant if the sample size is not large compare with the number of predictor in the model. The F- ratio is given by:

$$F = \frac{MSR}{MSE} \quad (2.33)$$

In order to work with this model there are requirements about the behaviour of the error term. $R^2 = 1$ is a 'perfect score', obtained only if the data points happen to lie exactly along a straight line; $R^2 = 0$ is perfectly lousy score, indicating that x_i is absolutely useless as a predictor for y_i [123], [124]. The sum of squared (SSR) is to measure the discrepancy between the data and an estimation model. A small SSR indicates a tight fit of the model to the data.

The Pearson correlation lies between -1 and 1. Values near 0 means no (linear) correlation and values near ± 1 means very strong correlation [125]. Table 2.29 gives a guideline on the strength of the linear relationship corresponding to the correlation coefficient value [126].

Table 2-29 Strength of Linear Relationship [126]

Correlation Coefficient Value	Strength of linear relationship
At least 0.8	Very strong
0.6 up to 0.8	Moderately strong
0.3-0.5	Fair
Less than 0.3	Poor

The model summary table provides the R and R^2 value. The value of R represents the degree of correlation. The R^2 value indicates how much of the dependent variable can be explained by the independent variables. The ANOVA table indicates the statistical significance of the regression noted that was applied. If the value given in the "Sig" column is less than 0.05, it indicates that overall the model applied is significntly good enough in predicting the outcome variable [127].

2.14 Types of Steels in Offshore Structures

The steel used in offshore structure shall comply with the general requirement of the standard and with the specific requirement of the grade concerned. The design and engineering practise for weldable structural steels for fixed offshore structure stated in Petronas Technical Standards classified the materials into 4 groups [25].

A. Type 1 Steel: Primary Structural Steel – High strength

Primary structural steel (high strength) is steel with yield strength of 344.7 MPa and over and used in members essential to the overall integrity of the structure and for other structural members of importance to the operational safety of the structure.

B. Type 2 Steel: Primary Structural Steel - High Strength with Through Thickness Properties.

Primary structural steel (high strength) with through thickness properties, is steel with a yield strength of 344.7 MPa and over and used in members essential to the overall integrity of the structure, where stress concentrations are high and where the stresses in the through thickness direction may lead to lamellar tearing.

C. Type 3 Steel: Primary Structural Steel- Mild Steel

Primary structural steel (mild steel) is steel with yield strength between 248.2 MPa and 344.7MPa and used in members essential to the overall integrity of the structure and for other structural members of importance to the operational safety of the structure.

D. Type 4 Steel: Primary Structural Steel- Mild Steel with Through Thickness Properties.

Primary structural steel (mild steel) with through thickness properties is steel with a yield strength between 248.2 MPa and 344.7MPa and used in members essential to the overall integrity of the structure, where stress concentrations are high and where the stresses in the through thickness direction may lead to lamellar tearing.

2.15 Corrosion Behaviour of Metals and Alloy

There are differences on the corrosion behaviour of metals and alloys from one zone to another. The carbon and low alloy steels do not have satisfactory performance in splash zone. Anderson and Ross [128] had found that the austenitic grades performed much better than martensitic and ferritic grades. Austenitic is metallic non-magnetic solid solution of iron and an alloying element. The martensitic is a very hard form of steel crystalline structure. In splash zone, carbon steel is less resistant than Ni, Cu and P alloyed steels. Besides that, it was found that Mn, P and Al had measurable influence on corrosion rates of low carbon steels under tidal exposure. The rate of attack in splash zone was much higher than the atmosphere and deep submerged zone after 5 years exposure test [129].

The laboratory immersion test technique was used to conduct the experiment. Rectangular test specimens of different alloys with 50x20x2 mm dimension were utilized in the experimental work. The specimens were exposed to seawater under different levels. The test specimens were abraded on 400 grit SiC paper to remove the corrosion by product. Weight loss coupon method technique had been used to determine the corrosion rates [129].

The corrosion rates of the specimens at semi submerged location for all the tests are higher than the other locations. The most affected area in test specimens was found at water line zone. This attack could be due to the formation of differential aeration cell. Due to low oxygen solubility in water the oxygen concentration will be higher above the water surface.

The carbon steel 304SS and 316L SS have been markedly affected by water line corrosion. With increase of nickel content in copper base alloys the resistance to water line corrosion increase. Titanium addition to Incoloy 825 has beneficial effect at semi submerged location in minimizing the pitting depth. Incoloy 825 is a nickel-iron-chromium alloy with additions of molybdenum, copper and titanium to provide exceptional resistance to various corrosive environments [128].

2.16 Summary

The purpose of this chapter is to review the relevant literature on corrosion and emphasize the key matters. Studies on corrosion allowance in Malaysia for offshore steel structures have not been systematically undertaken nor have they been reported in literature. There are a number of studies which indicate that corrosion is a complex and unpredictable process. The prediction of the likely corrosion loss of material is still rather simplistic and not well developed despite some quite extensive, long term experimental test programs [11]. The unpredictable condition of the corrosion progress and the uncertainties related to material and environment properties make the nature of corrosion complex. Thus, the average value of the corrosion growth rate may be miscalculated.

The current study which collects real inspection data will enhance the knowledge of researchers on the subject of corrosion. It is vital to gather the assessment systematically and carry out analysis on inspection data, and develop practical guidelines. The corrosion analysis is an incorporating empirical model based on field data study and taking account into the parameters affecting the data to obtain the best outcome of corrosion assessment. All these factors will be taken into account in this project to achieve the optimum results.

Since the composition of different elements in the test specimen affects the rate of corrosion, this will be taken into account in this project. The test specimens used will be chosen according to the requirements in Petronas Technical Standard.

CHAPTER 3

METHODOLOGY

3.1 Introduction

Corrosion is a major problem affecting the useful life of marine and offshore structures. Due to very large replacement costs, there is increasing emphasis to maintain existing structures in service for longer time. Thus there is interest to predict corrosion rates at a location. This work measures the rates of corrosion in type 3 steel at the coastal area of Lumut using corrosion coupons kept immersed in sea water. The objectives of the work have been stated in Chapter 1. The methodology to achieve the objectives consists of the following:

1. Fabrication and set up of the experiment for determination of marine corrosion rates of type 3 steel at Lumut.
2. Collection and processing of corrosion coupons at three months interval over a period of 2 years.
3. Chemical Cleaning of Coupons Using ASTM G1 Provision.
4. Determination of the Standard Deviation of Percentage Weight Loss in corrosion coupons.
5. Determination of climatic parameters at Lumut.
6. Determination of chemical composition of type 3 steel coupons obtained from fabricators.
7. Analysis of the data.

These are explained in detail in the following sections.

3.2 Fabrication and Set Up of the Experiment for Determination of Marine Corrosion Rates of type 3 steel at Lumut.

This part explains the step-by step procedures to set up the experimental work at Boustead Shipyard, Lumut.

3.2.1 Fabrication of Coupons and Frames.

The corrosion loss has been obtained under field exposure conditions. Laboratory experiments mainly use artificial seawater in which it is difficult to generate the biotic marine conditions. The experiment is confined to corrosion in relatively shallow seawaters at Lumut, Perak. The depth is not expected to have huge impact on corrosion loss and microbiological effect is expected to be of importance.

Corrosion coupons are inexpensive methods for monitoring the corrosion rate in any system or structure effectively (Figure 3.1). The reliability of the data depends very much on the surface finish, coupon placement, and test duration.

Figure 3-1Different types of Corrosion Coupons

Corrosion coupon testing is an in-line monitoring technique where coupons are placed directly in the process stream and extracted for measurement. The monitoring technique gives a straightforward measurement of metal loss that allows obtaining the general corrosion rate and the results are independent of the phase of the environment in which the measurement is performed. There are many advantages in corrosion coupon testing. It is simple and direct principle, which provides specimens for post test examinations. It also allows comparison between different alloys and inhibitors. There are limitations in using corrosion coupon testing because it measures only the average corrosion rate during the time of exposure. Besides this, the corrosion rates can only be obtained after coupon removal and short exposure period can yield unrepresentative corrosion rates especially for alloys that form passive films such as stainless steels.

ASTM G311 [130] recommends minimum exposure time in hours as:

Exposure with hours = 2000/ Expected corrosion in mpy........................(3.1)

This if the corrosion rate of one mil per year (0.001 inches) is expected, the minimum recommended exposure time would be 2000 hours or 83 1/3 days. The corrosion rates may be higher under short-term exposure (15 to 45 days) compares to long-term exposures [130]. Longer exposures (60 to 90 days) are required to develop bacterial fouling on the coupons [129]. In this case, this experiment is conducted for 2 years duration starting March 2010 until March 2012.

The surface finish of the coupons affects the accuracy of the results. Many coupons are polished on aluminium oxide or silicon carbide abrasive paper, thus contaminants imbedded in the coupon, modifying the chemistry of the surface. In this case, Sample 1 and Sample 2 undergo a finishing technique by using double disc grinders to minimize the contamination of the coupon surface.

Experimental Set up: The experiment was conducted at BOUSTEAD Naval Shipyard Sdn. Bhd. in Lumut. This site was classified as a marine-industrial site. It is a highly industrial area, which is located near the sea coast, thus it is a combination of both marine and industrial environments. Type 3 steels were used in this study. Each corrosion coupon is pre-weighed to an accuracy of two decimal places. The corrosion coupons were positioned on 3 different positions, atmospheric zone, splash zone and fully immersed zone. The tests were carried out during the period 2010-2012. The corrosion coupons are then removed every 3 months and sent to University Teknologi

Petronas laboratory. They were cleaned in respective pickling solutions as described in the ASTM norms G1, dried and weighed again [131].

The coupons will be typically photographed as received, cleaned of any attached debris and deposits, visually inspected, dried and re-weighed, and then photographed again to show surface conditions. The corrosion rate of the coupon is based upon the weight of material lost over its time in service. The set-up of the experiment is shown in Figure 3.2 and Figure 3.3.

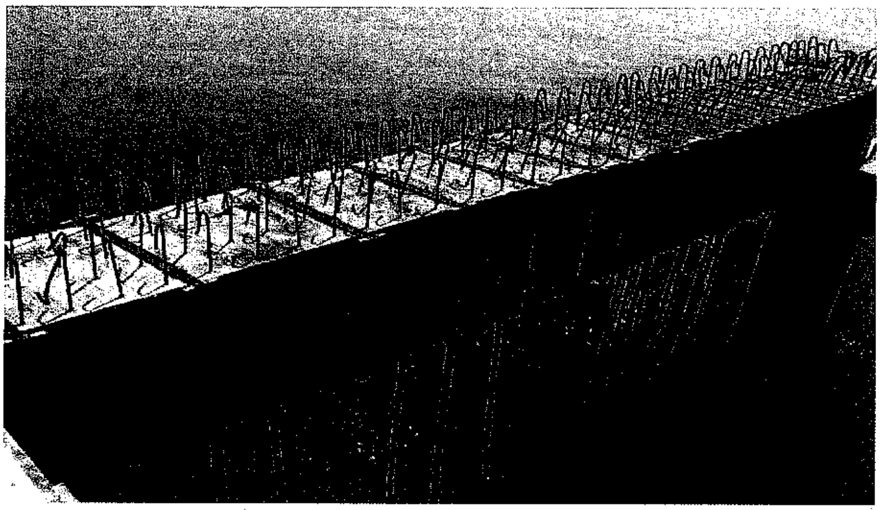


Figure 3-2 Boustead Naval Shipyard Sdn. Bhd. -Beam with Frames and Corrosion Coupons.

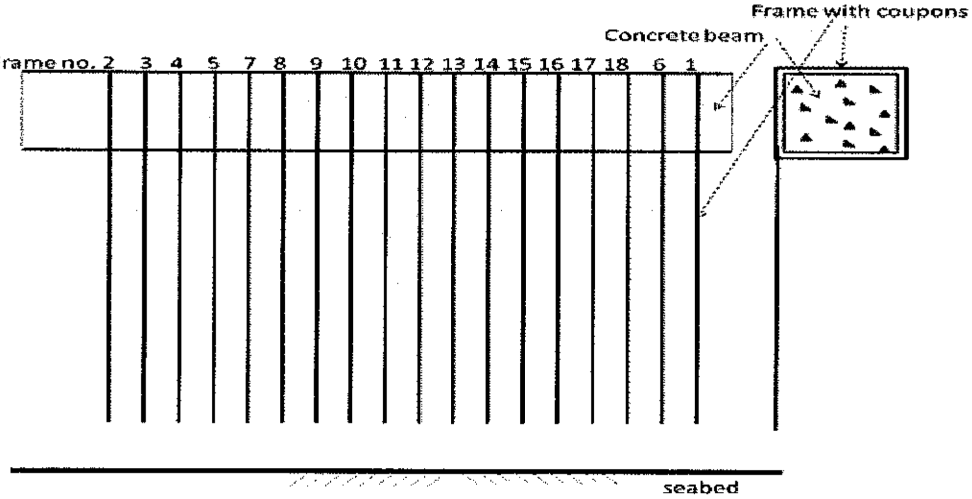


Figure 3-3Experimental Set Up for Measuring Corrosion Rate

Exposure locations play an important role in determining meaningful results. The Boustead Shipyard Sdn. Bhd. was selected to set up the experiment because it is a safe and secure location. This ensures that the set-up of the experiment would not be tampered. Besides that this area meets the requirements to conduct this experiment simulating the offshore structural condition eg. fully immersed zone, splash zone and atmospheric zone.

3.2.2 Experiment Procedure

The experimental procedure is explained step by step as follows.

1. Fabrication of two sets of corrosion coupons of Type 3 Steel which consist of mild Steel from two different sources (namely Japan and China) and hence will have varying chemical compositions.
2. Each of the corrosion coupons are stamped with number for identification purposes.
3. At the atmospheric and the fully immersed zone, 73 mm strip coupons are installed. The dimension of the corrosion coupons will be ~73x22x3.8mm with one mounting hole.
4. At the splash zone, 152 mm strip coupons are installed since the tide level is likely to fluctuate more than 76 mm. The dimensions of the 152" strip coupon are ~152mm x 22mm x 3.8mm.
5. Four coupons are placed on each zone; atmospheric, semi-submerged and totally submerged zones. Metal to metal contact with coupons are eliminated by placing rubber, non conductive material to prevent galvanic effects. The disposition of the four coupons is shown in Figure 3.4.
6. The samples are then removed every 3 months for chemical cleaning to obtain the results.

7. The corrosion coupons are cleaned to remove the corrosion by-product by scraping with sand paper and by pickling.

8. The rate of corrosion loss was obtained as the average of three/four specimens for each exposure period.

9. Weight loss of coupon method will be used to determine the corrosion rates.

10. The overall error from this experiment is estimated at ± 1%.

11. The results are compared with the recommendations of the code.

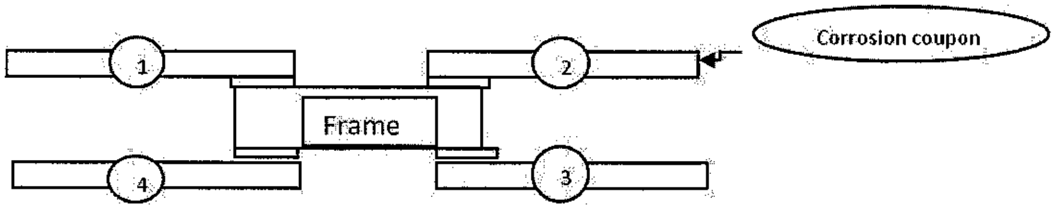


Figure 3-4Disposition of the four corrosion coupons placed at each zone – Plan View at One Level.

Appendix A shows the process of the fabrication and installation of corrosion coupons and frames displayed in pictures.

3.3 Collection and Processing of Corrosion Coupons at Three Months Interval over a Period of 2 years

The samples are collected every three months and cleaned. The method for cleaning corrosion Coupons after collection is explained below.

Sample 1 and sample 2 collected are rinsed with distilled water; air dried and is placed in a sealed bag. Plastic bags treated with vapour phase corrosion inhibitors are useful. A duplicate uncorroded corrosion coupon should be cleaned by the same procedure being used on the corroded coupons to obtain the mass loss of the base metal. The extent of metal loss causing from cleaning can be used to correct the corrosion mass loss.

Chemical cleaning method includes immersion of the corrosion coupons in a particular solution that is catered to get rid of the corrosion products with minimal dissolution of any base metal. Chemical cleaning is often followed by light brushing or ultrasonic cleaning in reagent water to remove loose products.

3.3.1 Chemical Cleaning of Coupons using ASTM G1 Provision

1. The corrosion coupons are cleaned in a mixture of 1000 mL hydrochloric acid (HCl), 20g antimony trioxide (Sb_2O_3), 50g stannous chloride ($SnCl_2$) and at the same time the mixture are stirred vigorously for 25 min at 23°C. Longer times may be required in certain instances.

2. The reagent water is mixed with 50g sodium chloride (NaOH) and 200g granulated zinc to make a mixture of 1000mL at 90°C. Corrosion coupons are submerged in the mixture for 40 minutes. Caution should be exercised in the use of any zinc dust since spontaneous ignition upon exposure to air can occur.

3. The reagent water is mixed with 200g sodium hydroxide (NaOH), 20 g granulated zinc to make another 1000 mL mixture. The temperature of the mixture should also be 90°C. The corrosion coupons are cleaned in the mixture for 30 to 40 minutes.

4. 200g diammonium citrate ($(NH_4)_2HC_6H_5O_7$) is added into the reagent water to make a 1000mL mixture. The corrosion coupons are cleaned in the mixture for 20 min at 75 to 90°C. Depending upon the composition of the corrosion product, attack of base metal may occur. 500mL of hydrochloric acid (HCl, sp gr1.19), 3.5 g of hexamethylene tetramine are mixed with the reagent water to make 1000mL mixture. Coupons are neutralized in the mixture for another 10 min at 20-25°C. Longer time may be required in certain instances.

5. Lastly, the corrosion coupons are neutralized in the molten caustic soda (NaOH) with 1.5-2.0 % sodium hydride (NaH) for 20 min at 370°C.

Appendix B shows a flow chart of the experimental work.

3.4 Determination of the Standard Deviation of Percentage Weight Loss in Period of Two Years.

This part explains the statistical analysis with the main objective to determine the accuracy of the data collected by a 100 (1-α) % confidence interval for the weight after exposure mean of the form:-

$$Y \pm Z\alpha/2 \ \hat{SE}(y) \qquad (3.2)$$

where Zα/2 refers to the value that is exceeded with probability α/2 for the standard normal distribution. This is an approximate confidence interval for the data from this distribution, based on the result that data means tend to be normally distributed even when the distribution being sampled is not. The interval is valid providing the distribution being sampled is not very extreme in the sense of having many tied values or a small proportion of very large or very small values [132].

The mean of the weight loss can be obtained as follow:-

$$\text{Mean} = \frac{\text{Sum of Initial Weight of Sample 1} - \text{Sum of Final Weight of Sample 1}}{\text{Number of Sample}} \quad \ldots\ldots. (3.3)$$

$$\textit{Standard Deviation} = \sqrt{\frac{\{\textit{Sum (Weight Loss Sample} - \textit{Mean)}\}^2}{\textit{Number of Sample}}} \quad \ldots\ldots\ldots\ldots\ldots (3.4)$$

3.5 Determination of climatic parameters at Lumut

The data collection is vital in this study. There are many parameter involved in this studies which include the mean relative humidity and mean temperature at Lumut, Perak since this experiment was conducted at Lumut, Perak. The mean relative humidity and mean temperature was obtained from Malaysia Meteorology Department, for the station at Sitiawan (04°13' N 100°42' E) for a period of 8 years (2005-2012).

3.6 Determination of Chemical Composition of type 3 steel obtain from fabrictors.

The chemical composition of sample 1 and 2 must be determined accurately in order to ensure the desired metallurgical properties. Thus, sample 1 and 2 were sent to SIRIM QAS International Sdn. Bhd. to determine the alloy and residual elements in carbon and low-alloy steels. Optical Emission Vacuum Spectrometric analysis of Carbon and Low Alloy Steel is the standard test method to obtain the elemental composition. This ASTM standard is issued under the fixed designation E415 [133].

3.6.1 Summary of the Test Method

The most excessively affected element like arsenic boron, carbon, nitrogen, phosphorus, sulphur and tin lie in the vacuum ultra violet region. The air in this entire area absorbs the radiation by creating vacuum in the spectrometer and flushing the spark chamber with argon. A capacitor discharge is formed between the flat, ground surface of the disk specimen and a conically shaped electrode. At a predetermined intensity time integral of a selected iron line, the discharge is disappeared or at a predetermined time, the relative radiant energies or concentrations of the analytical lines are recorded. The duplicate percentage concentration readings for each sample are averaged to obtain the results [133].

3.7 Data Analysis

From the data collected from the experiment, the following analyses are carried out:

3.7.1 Nature of corrosion

Every three months when one frame is removed from the site, photographs of the frame as well as the coupons at different levels /zones are taken. The intensity and nature of marine growth is observed.

The coupons are cleaned according to the procedure and the surface of the coupons is again photographed. The cleaned sample will indicate the type of corrosion predominant at different zones as well as at different time periods.

3.7.2 Directional corrosion and coefficient of variation of corrosion loss

The weight losses in the four samples placed at the same level gives indication of the directional effect of corrosion. The variation in corrosion between samples placed at the same level is also determined at different levels and time periods.

3.7.3 Rate of corrosion

The rate of corrosion is determined as follows. The initial total surface area of the specimen and the mass lost during the test period are obtained. The average corrosion rate is calculated as follows:

$$\text{Corrosion Rate} = (K \times W)/(A \times T \times D) \tag{3.6}$$

where K = a constant, T= time of exposure in hours, A= area in cm^2, W= mass loss in grams, and D= density in g/cm^3

The corrosion rates can be expressed in many units. Using the units in T, A, W and D, the corrosion rate can be calculated in a variety of units with the appropriate value of K as given in Table 2.1.

Corrosion loss can also be determined using the weight loss measurement without taking constant (k) into consideration. This can then be expressed in several ways:

(1) Percent weight change is calculated as:

$$\%\_wt\_change = \frac{Original\_wt - Final\_wt}{Original\_wt} \times 100 \tag{3.7}$$

(2) The metal loss in mm can be calculated using expression

$$Metal\_loss = W \times \frac{0.01}{DA} \tag{3.8}$$

(3) Loss of metal thickness per unit time, given by the following expression

$$mm/yr = W \times \frac{87.6}{DAT} \tag{3.9}$$

W = weight loss in milligrams; D = metal density in g /cm^3; A = area of sample in cm^2; T = time of exposure of the metal sample in hours.

(4) Loss of metal thickness per unit time can be expressed using Engineering Units of mils per year. A mil is one thousandth of an inch.

$$mpy = W \times \frac{534}{DAT} \tag{3.10}$$

W = weight loss in milligrams; D = metal density in g /cm^3; A = area of sample in square inches; T = time of exposure of the metal sample in hours.

(5) Weight loss in milligrams per square decimeter per day (mdd) is given by

$$mdd = W \times \frac{100}{AT} \tag{3.11}$$

where T is the exposure time in days

W = weight loss in milligrams; A = area of sample in cm^2.

(6) Weight loss in grams per square meter per year

$$Wt\_loss(gm/m^2/yr) = mdd \times 36.5 \tag{3.12}$$

The rate of corrosion obtained is also compared with the corrosion rate obtained from experiment at Kuala Terengganu, Malaysia [18].

3.7.4 Analysis of data on climatic parameters at Lumut, Perak

a. Temperature

The records of 24 hour mean temperature was recorded by Malaysia Geological Department since 2005 to 2012. Thus, the temperature was obtained from Malaysia Meteorology Department. The monthly average seawater temperature and atmospheric temperature versus the corrosion rate obtained will be plotted to correlate the effect of temperature towards the corrosion rate for sample 1 and sample 2.

b. Humidity

Atmospheric air is a mixture of dry air and water vapour. Lumut is an industrial and coastal area hence gases such as SO_2, Cl_2 and H_2S and particulates of NaCl and other salts are present [133]. The air humidity is characterized by the indices RH, absolute humidity, moisture content and specific air humidity.

The 24 hour mean relative humidity recorded by Malaysia Geological Department from 2005 to 2012 is available.

c. pH

The pH scale measures how acidic or basic a substance is as shown in Figure 3.5. The pH scale ranges from 0 to 14. A pH of 7 is neutral. A pH less than 7 is acidic. A pH greater than 7 is basic. The concentrations of hydrogen ions and indirectly hydroxide ions are given by a pH number. pH is defined as the negative logarithm of the hydrogen ion concentration.

The equation is:

$$\text{pH} = -\log [H^+] \tag{3.13}$$

$$\text{similarly, pOH} = -\log [OH^-] \tag{3.14}$$

$$\text{and p Kw} = -\log [Kw] \tag{3.15}$$

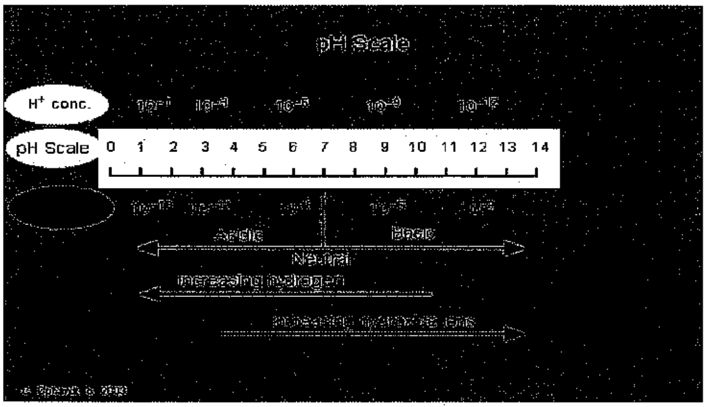


Figure 3-5 pH scale [135]

Digital pH pen was used to obtain the seawater pH. Table 3.1 shows the digital pH pen specification.

Table 3-1 Digital pH Pen Specification

Feature	**Description**
Measuring range	0.0 to 14.0pH
Resolution	0.1 pH
Accuracy	± 0.1 pH(at 20°C/68°F)
Operating temperature	0°C to 50°C(32°F-122°F)

The seawater pH can be measured by turning on the pH pen and immersing the probe end of the pen into the water. The pen is swirled around the seawater to dislodge any air bubbles. A reading can be obtained from the meter. The pH value on the reading is checked and the pen is adjusted so that the reading displays 7.0. The pen is then cleaned by rinsing it under running water. Next is immersed the pen in the seawater to test its pH level. The pen is swirled around the seawater to dislodge air bubbles and ensure a more accurate reading. The value is recorded and the pH pen is removed from the seawater. The pen is washed in running water to avoid cross contamination and prevent incorrect readings.

PH has a variable effect on corrosion. At lower pH, corrosion rate is high due to acidic corrosion, while, at intermediate pH of 8.5 to 12, it drops down due to formation of passive layer and, at higher pH, the corrosion is severe due to caustic embrittlement.

3.7.5 Analysis and interpretation based on the chemical composition of the steel samples.

The chemical compositions of the samples are tabulated in Table 4.9 and Figure 4.18. The chemical compositions of the sample1 and sample 2 are compared. The aim was to see whether there are differences and to see whether this has any effect on the corrosion rate.

1. Analysis of the effect of marine growth on corrosion rates

Fouling on panels was assessed, exposure-wise, in terms of biomass. The biomass was calculated after scrapping off the mass adhered on the metal surface and drying it in an air oven for an hour at 100°C. The equation 3.16 is used to calculate biomass settlement on sample 1 and sample 2.

$$Biomass(g/cm2) = \frac{Wt\_after\_drying\_in\_oven - Wt\_after\_biomass\_removed}{Area\_sample(cm2)} \tag{3.16}$$

Biomass settlement on sample 1 and sample 2 in Lumut seawater for different exposure periods is plotted and shown in Figure 4.20-4.23. It is further attempted to see whether marine growth has any effect on the corrosion rate.

3.7.6 Fitting Regression Models to the Data

The effectiveness and efficiency of statistical data analysis have been greatly enhanced by the availability of excellent computer packages. Typical statistical software among others, includes the Statistical Package for the Social Science (SPSS), Statistical Analysis System (SAS), Minitab and Microsoft Excel. In this study, SPSS and Microsoft Excel have been chosen as the computer programme for data analysis.

(a) Regression using SPSS

Multiple linear regressions was applied to the data to determine the relationship between the corrosion rate, the times of exposures of the coupons, seawater surface temperature, seawater pH, salinity and fouling organism of the coupons.

In the current study, a sample size of 7 has been included in the analysis. The independent variables are fouling load, months, temperature, salinity and pH. The dependent variable is corrosion rate. The variables are entered into spread sheet for regression analysis as shown in Table 3.2.

Table 3-2 Variables Entered

Model	Variables Entered	Variables Removed	Method
1	FL, TEMP, PH, MONTHS, SALINITY[a]	.	Enter

a. All requested variables entered.

b. Dependent Variable: C.R

To perform the regression, click on Analyze\Regression\Linear as shown in Figure 3.6. The corrosion rate is placed in the Dependent box and time of exposure (months) temperature, pH, salinity and fouling load are placed in the Independent box.

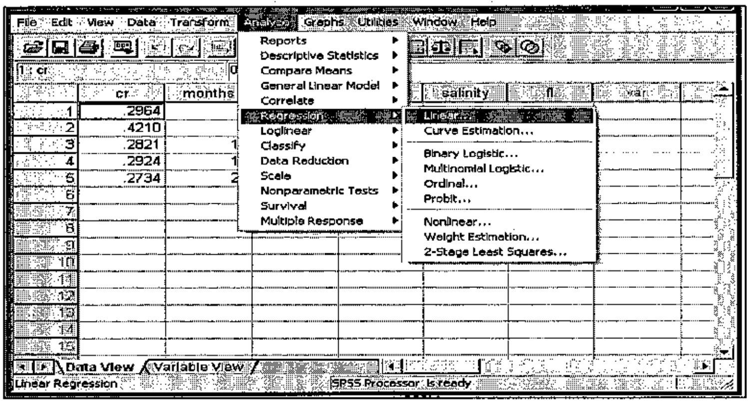
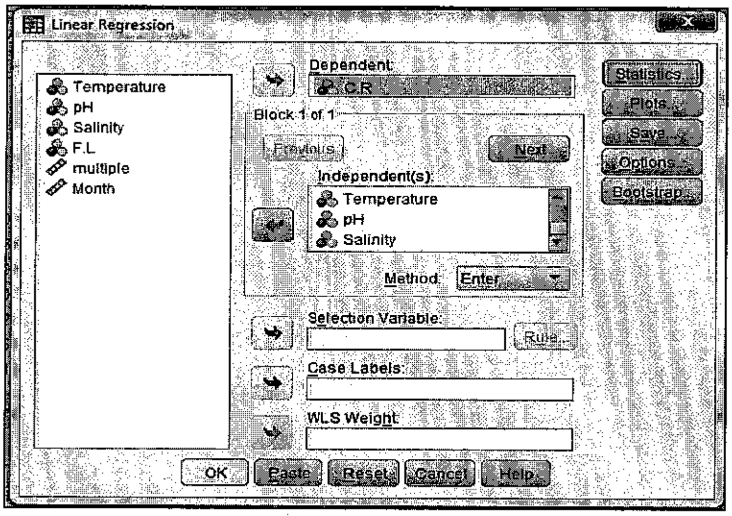


Figure 3.6 Starting the procedure.

The variables are chosen from the list in the variable box. The "CR" which is highlighted is kept in the box labelled Dependent. The pH, salinity, temperature, time of exposure (months) and fouling load are chosen from the list in the variable box and moved into the box called Independent(s) by clicking the arrow. Descriptive statistics option is chosen by clicking the button labelled "Statistic" as shown in Figure 3.7.



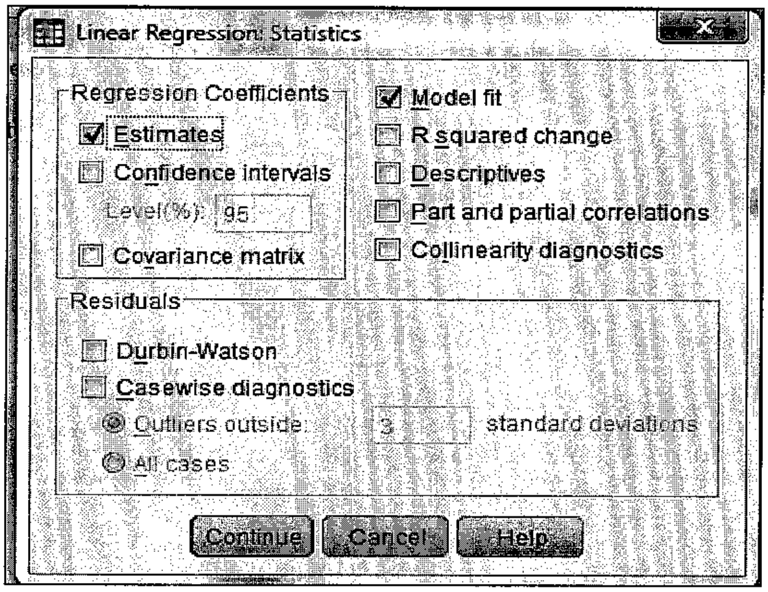
Dependent: C.R

Independent(s): Temperature, pH, Salinity

Method: Enter

Figure 3.7 Linear Regression Input: - "Dependent" and "Independent"

This analysis does not require additional statistics, so the "Continue" button is clicked as shown in Figure 3.8.



☑ Estimates

☐ Confidence intervals

Level(%): 95

☐ Covariance matrix

☑ Model fit

☐ R squared change

☐ Descriptives

☐ Part and partial correlations

☐ Collinearity diagnostics

☐ Durbin-Watson

☐ Casewise diagnostics

● Outliers outside: 3 standard deviations

○ All cases

Figure 3.8 Requesting Statistics

The OK button is clicked to run the Multiple Linear Regression procedure. On the menu bar of the SPSS Data Editor window, Analysze> Correlate>Bivariate is clicked as shown in Figure 3.9. The correlations among the variables are obtained by clicking correlations icon. The Ctrl key is held down to choose the variables.

The arrow button is clicked to add selected variables to the Variables window as shown in Figure 3.10.

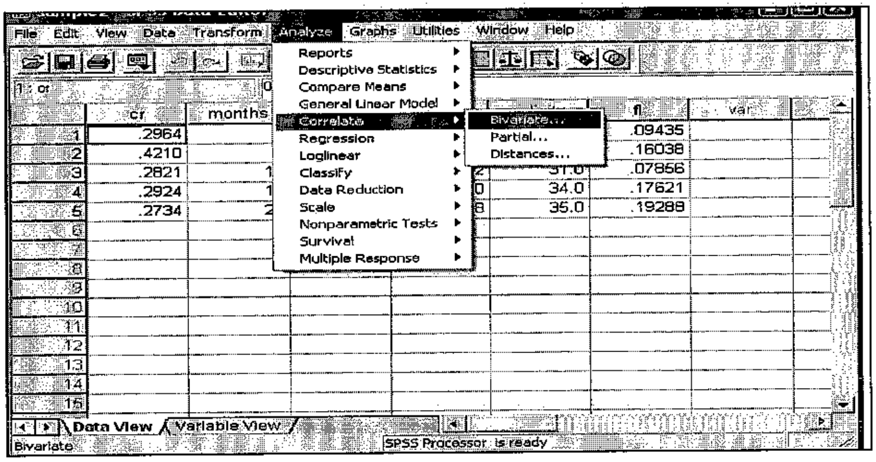
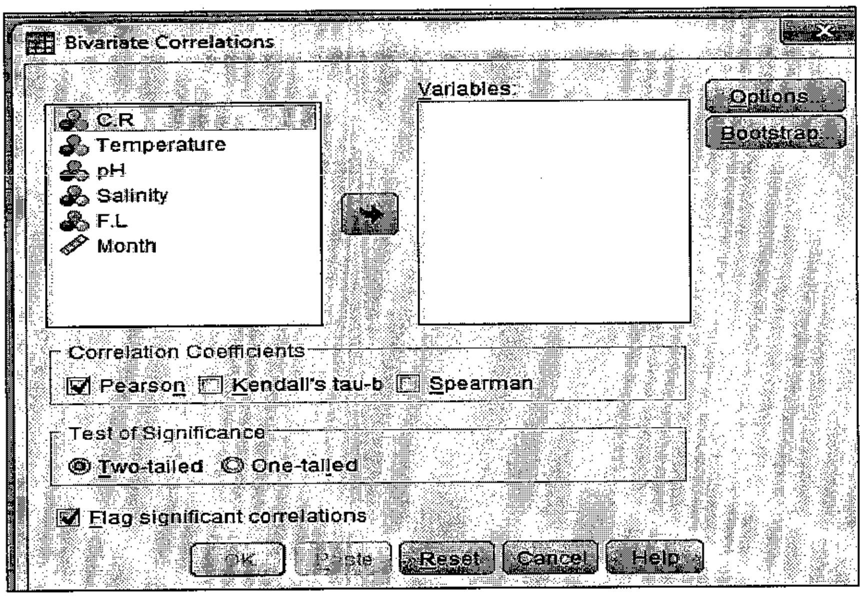


Figure 3.9 Correlation Icon



Correlation Coefficients

☑ Pearson ☐ Kendall's tau-b ☐ Spearman

Test of Significance

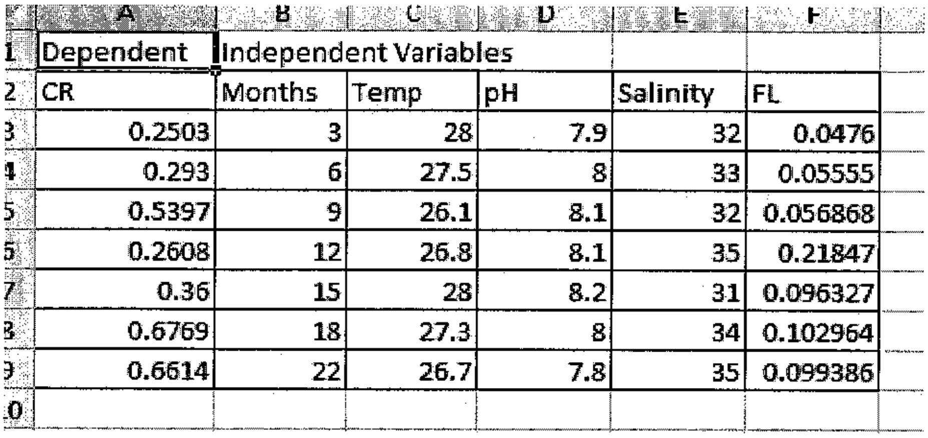
● Two-tailed ○ One-tailed

☑ Flag significant correlations

Figure 3.10 Bivariate Correlation

(b) Regression Using Microsoft Excel

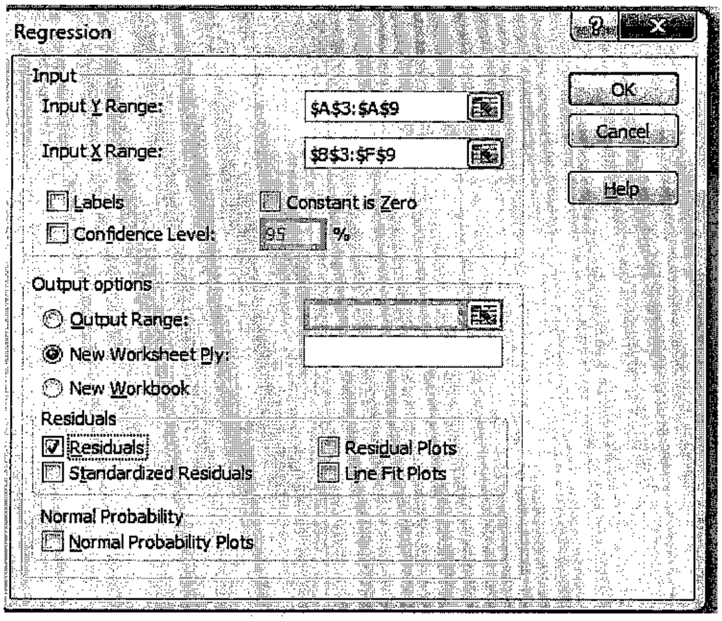
The spread sheet input table for regression analysis is prepared in the following format as shown in Figure 3.11.



	A	B	C	D	E	F
1	Dependent	Independent Variables				
2	CR	Months	Temp	pH	Salinity	FL
3	0.2503	3	28	7.9	32	0.0476
4	0.293	6	27.5	8	33	0.05555
5	0.5397	9	26.1	8.1	32	0.056868
6	0.2608	12	26.8	8.1	35	0.21847
7	0.36	15	28	8.2	31	0.096327
8	0.6769	18	27.3	8	34	0.102964
9	0.6614	22	26.7	7.8	35	0.099386
10						

Figure 3.11Regression Input for Microsoft Excel.

To perform the regression analysis from the Microsoft Excel, Tool\Data Analysis\Regression are clicked and the input dialog box will pop out as shown in Figure 3.12.



Regression

Input

Input Y Range: $A$3:$A$9

Input X Range: $B$3:$F$9

☐ Labels ☐ Constant is Zero

☐ Confidence Level: 95 %

Output options

○ Output Range:

● New Worksheet Ply:

○ New Workbook

Residuals

☑ Residuals ☐ Residual Plots

☐ Standardized Residuals ☐ Line Fit Plots

Normal Probability

☐ Normal Probability Plots

Figure 3.12 Regression Input

The “Input Y range” refers to the spread sheet cells containing the dependent variable Y and the “Input X range” to those containing independent variable X (eg, X_1, X_2, X_3....etc). If we do want to form the model through the origin, leave the “Constant is Zero” box unchecked.

3.8 Summary

The location of the regression output can be selected as another worksheet or a new workbook. These are options for choosing Residual, Standardized Residuals, Residual Plots, Line fit plots and normal probability plots.

The output will be in tabular form in another work sheet and consists of (1) Regression Statistic, (2) ANOVA (Analysis of Variance) and (3) Residual Output. The meaning of these output have been explained in the literature review in section 2.13 and in the Chapter 4 in section 4.3.8 and 4.4.10.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

There is an increasing need to predict corrosion rates in marine and offshore structures due to the increasing number of ageing structures and the high replacement costs. The main aim of the work is to develop time based corrosion model for mild steel under marine exposure using experimental field data. The sub objectives have been stated in section 1.3. The methodology adopted for the work is described in Chapter 3. This chapter presents the results of the study.

Section 4.2: Presents the details of the data collected.

Section 4.3: Presents the results of the data analysis in the following order:-

- 4.3.1 Climate parameters at Lumut.
- 4.3.2 Characteristic of the Seawater at Lumut.
- 4.3.3 Physical Condition of the frames and coupons.
- 4.3.4 Statistical Variation of Corrosion Loss in Samples.
- 4.3.5 Percentage weight reduction, corrosion loss with time and corrosion rate.
- 4.3.6 The Chemical Composition of the samples.
- 4.3.7 Fouling Load.
- 4.3.8 Fitting Multiple Parameter Regression Models to the Data.

Section 4.4: Analysis of the Results and Discussion. In this section, the results presented in section 4.3.1 to 4.3.8 are analysed and discussed. The discussion are presented in the following order.

4.4.1 Climate parameters at Lumut

4.4.2 Marine Water Quality

4.4.3 Analysis of physical condition of coupons.

4.4.4 Standard Deviation of Percentage Weight Loss

4.4.5 Percentage weight loss, Corrosion loss with time and corrosion rate.

4.4.6 Comparison of corrosion rate.

4.4.7 Chemical Composition Analysis

4.4.8 Fouling Load Analysis.

4.4.9 Time Based Corrosion Model

4.4.10 Analysis of the results of the Multiple Linear Regression by SPSS.

Section 4.5: Methods of Increasing Effective Life of Marine Steel Structures.

4.2 Details of the Data Collected.

Climatic data, which includes the monthly variation of temperature and humidity, are collected from Malaysia Meteorology Department for a period of 8 years.

The seawater characteristics are obtained through laboratory analysis. The chemical compositions of sample are obtained from SIRIM QAS International Sdn. Bhd who used the Optical Emission Vacuum Spectrometric Analysis. The corrosion coupons kept at the marine location at Boustead Shipyard, Lumut are collected at three months interval over a period of 2 year to obtain the weight loss data and fouling load data.

4.3 Data and Results of Data Analysis

The details of the data and results of the data analysis are explained in the following section.

4.3.1 Climatic Parameters at Lumut

The monthly variation of temperature and humidity are tabulated below.

4.3.1.1 General

Malaysia, lying between latitudes ½ ° to 7 ° N and longitude 100 ° to 119 ½ ° E, has tropical climate. The average temperature is 27.5 ° C and average rainfall is 2409 mm. The mean relative humidity is 62.6%. Lumut, located on the northwest shores of Peninsula gains importance from the location of Royal Malaysian Navy, Naval shipyard, Marine Terminal, Industrial Park and the various industries located there. The climate at the coast of Lumut can be classified as "marine tropical". This site was classified as a marine-industrial site. It is a highly industrial area, which is located near the seacoast and hence, it is a combination of both marine and industrial environments.

4.3.1.2 Monthly Variation of Temperature and Humidity

Average monthly 24 hours mean temperature and humidity are given in Table 4.1-4.2. The average annual temperature in this area is around 26.1- 28.7°C, average relative humidity 77.9 to 86.3%. The relationship between corrosion rate and relative humidity is shown is Figure 4.1. In this figure, it is to be noted that the variation of RH is continuous where as the corrosion rate values correspond to the times at which the samples are retrieved from the test location.

Table 4-1 Average Monthly 24 Hour Mean Temperature in °C at Lumut, Perak

Year Month	2005	2006	2007	2008	2009	2010	2011	2012
Jan.	27.0	26.8	26.8	27.0	26.3	27.0	26.1	26.7
Feb.	28.2	27.2	27.1	27.0	27.0	28.2	27.3	28.1
Mar.	28.2	27.7	27.5	26.5	26.9	28.3	26.8	27.9
Apr.	28.0	27.4	27.5	27.1	27.7	28.5	27.6	
May	28.0	27.3	28.2	27.5	28.0	28.7	28.1	
Jun.	28.1	27.4	27.7	27.1	28.3	28.0	28.0	
Jul.	27.6	27.5	27.2	26.7	27.4	27.6	27.6	
Aug.	27.7	27.4	27.1	26.8	27.2	28.0	27.1	
Sep.	27.8	26.7	27.3	26.9	27.3	27.5	27.3	
Oct.	26.8	27.1	26.6	26.9	27.2	28.0	27.5	
Nov.	26.5	26.7	26.5	26.9	26.7	27.0	26.9	
Dec.	26.5	27.0	26.3	26.6	27.0	26.1	26.9	
Annual	27.5	27.2	27.2	26.9	27.3	27.7	27.2	

Table 4-2 Average Monthly 24 Hours Mean Relative Humidity in (%)

Year Month	2005	2006	2007	2008	2009	2010	2011	2012
Jan.	83.0	83.6	83.3	84.9	82.4	84.3	84.7	84.4
Feb.	79.3	82.0	79.9	77.9	82.0	81.3	80.1	80.2
Mar.	79.9	81.9	80.3	85.4	84.0	80.1	83.6	82.7
Apr.	81.5	83.7	82.9	84.0	82.4	82.0	81.6	
May	82.0	84.0	79.2	81.9	81.7	83.0	81.4	
Jun.	81.0	81.3	82.4	83.6	79.6	81.6	81.3	
Jul.	80.8	81.0	83.2	84.3	81.7	81.7	79.9	
Aug.	79.4	80.1	82.0	83.3	83.6	80.3	82.5	
Sep.	80.6	84.5	82.0	82.9	83.8	81.7	82.0	
Oct.	84.3	83.5	85.5	83.8	83.9	79.2	82.3	
Nov.	85.9	85.6	85.6	85.6	86.3	84.3	85.3	
Dec.	86.3	84.1	85.1	84.0	84.9	86.1	85.9	
Annual	82.0	82.9	82.6	83.5	83.0	82.1	81.9	

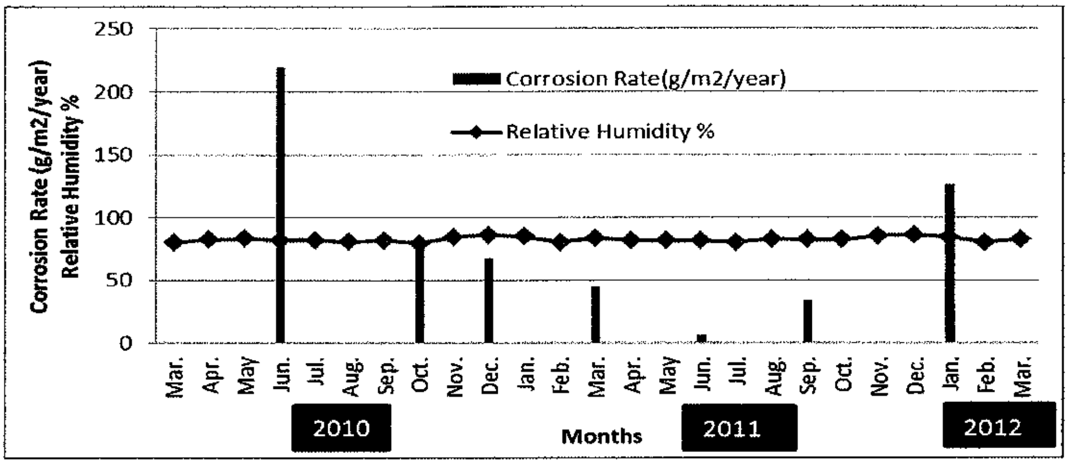


Figure 4-1 Relationship of Average Relative Humidity in % and Corrosion Rate (g/m^2/year) at Atmospheric Zone for the Corrosion Test Period.

4.3.2 Seawater Parameters of the Experiment

The experiment is conducted in the seawater at Lumut, Malaysia over a two year period. The characteristics of seawater are obtained by laboratory analysis (Table 4.3). The density of steel is taken as 7.86g/cc [136].

Table 4-3 Characteristics Of Seawater At Lumut

Characteristic	Minimumm	Maximum
Surface temperature (C)	26.1	28.3
Salinity(ppt)	31	35
pH	8.2	7.8

Table 4.4 shows the percentage by which various parameters exceed the standard values given in column 8 of the table.

Table 4-4 Marine Water Quality Parameters Exceeding Standards (%) for period 2005-2010 of Perak Darul Ridzuan.

Year	2005	2006	2007	2008	2009	2010	Standards (Table 2.10)
1	2	3	4	5	6	7	8
No of Stations	13	13	13	13	7	7	-
No of samples	74	52	66	68	42	14	-
Total Suspended Solid	100	100	66	58	51	54	100mg/L
Oil & Grease	100	12	82	97	69	14	5 µg/L
E-Coli	77.36	64	48	44	20	14	200 E. Coli/100ml
Cadmium	0	0	7	14	54	0	10 µg/L
Chromium	0	0	7	2	60	93	48 µg/L
Mercury	NA	0	0	NA	NA	0	50 µg/L
Lead	36.84	56	24	73	66	0	50 µg/L
Arsenic	0	0	0	0	0	0	50 µg/L
Copper	2.79	0	28	58	100	39	10 µg/L

4.3.3 Physical Condition of the Frames and Coupons

The surface condition of the samples was studied to understand the nature and intensity of corrosion. For the two sets of sample (sample 1 and 2), the observation was done on atmospheric zone, splash zone and immersion zone. Figure 4.2 show the frames of sample 1 on retrieval from the testing area.

At 3 months, the frame was covered mainly by barnacles and at 6 months, the coupons at tidal were densely covered by barnacles, plankton, algae, and bryozoans. At 9 months, the coverage of barnacles, plankton and algae is lesser compared to at 6 months. The nature of the surface of the coupons collected at 6 months did not seem to differ from the coupons collected at 3 months.

At 12 months, bacteria like structures appeared to attach to the surfaces of the tidal and submerged coupons. The bacteria were orange in color. It was difficult to differentiate amorphous inorganic deposits from bacteria. The coupons were covered by barnacles and algae at certain surface area.

At 15 months and 18 months, the surfaces of the coupons were extensively removed, exposing thinner coupon. Thick fibrous materials were entrapped and attached to the coupons. After removing the living barnacles and the corrosion products from samples located at splash zone, the sample 1 and sample 2 surfaces which had been under the bases of the organisms stand out as relatively smooth plateaus surrounded by depressed and pitted areas where corrosion has taken place.

At 22 months, very thick fibrous materials in orange, reddish and greenish colour were entrapped and attached to the samples and it is difficult to be removed at tidal zone. Mussels were attached to the frames located at the immersion zone.

Figure 4.3 show the frames of sample 2 on retrieval from the testing area. At 6 months, the coupon was covered mainly by barnacles and plankton at tidal zone. At 12 months, bacteria like structures appeared to attach to the surfaces of the tidal and submerged coupons. The bacteria were orange in color. At 15 months, dense plankton, barnacles and algae covered the coupons at tidal and submerged zones of the frames. The coupons condition at 18 months was similar to those at 15 months. Some of the coupons exposed were covered with black deposits and some appeared to be in bluish/green deposits. However, the coupons were mostly dull.

At 22 months, a heavy growth in which mussels predominated the lower part of the frame which is the immersion zone. Bacteria/fouling at this zone were bright orange and greenish very soft, covering the sample surface and very easy to remove, which is completely different from tidal zone. Dense plankton and barnacles covered the coupons at tidal zone and it is difficult to be removed.

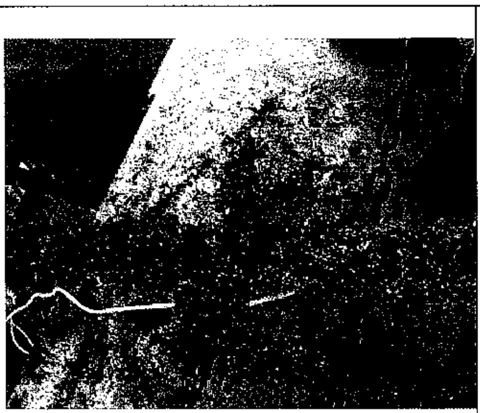
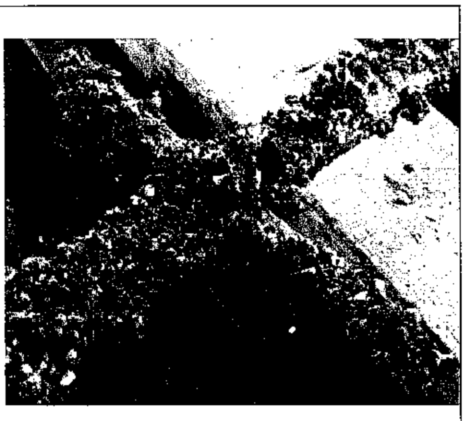
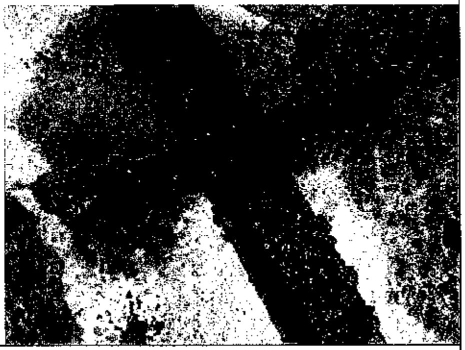
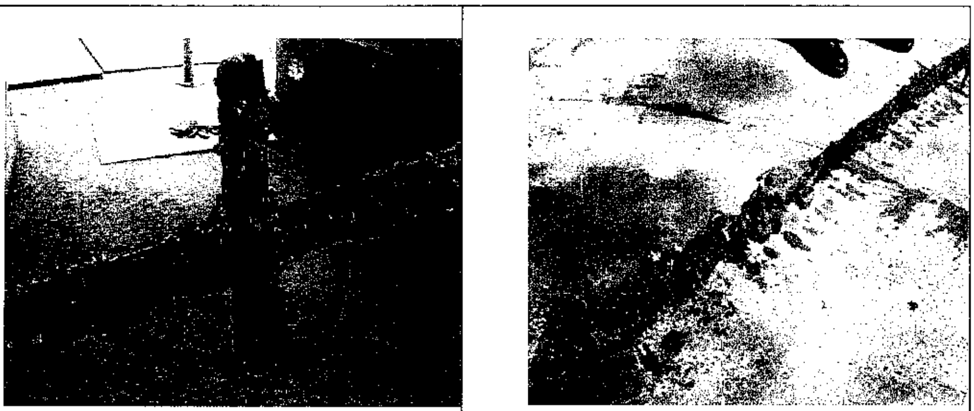
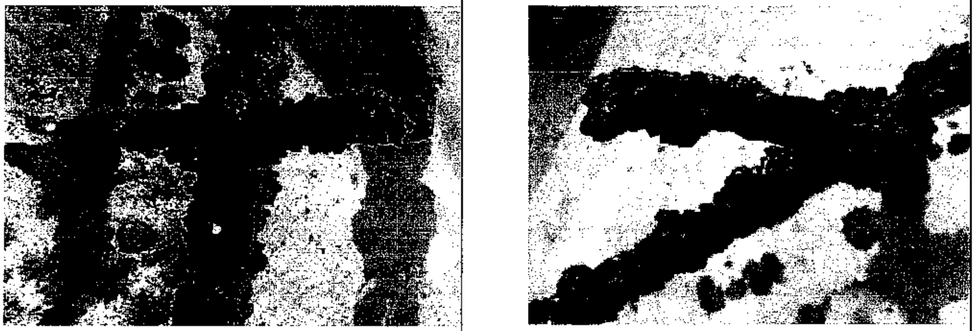
	
June 2010	September 2010
	
December 2010	March 2011
	
June 2011	September 2011
	
December 2011	March 2012

Figure 4-2Frames of sample 1 on retrieval from the testing area at 3,6,9,12,15, 18, 22 and 24 months



September 2010

March 2011



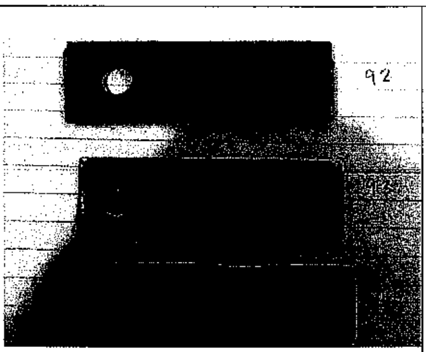
June 2011

September 2011

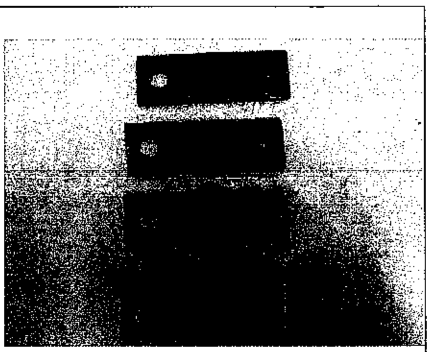
January 2012

Figure 4-3Frames of sample 2 on retrieval from the testing area at 6, 12, 15, 18, and 22 months

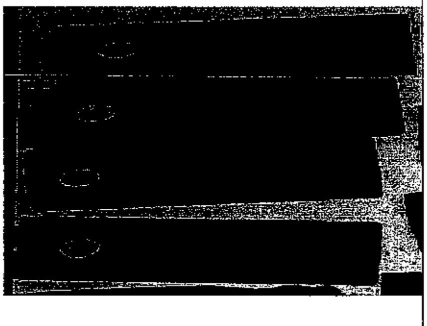
Figure 4.4 shows the sample 1 at atmospheric zone, which have been cleaned of the marine growth.



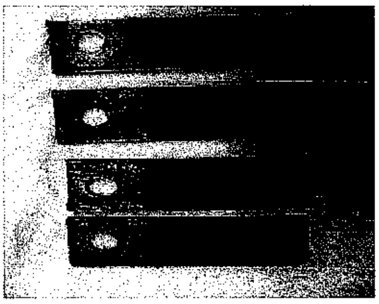
June 2010



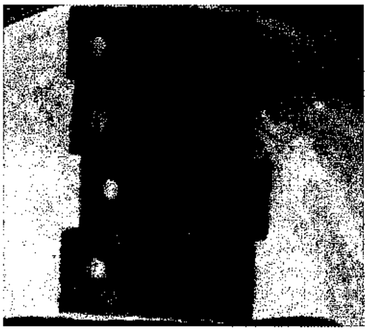
September 2010



December 2010

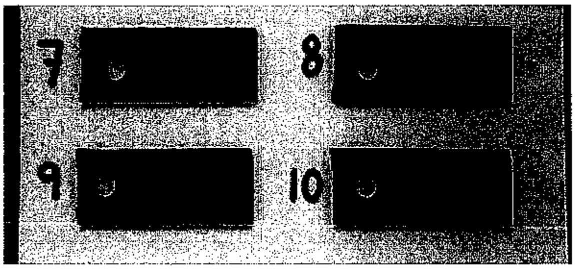


March 2011



June 2011

September 2011

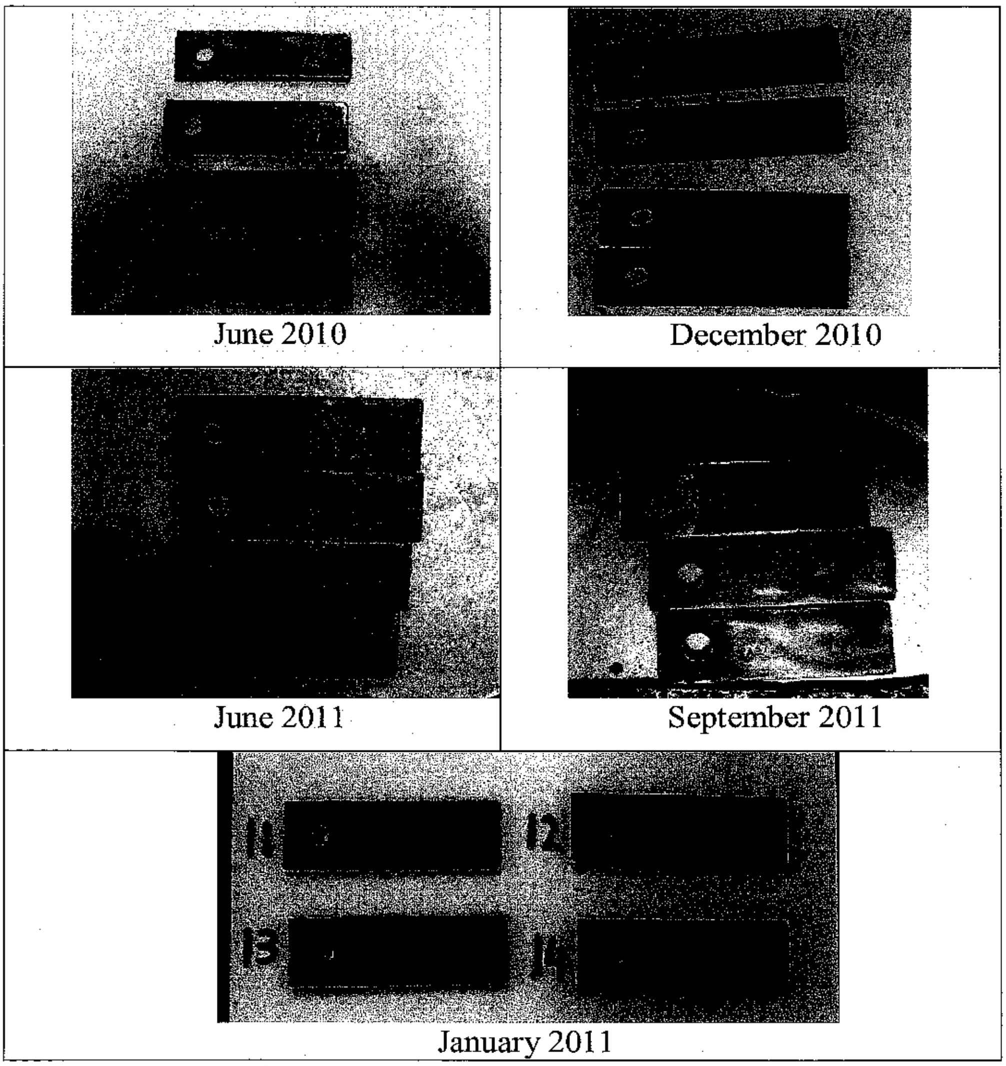


January 2011

Figure 4-4Cleaned coupons of sample 1 at Atmospheric zone at 3, 6, 12, 15, 18 and 22 months

At the atmospheric zone, the coupons of mild steel 1 exposed were golden/brown. Other predominant features observed include rust-like deposits scattered throughout the coupon surface. A lesser amount of deposits formed around the punched hole than on the surface exposed to the environment. The surfaces of the coupons showed that the corrosion pattern at atmospheric is essentially free from pitting and showed signs of uniform corrosion.

Figure 4.5 shows the coupons of sample 2 at atmospheric zone which have been cleaned of the marine growth. The coupons were golden brown with brown deposits. No pitting corrosion is observed.



June 2010

December 2010

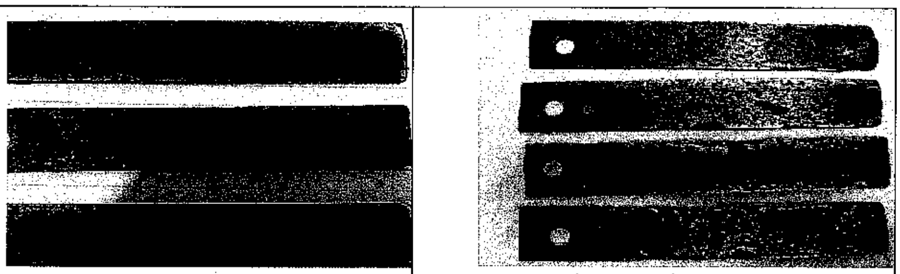
June 2011

September 2011

January 2011

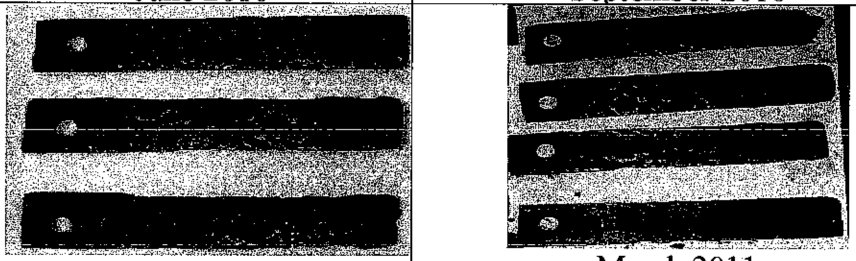
Figure 4-5Cleaned coupons of sample 2 of Atmospheric zone at 6, 12, 15, 18 and 22 months

Figure 4.6 shows the sample 1 at splash zone which have been cleaned of the marine growth.



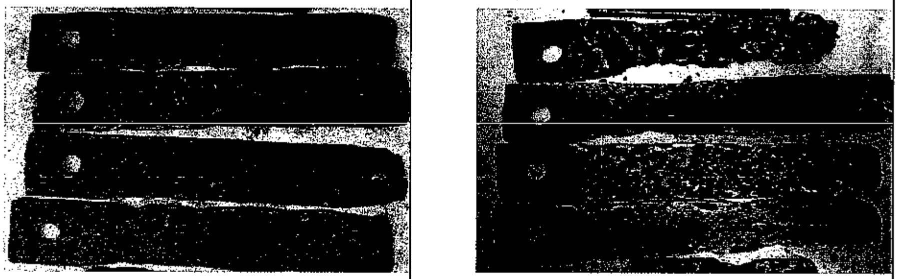
June 2010

September 2010



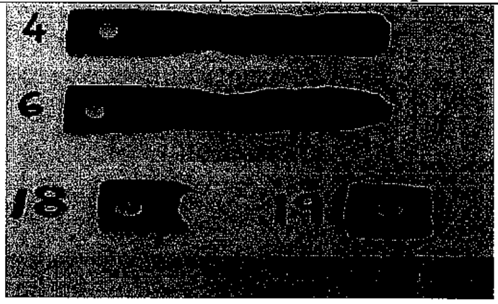
December 2010

March 2011



June 2011

September 2011



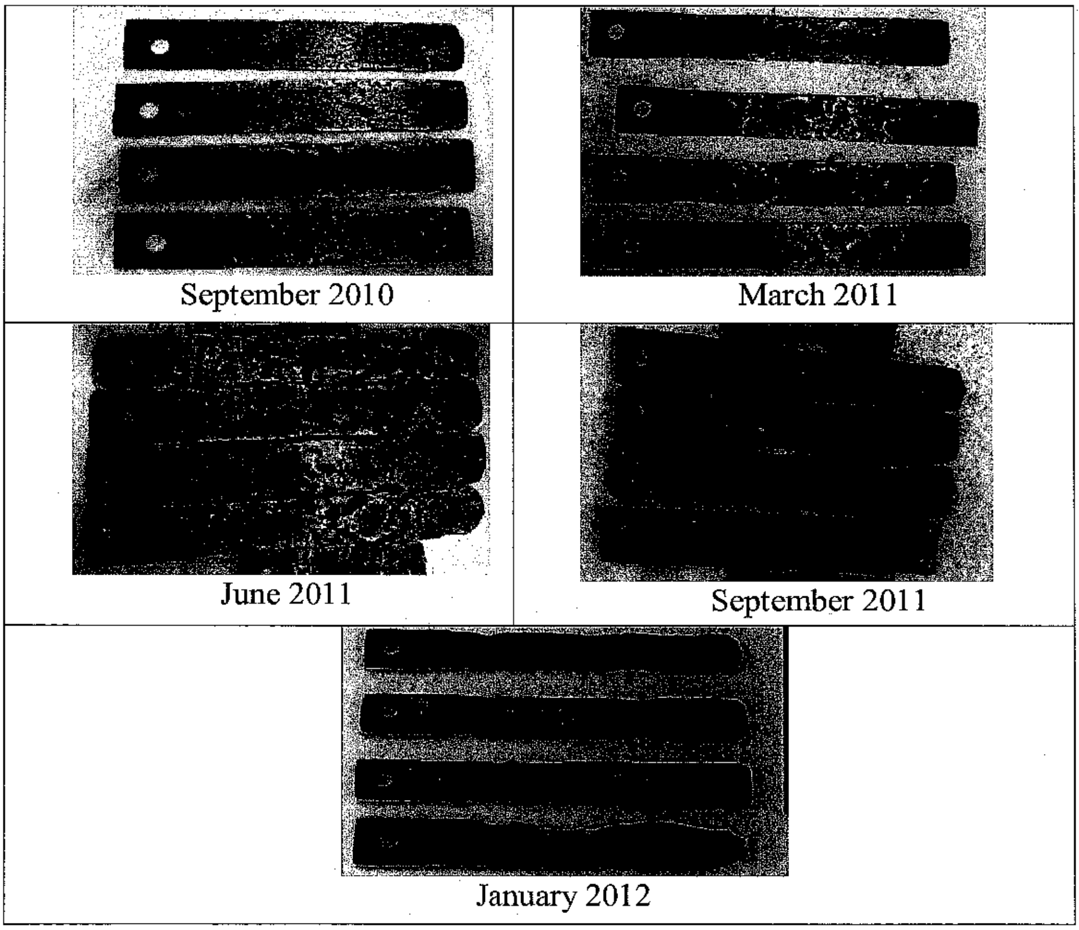
January 2012

Figure 4-6Cleaned coupons of sample 1 of Splash Zone at 3, 6, 12, 15, 18, and 22 months.

At 3 months, the coupons showed signs of small pits and at 6 months, the coupons showed more small pits. Based on close visual examination, the surface of each segment of the coupons showed pitting corrosion occurred. Large pits are observed at

9 months and 12 months. The thickness of the coupons was reduced. At 12 months, the coupons were not in rectangular shapes. Most of the pits were divided into smaller segments. At 15 months, the coupons were thinner and the shapes were irregular. At 18 months, pits were deeper and the edge of the coupons were mostly eaten up therefore the size of coupons were smaller compared to the original samples. At 22 months, 50% of the coupons were gone for two coupons and the thickness of another two coupons reduced more than 50% even though 70% of the coupons remained.

Figure 4.7 shows the coupons of sample 2 at splash zone which have been cleaned of the marine growth. At 6 months, the formation of pit is less compared to coupons collected at 12 months. Broad, shallow pitting and less developed pitting randomly scattered over the coupon' surface collected at 6 months was observed.


September 2010

March 2011

June 2011

September 2011

January 2012

Figure 4-7Cleaned coupons of sample 2 from splash zone at 6, 12, 18 and 22 months.

At 12 months, dark and golden brown rust deposits were clearly visible on the pits. An interesting observation is the closely spaced and highly developed pitting observed on the coupons collected at 18 months. At 22 months, the sample 2 is out of shape (not rectangular) and the thickness is reduced due to broad pit scattered over the coupon's surface.

Figure 4.8 shows the sample 1 from immersed zone cleaned of the marine growth.

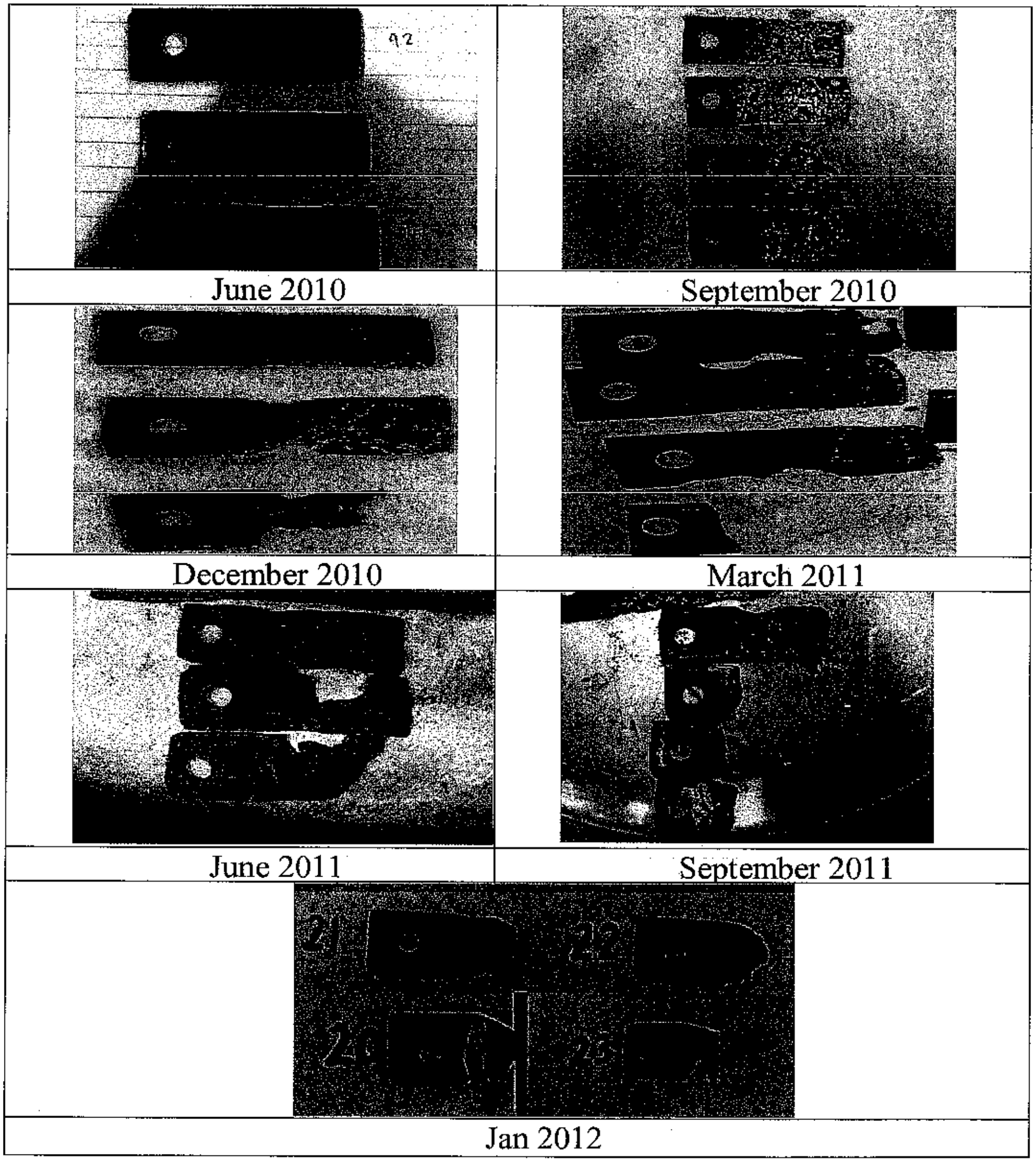
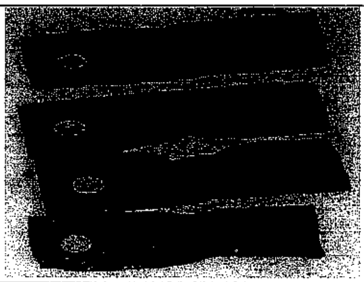

June 2010
September 2010
December 2010
March 2011
June 2011
September 2011
Jan 2012

Figure 4-8Corrosion coupons of sample 1 from immersed zone at 3, 6, 9, 12, 15, 18, and 22 months

The coupons collected at 3 months were still in rectangular shape. Small pits were developed and scattered on the surface of the coupons. At 9 months, the coupons were smaller in size and this indicates the start of severe corrosion. At 12 months, the coupons were badly corroded. One of the coupons was left with quarter of the original size. At 15 months a large central pit and other less developed pitting scattered over the surface were observed at the immersion zone. In contrast, the type of pitting seen at month 18 appears to be very aggressive and showing little or no obvious sign of pits. Nearly 70% of the coupons were gone. At 22 months, the coupons are very thin and it is nearly 50% of the coupons were gone. The shape of the coupons are odd.

Figure 4.9 show the sample 2 from immersed zone which have been cleaned of the marine growth.

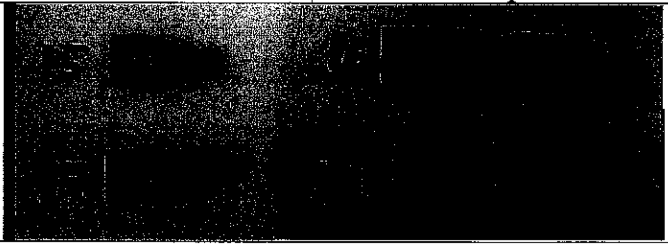
September 2010



March 2011

June 2011

September 2011



January 2012

Figure 4-9Corrosion coupons of Sample 2 from immersed zone at 6, 12, 15, 18 and 22 months

At 6 months, large pits were developed and scattered on the surface of the coupons. At 12 months, the coupons were thin and deeper pits developed. Closely spaced pitting was obviously scattered on the coupons. The shapes of the coupons started to change. At 15 months, larger pits were developed. Few portions of the coupons were lost. Other predominant features observed include rust like deposit mostly in the pits region.

At 18 months, the coupons were thinner and the sizes of the coupons were smaller than the original size. Rust like deposits were observed in the pits region. At 22 months, there are few parts of the coupons were gone and two of the coupons nearly lost 70% of the metal.

4.3.4 Statistical Variation of Corrosion Weight Loss in Samples

Since four coupons were placed at each level, it gives opportunity to study the variation of the weight loss. The mean weight loss, the standard deviation and the coefficient of variation at different levels are tabulated in Table 4.5 for sample 1 and Table 4.6 for sample 2. Figure 4.10 and Figure 4.11 show the mean weight loss with time and the corresponding standard deviation for sample 1 and sample 2 respectively.

Table 4-5 The Mean and Standard Deviation of Weight Loss at different Levels for Sample 1.

Zone	Mean	Standard Deviation
	Month: 3	
Atmospheric Zone	0.65	0.06
Splash Zone	5.58	3.05
Fully Immersed	16.90	7.46
	Month:6	
Atmospheric Zone	0.47	0.03
Splash Zone	12.82	6.61
Fully Immersed	15.86	10.24

Table 4.5: (Continued) The Mean and Standard Deviation of Weight Loss at different Levels for Sample 1

	Month:9	
Atmospheric Zone	0.58	0.01
Splash Zone	31.75	17.00
Fully Immersed	38.47	13.71
	Month:12	
Atmospheric Zone	0.54	0.30
Splash Zone	24.08	15.91
Fully Immersed	48.59	8.71
	Month: 15	
Atmospheric Zone	0.92	1.02
Splash Zone	43.33	15.26
Fully Immersed	58.71	18.62
	Month: 18	
Atmospheric Zone	0.76	0.34
Splash Zone	80.40	18.84
Fully Immersed	59.64	19.29
	Month: 22	
Atmospheric Zone	2.27	0.25
Splash Zone	89.95	30.72
Fully Immersed	63.04	4.79

Table 4-6 The Mean, Standard Deviation and the Cofficient of Variation at different Levels for Sample 2.

Zone	Mean	Standard Deviation
	Month:6	
Atmospheric Zone	0.39	0.03
Splash Zone	6.61	0.96
Fully Immersed Zone	15.42	5.22

Table 4.6: (Continued) The Mean, Standard Deviation and the Cofficient of Variation at different Levels for Sample 2.

	Month: 12	
Atmospheric Zone	0.21	0.15
Splash Zone	20.06	7.07
Fully Immersed Zone	34.24	13.32
	Month:15	
Atmospheric Zone	0.08	0.04
Splash Zone	22.61	15.16
Fully Immersed Zone	41.52	9.84
	Month: 18	
Atmospheric Zone	0.07	0.04
Splash Zone	27.82	6.16
Fully Immersed Zone	49.35	3.55
	Month: 22	
Atmospheric Zone	0.36	0.05
Splash Zone	26.06	10.68
Fully Immersed Zone	62.35	6.28

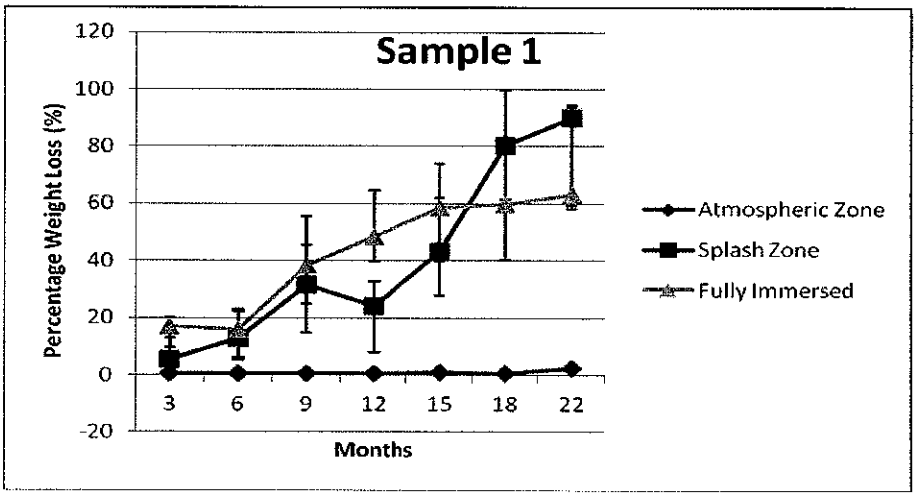


Figure 4-10Mean Weight Loss and standard deviation of Sample 1 at 3, 6, 9, 12, 15, 18, and 22 months.

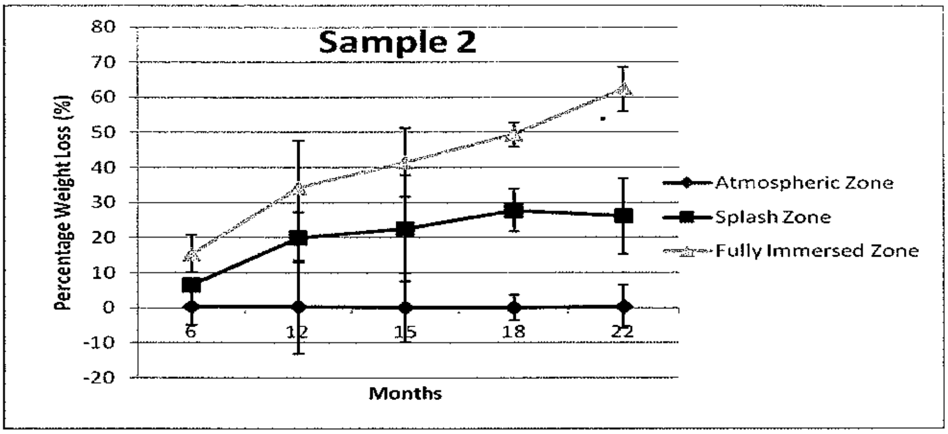


Figure 4-11Mean Weight Loss and Standard deviation of Sample 2 at 6, 12, 15, 18 and 22 months.

4.3.5 Percentage weight reduction, Corrosion loss (mm) with Time and Corrosion rate (mm/year)

In this study, an extensive amount of data on corrosion at Boustead Shipyard, Lumut was gathered through experiment on corrosion coupons from 2010 to 2012. The data were collected for two different samples, named Sample 1 and Sample 2. Sample 1 and 2 consist of three sets of data obtained from atmospheric zone, splash zone and fully immersed zone. Using the data, the percentage weight reductions, corrosion loss (mm) with time and corrosion rate in mm/year were calculated and tabulated (Table 4.7 and 4.8).

Table 4-7 Calculation of percentage weight reduction, corrosion loss with time and corrosion rate for sample 1.

Time	Initial Measurements					Final	weight loss	Metal loss	Corrosion rate			
	wt	thick	breadth	length	area	wt						
mths	(g)	(cm)	(cm)	(cm)	(cm^2)	(g)	%	mm	mmpy	mpy	mdd	g/m^2/yr
1	2	3	4	5	6	7	8	9	10	11	12	13
Atmospheric zone												
3	31.67	0.284	2.446	6.736	38.156	31.47	0.65	0.0069	0.0279	1.10	6.01	219.7
7	30.46	0.274	2.393	6.776	37.453	30.31	0.47	0.0049	0.0099	0.39	2.14	78.0
9	31.63	0.285	2.455	6.800	38.674	31.45	0.54	0.0057	0.0086	0.34	1.86	67.7
12	31.14	0.288	2.439	6.728	38.092	30.97	0.55	0.0057	0.0057	0.22	1.22	44.6
15	31.63	0.282	2.469	8.507	48.185	31.59	0.11	0.0010	0.0008	0.03	0.17	6.1
18	31.56	0.284	2.437	8.432	47.284	31.32	0.76	0.0064	0.0043	0.17	0.94	34.2
22	31.80	0.282	2.441	6.817	38.387	31.08	2.27	0.0239	0.0161		3.47	126.8
Splash zone												
3	65.30	0.290	2.437	13.565	75.421	61.63	5.61	0.0618	0.2503	9.86	53.9	1969.8
7	64.70	0.283	2.359	13.555	72.968	56.40	12.82	0.1447	0.2930	11.54	63.2	2305.6
9	65.95	0.290	2.424	13.470	74.519	45.14	31.55	0.3552	0.5397	21.25	116.3	4246.6
12	63.83	0.286	2.427	13.555	74.953	48.45	24.10	0.2611	0.2608	10.27	56.2	2052.0
15	65.19	0.283	2.441	11.837	65.852	42.20	35.28	0.4443	0.3600	14.17	77.6	2832.6
18	64.38	0.288	2.428	11.835	65.678	12.62	80.40	1.0026	0.6769	26.65	145.9	5326.6
22	64.34	0.287	2.438	13.532	75.160	6.47	89.95	0.9796	0.6614	26.05	142.6	5204.5
Immersion zone												
3	31.28	0.283	2.391	6.784	37.647	26.04	16.75	0.1771	0.7173	28.24	154.6	5644.8
7	31.66	0.277	2.450	6.759	38.208	26.61	15.93	0.1679	0.3401	13.39	73.3	2676.2
9	32.49	0.286	2.435	6.830	38.549	20.25	37.68	0.4040	0.6138	24.17	132.3	4829.6
12	31.09	0.288	2.436	6.721	38.013	15.95	48.69	0.5066	0.5060	19.92	109.1	3981.6
15	31.28	0.283	2.435	6.772	38.203	13.03	58.35	0.6079	0.4925	19.39	106.2	3875.5
18	31.54	0.279	2.435	6.739	37.938	12.69	59.76	0.6320	0.4267	16.80	92.0	3357.8
22	31.24	0.286	2.433	6.623	37.400	11.55	63.03	0.6698	0.4522	17.80	97.5	3558.1

Table 4-8 Calculation of percentage weight reduction, corrosion loss with time and corrosion rate for sample 2.

Time	initial					Final	weight loss	Metal loss	Corrosion rate			
mths	wt	thick	breadth	length	area	wt						
	(g)	(cm)	(cm)	(cm)	(cm^2)	(g)	%	mm	mmpy	mpy	mdd	g/m^2/yr
1	2	3	4	5	6	7	8	9	10	11	12	13
Atmospheric zone												
6	50.24	0.435	2.286	7.418	42.348	50.05	0.39	0.0059	0.0120	0.47	2.59	94.6
9	49.81	0.436	2.319	7.271	42.086	49.7	0.22	0.0033	0.0044	0.17	0.95	34.5
15	50.48	0.442	2.319	7.271	42.205	50.44	0.08	0.0013	0.0010	0.04	0.22	8.2
18	49.86	0.436	2.325	7.377	42.760	49.79	0.15	0.0022	0.0015	0.06	0.31	11.5
22	50.77	0.431	2.341	7.411	43.104	50.41	0.72	0.0107	0.0072	0.29	1.56	56.9
Splash zone												
6	106.74	0.435	2.243	11.08	61.291	99.69	6.61	0.1464	0.2964	11.67	63.91	2332.7
9	106.45	0.438	2.325	15.400	87.139	85.1	20.06	0.3118	0.4210	16.57	90.76	3312.6
15	107.15	0.477	2.325	15.400	88.530	82.92	22.61	0.3482	0.2821	11.11	60.81	2219.7
18	106.61	0.437	2.325	15.400	87.099	76.95	27.82	0.4331	0.2924	11.51	63.05	2301.2
22	106.72	0.437	2.332	15.410	87.380	78.91	26.06	0.4049	0.2734	10.76	58.94	2151.1
Immersion zone												
6	49.78	0.433	2.233	7.283	40.752	42.1	15.42	0.2397	0.4855	19.12	104.67	3820.3
9	50.45	0.434	2.321	7.387	42.712	33.18	34.24	0.5146	0.6948	27.36	149.80	5467.7
15	49.91	0.436	2.321	7.387	42.760	29.19	41.52	0.6166	0.4995	19.67	107.69	3930.8
18	50.12	0.434	2.324	7.387	42.762	25.39	49.35	0.7359	0.4968	19.56	107.11	3909.6
22	49.80	0.432	2.332	7.277	42.238	18.75	62.35	0.9352	0.6314	24.87	136.13	4968.7

4.3.5.1 Percentage Weight Loss

Figure 4.12 and Figure 4.13 shows the percentage weight loss at different zones with time for sample 1 and sample 2 respectively.

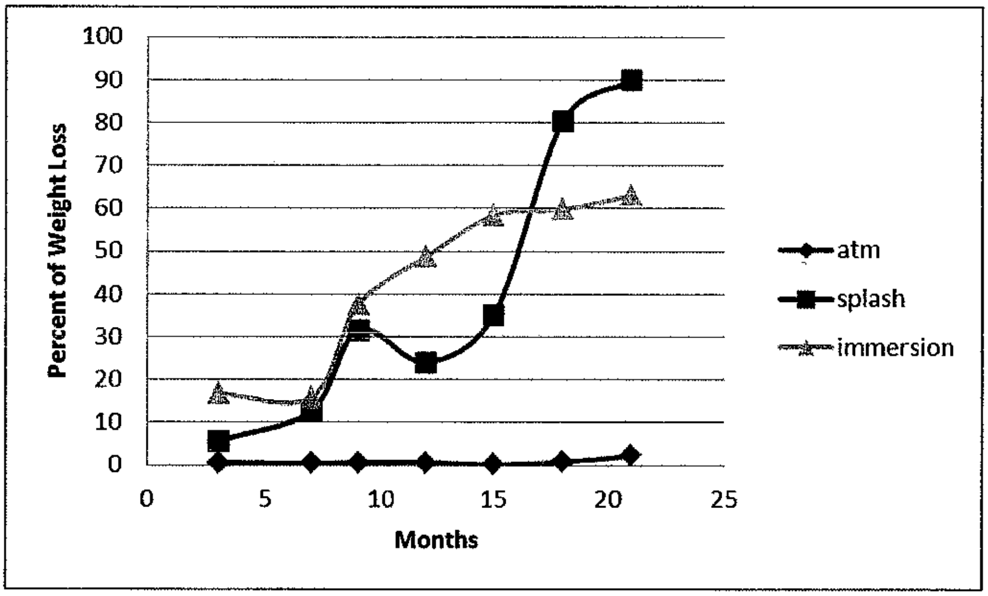


Figure 4-12Percentage weight losses (%) at 3, 6, 9, 15, 18 and 22 months for Sample 1

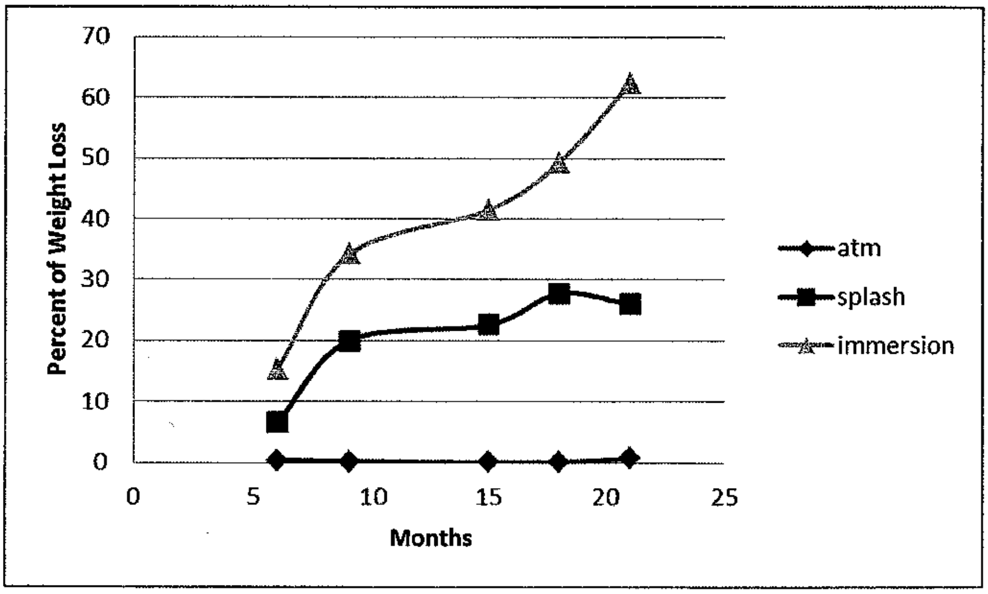


Figure 4-13Percentage weight losses (%) at 6, 12, 15, 18 and 22 months for Sample 2.

4.3.5.2 Corrosion loss (mm)

The profile for corrosion losses (mm) of sample 1 and sample 2 for 24 months of exposure in the seawater is shown in Figure 4.14 and Figure 4.15 respectively.

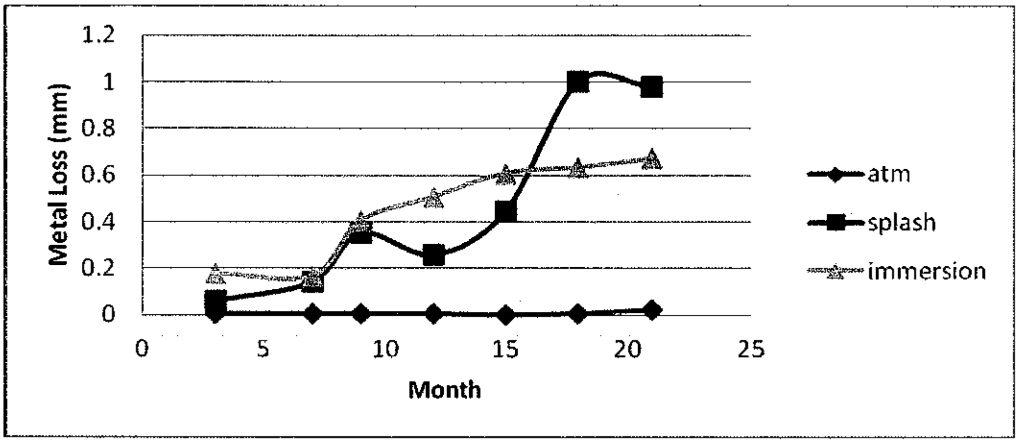


Figure 4-14Corrosion loss (mm) for sample 1 at 3, 6, 9, 15, 18 and 22 months for Sample 1

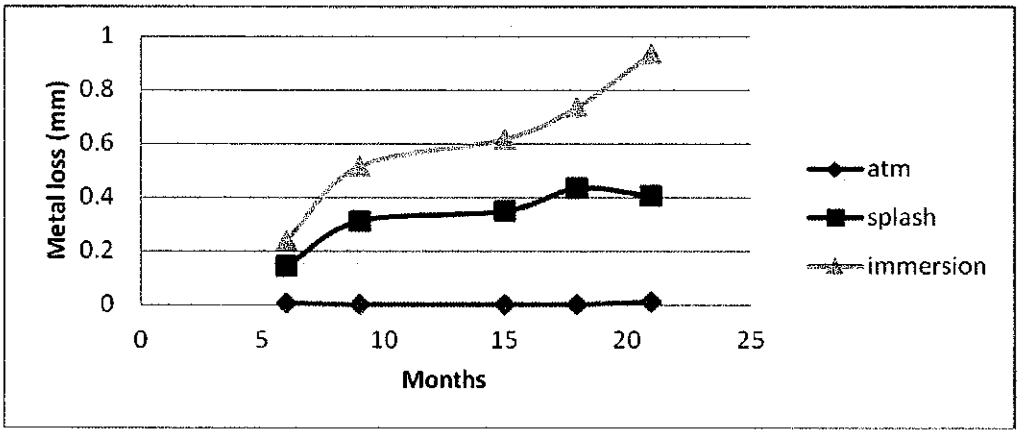


Figure 4-15Corrosion loss (mm) for sample 2 at 6, 12, 15, 18 and 22 months for Sample 2.

4.3.5.3 Corrosion Rate (mm/year)

The corrosion rate for sample 1 and sample 2 for various zones; atmospheric zone, splash zone and fully submerged zone at 3, 6, 9, 15, 18 and 22 months are shown in Figure 4.16-4.18 respectively.

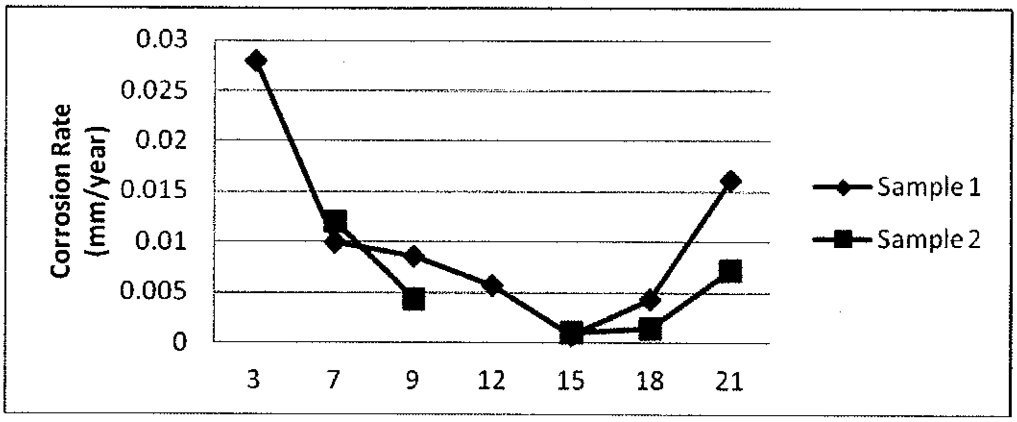


Figure 4-16Corrosion rate for Sample 1 and Sample 2 at Atmospheric Zone.

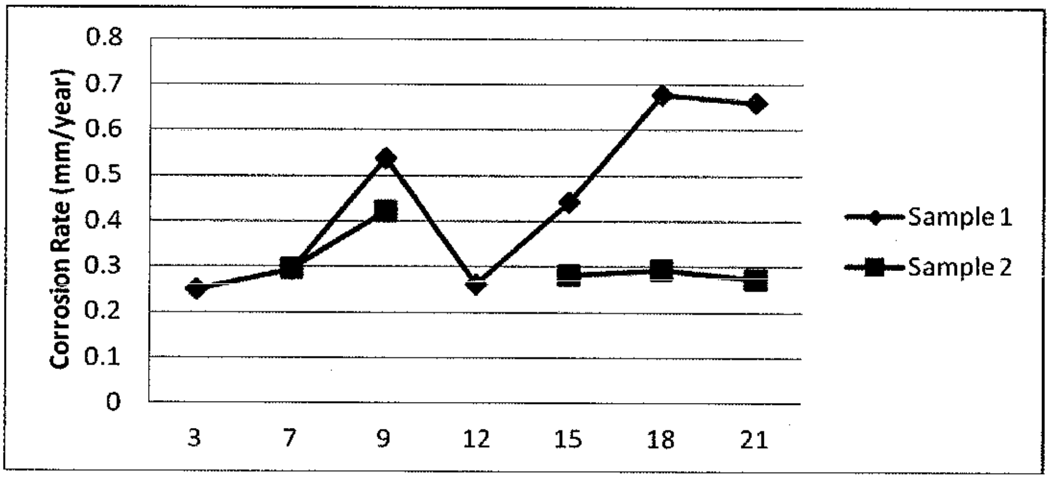


Figure 4-17Corrosion rate for Sample 1 and Sample 2 at Splash Zone.

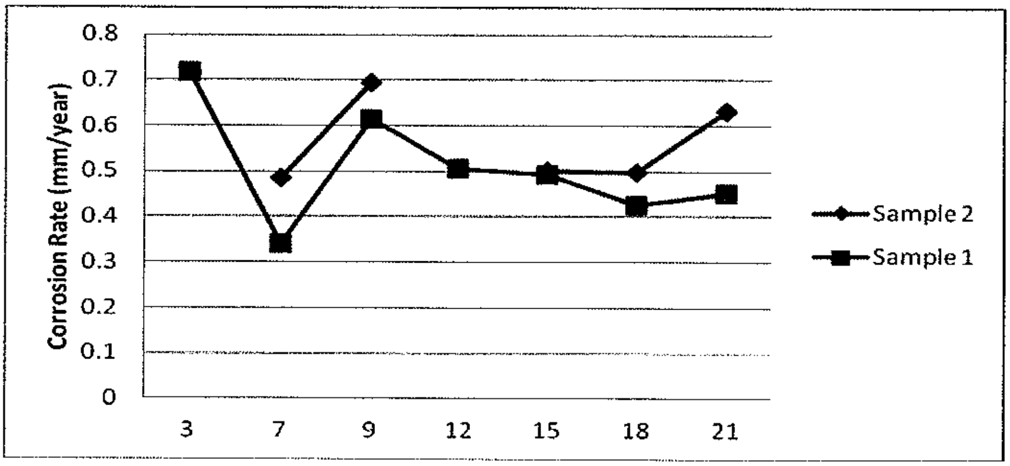


Figure 4-18Corrosion rate for Sample 1 and Sample 2 at Fully Submerged Zone.

4.3.6 The Chemical Composition of Samples

The sample used was mild steel with chemical composition listed in Table 4.9 based on test report from SIRIM QAS International. The chemical composition of the samples is presented as a pie chart (Figure 4.19). Note that in the figures only the percentage composition of the minor elements (excluding iron) has been shown.

Table 4-9 Chemical Composition of Sample 1 and Sample 2 Coupons.

ELEMENT	SAMPLE 1 (%)	SAMPLE 2 (%)
Carbon, C	0.088	0.058
Silicon, Si	0.369	0.149
Manganese, Mn	1.324	0.424
Phosphorus, P	0.007	0.007
Sulphur, S	0.003	0.002
Copper, Cu	0.019	0.14
Nickel, Ni	0.004	0.035
Chromium, Cr	0.063	0.071
Iron	98.123	99.14
Total	100	100

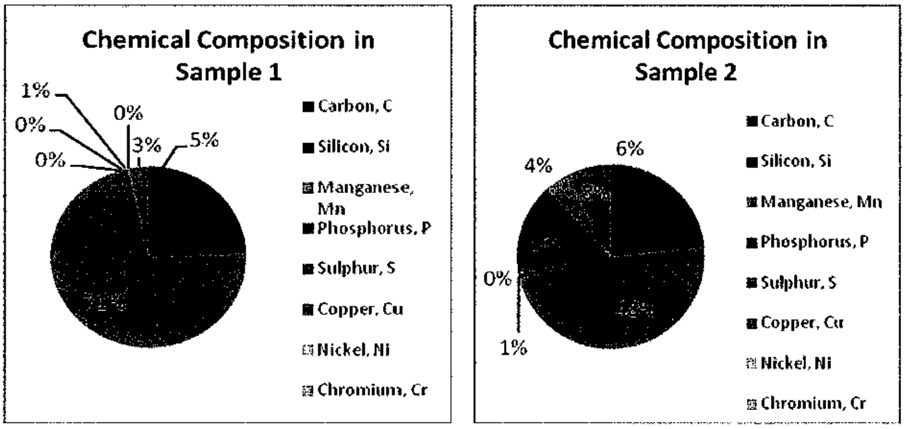


Figure 4-19Percentage Chemical Composition in Sample 1 and Sample 2 determined by SIRIM

4.3.7 Fouling Load

The variation of the fouling load (g/cm^2) and corrosion rate (mm/year) with time of sample 1 and sample 2 for splash zone and fully immersed zone are shown in Figure 4.20- Figure 4.23. Atmospheric zone did not show any fouling effect, as expected and hence has not been plotted.

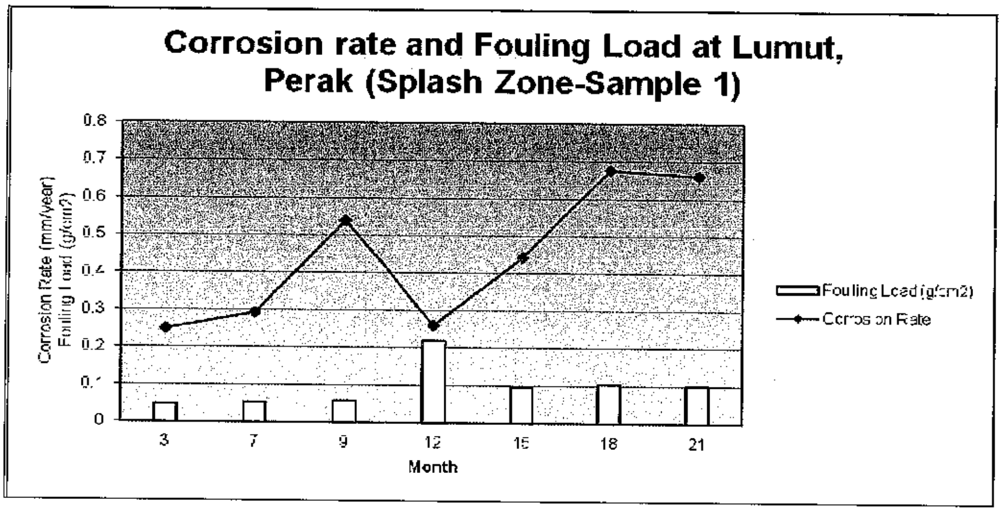


Figure 4-20Corrosion Rate and Fouling Load of Sample 1 in natural seawater, Lumut, Perak. (Splash Zone)

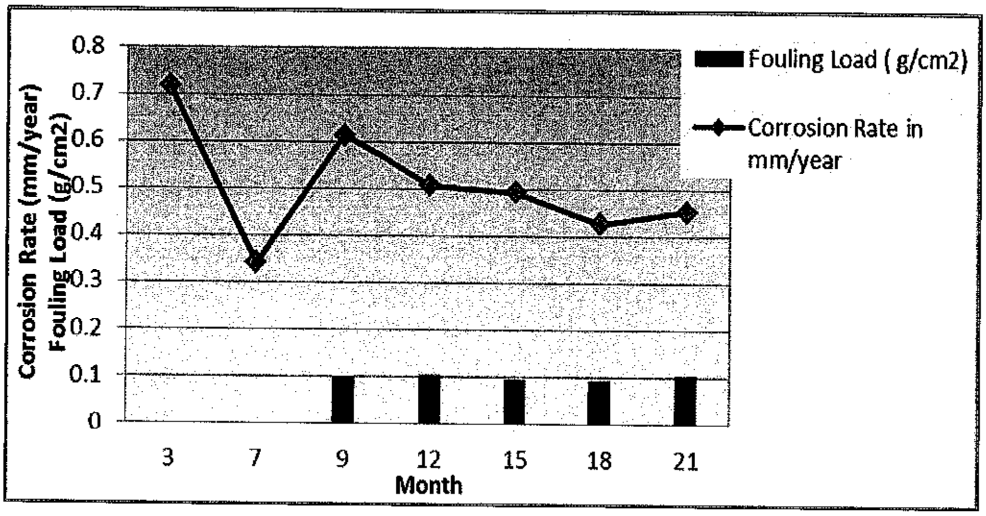


Figure 4-21Corrosion Rate and Fouling Load of Sample 1 in natural seawater, Lumut, Perak. (Fully Immersed Zone)

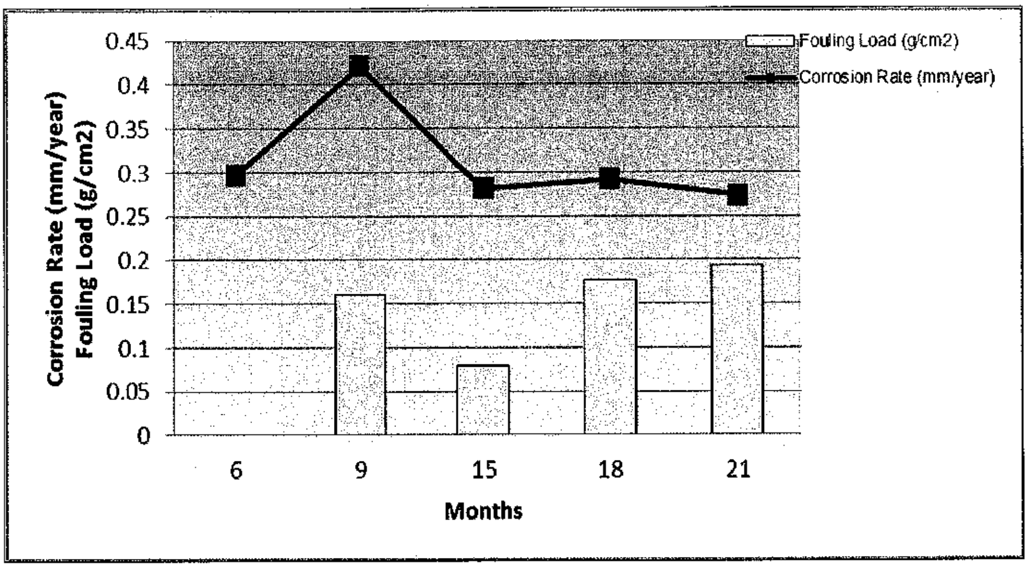


Figure 4-22Corrosion Rate and Fouling Load of Sample 2 in natural seawater, Lumut, Perak. (Splash Zone)

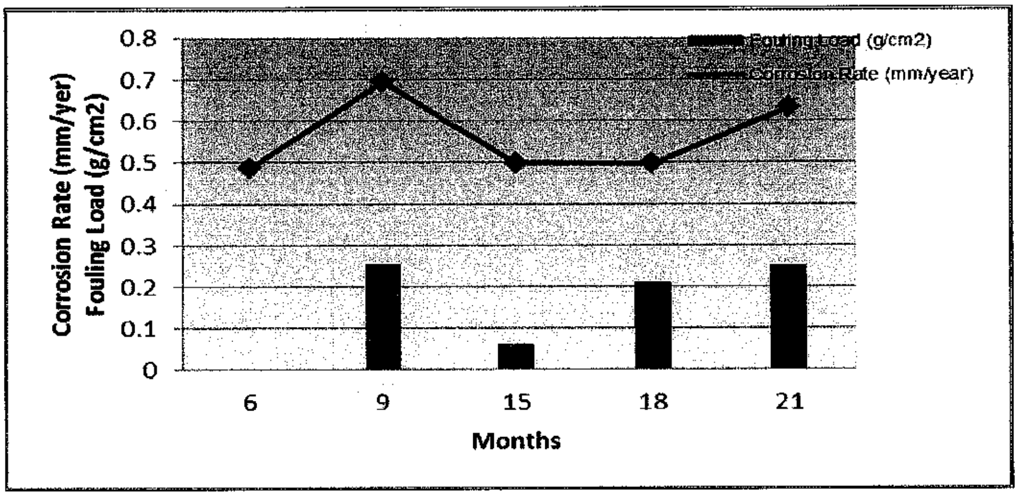


Figure 4-23 Corrosion Rate and Fouling Load of Sample 2 in natural seawater, Lumut, Perak. (Fully Immersed Zone)

4.3.8 Fitting Multiple Parameter Regression Models to the Data.

The mechanism of corrosion is due to various parameters. Corrosion that takes place in coupons located at splash zone is non- uniform, however it is assumed that to be uniform around the coupons surfaces to simplify the analysis.

Other effects such as dissolved oxygen and flow effect are not considered this time, although they may influence the rate of corrosion. The regression analysis helps to identify or estimate the effect of the chosen predicted variables on the corrosion rate. Only sample 1 located at splash zone is analyzed because the data collected is sufficient to generate multiple linear regression equation. The data is analysed using SPSS and Microsoft Excel. The dependent variable (CR) and the independent variables (months, temperature, pH, salinity and fouling load) parameters considered in this analysis are shown in Table 4.10.

Table 4-10 The result of the data for seawater surface temperate, pH, salinity, and fouling loads over the study period by months.

CR (mm/yr)	Months	Temperature °C	pH	Salinity (ppm)	FL (g/cm^2)
0.2503	3	28	7.9	32	0.0476
0.2930	6	27.5	8	33	0.0556
0.5397	9	26.1	8.1	32	0.0569
0.2608	12	26.8	8.1	35	0.2185
0.3600	15	28	8.2	31	0.0963
0.6769	18	27.3	8	34	0.1030
0.6614	22	26.7	7.8	35	0.0994

**CR= Corrosion rate, Temp=Temperature, FL= Fouling Load

The coefficient of determination, R^2 is shown in Table 4.11 and Table 4.12.

Table 4-11 Model Summary by SPSS

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.945^a	.893	.355	.150558

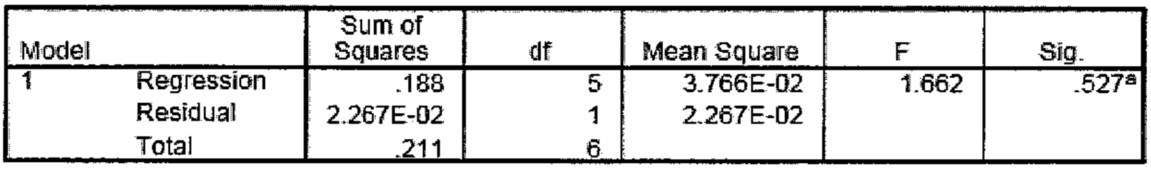
a. Predictors: (Constant), FL, TEMP, PH, MONTHS, SALINITY

Table 4-12 Model Summary by Microsoft Excel

Regression Statistics	
Multiple R	0.9487
R Square	0.8999
Adjusted R Square	0.3997
Standard Error	0.1453
Observations	7

According to the results generated, the values obtained by SPSS and Microsoft EXCEL are very similar. The sum of squares terms and related statistics are summarized in Table 4.13 – 4.14.

Table 4-13 ANOVA by SPSS



Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.188	5	3.766E-02	1.662	.527ᵃ
	Residual	2.267E-02	1	2.267E-02		
	Total	.211	6			

a. Predictors: (Constant), FL, TEMP, PH, MONTHS, SALINITY

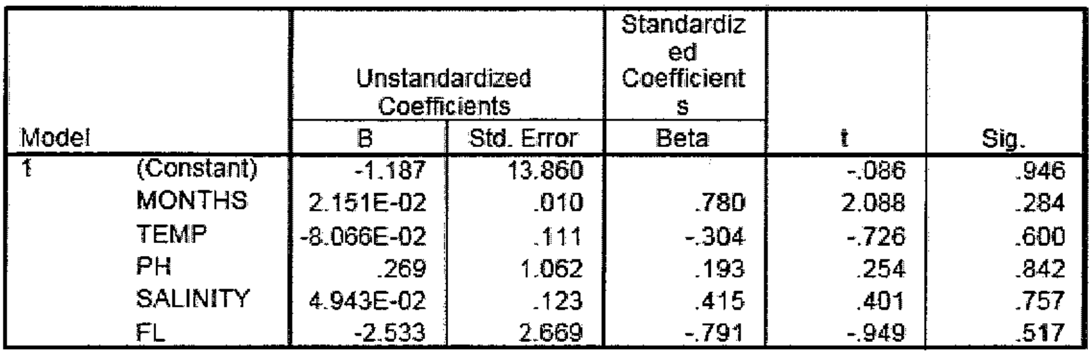
b. Dependent Variable: C.R

Table 4-14 ANOVA by Microsoft Excel

ANOVA					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	5	0.1899	0.0380	1.7989	0.5105
Residual	1	0.0211	0.0211		
Total	6	0.2110			

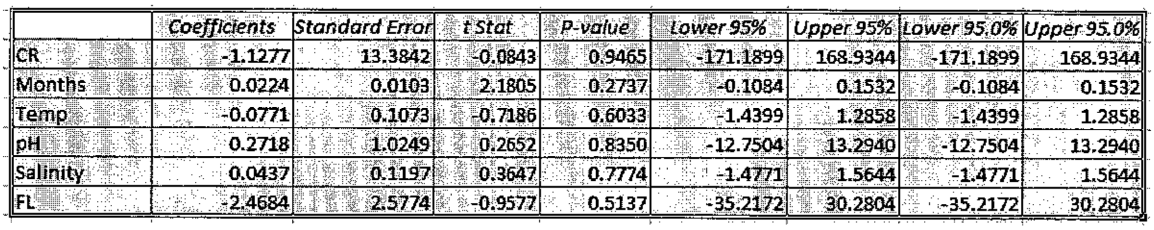
The coefficients for each of the variables are shown in Table 4.15 and Table 4.16. Each coefficient indicates the amount change one could expect in corrosion rate given one unit change in the value of that variable, given that all other variables in the model are held constant.

Table 4-15 Coefficients of variables that affect corrosion by SPSS



		Unstandardized Coefficients		Standardized Coefficients		
Model		B	Std. Error	Beta	t	Sig.
1	(Constant)	-1.187	13.860		-.086	.946
	MONTHS	2.151E-02	.010	.780	2.088	.284
	TEMP	-8.066E-02	.111	-.304	-.726	.600
	PH	.269	1.062	.193	.254	.842
	SALINITY	4.943E-02	.123	.415	.401	.757
	FL	-2.533	2.669	-.791	-.949	.517

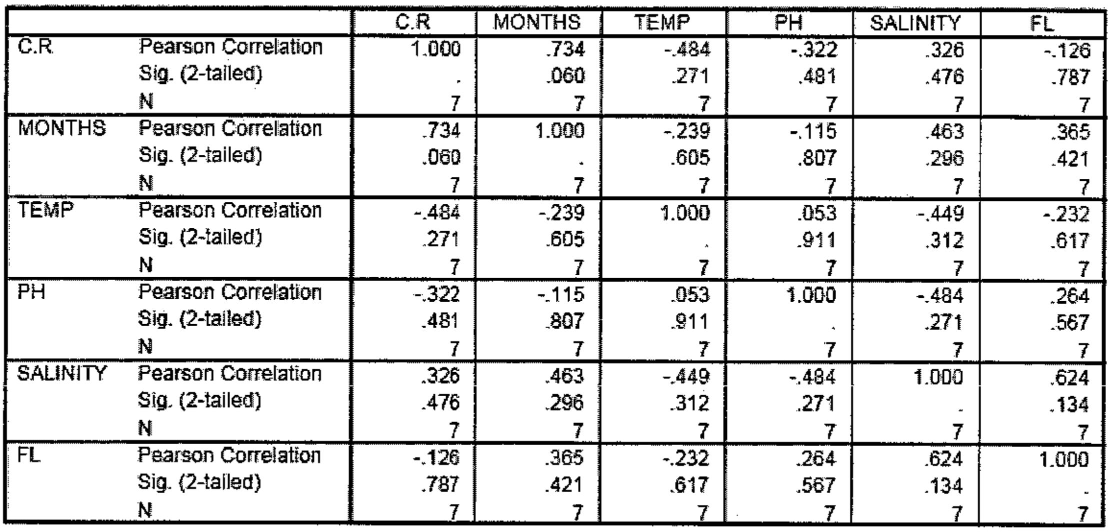
Table 4-16 Coefficient of variables that affect corrosion by Microsoft Excel



	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
CR	-1.1277	13.3842	-0.0843	0.9465	-171.1899	168.9344	-171.1899	168.9344
Months	0.0224	0.0103	2.1805	0.2737	-0.1084	0.1532	-0.1084	0.1532
Temp	-0.0771	0.1073	-0.7186	0.6033	-1.4399	1.2858	-1.4399	1.2858
pH	0.2718	1.0249	0.2652	0.8350	-12.7504	13.2940	-12.7504	13.2940
Salinity	0.0437	0.1197	0.3647	0.7774	-1.4771	1.5644	-1.4771	1.5644
FL	-2.4684	2.5774	-0.9577	0.5137	-35.2172	30.2804	-35.2172	30.2804

The correlations among the variables in the regression model are shown in Table 4.17.

Table 4-17 Correlations of variables that affect corrosion.



		C.R	MONTHS	TEMP	PH	SALINITY	FL
C.R	Pearson Correlation	1.000	.734	-.484	-.322	.326	-.126
	Sig. (2-tailed)	.	.060	.271	.481	.476	.787
	N	7	7	7	7	7	7
MONTHS	Pearson Correlation	.734	1.000	-.239	-.115	.463	.365
	Sig. (2-tailed)	.060	.	.605	.807	.296	.421
	N	7	7	7	7	7	7
TEMP	Pearson Correlation	-.484	-.239	1.000	.053	-.449	-.232
	Sig. (2-tailed)	.271	.605	.	.911	.312	.617
	N	7	7	7	7	7	7
PH	Pearson Correlation	-.322	-.115	.053	1.000	-.484	.264
	Sig. (2-tailed)	.481	.807	.911	.	.271	.567
	N	7	7	7	7	7	7
SALINITY	Pearson Correlation	.326	.463	-.449	-.484	1.000	.624
	Sig. (2-tailed)	.476	.296	.312	.271	.	.134
	N	7	7	7	7	7	7
FL	Pearson Correlation	-.126	.365	-.232	.264	.624	1.000
	Sig. (2-tailed)	.787	.421	.617	.567	.134	.
	N	7	7	7	7	7	7

Correlation is significant at the 0.1 level (2-tailed)

4.4 Analysis of the Results.

The following sections are the analysis of results obtained from this research.

4.4.1 Climate parameters at Lumut

Discussions in this section are based on data presented in section 4.3.1. Corrosion is more severe in humid environments than in dry environments. Marine environments like Lumut typically have high percentage of relatively humidity (RH) [137]. The thickness of the absorbed layer of water on the sample surface increases with RH and eventually the corrosion rates also increase. The marine environment contains salt concentration. The presence of sodium chloride (NaCl) requires 77% RH to make the sample surface wet [138].

The RH at Lumut is around 82% thus exceeding 77% and the high RH provides sufficient moisture for corrosion to proceed. The critical humidity level is a variable that depends on the nature of the corroding sample, the tendency of corrosion products and surface deposits to absorb moisture and the presence of atmospheric pollutants. In this case, the pollutants are not analyzed.

Temperature plays an important role in atmospheric corrosion. Sample surface will remain warmer than the humid air surrounding them and do not collect condensation until some time after the dew point has been reached as the ambient temperature drops in the evening [136]. The lagging temperature of the sample will tend to make them act as condensers, maintaining a film of moisture on their surface as the temperature increases in the surrounding air.

4.4.2 Marine Water Quality

The discussions in this section are based on the data presented in section 4.3.2. Table 4.4 shows that the surface temperatures are varying between 26.1 – 28.3°C. The salinity varies between 31 and 35ppt; and pH between 7.8 to 8.2.

The main sources of E.coli were from untreated or partially treated domestic, animal waste and uncontrolled sewage from coastal premises. Referring to Table 4.4, e. coli readings registered 14% excess in 2010. These reading exceeded the recommended MWQCS (Table 2.10) of 100ml/L.

Total suspended solid in marine coastal is mainly caused by land- based activities which include uncontrolled land clearing for development and agriculture activities as well as coastal development. The total suspended solid in 2010 is 54% exceeding the MWQCS recommended values (Table 2.10). The presence of oil and grease in Lumut is from oil discharge and leakages by vessels. Table 4.4 shows the level of oil and grease of 14% exceeded the standard. Heavy metals pollution was comparatively high with copper and chromium exceeding the MWQCS recommended values (Table 2.10) by 93%, while cadmium, mercury, lead and arsenic did not exceed the limit. In conclusion, seawater at Lumut is polluted by oil, grease and heavy metals. Water pollution accelerates corrosion of steels, especially in harbors where levels of oxygenation of the waters may be low and where there may be industrial and shipping wastes.

Table 4.4 indicates that the levels of E-Coli, total suspended solid, oil and grease and some heavy metals exceeded the recommended maximum values by MWQCS.

4.4.3 Analysis of Physical Condition of Coupons.

Detailed descriptions of the condition of the coupons on retrieval were presented in section 4.3.3. Generally, the frames retrieved from the experimental site, Lumut were covered by fouling organisms. (Figure 4.2-4.9). Highly developed pitting observed in the splash zone compared to the broad, shallow pitting, often with a large central pit and other less developed pitting randomly scattered over the surface observed in the immersion zone. According to pitting theory, aerobic corrosion conditions a dominant pit will tend to inhibit surrounding less developed pits and generate a cathodic zone around it. Closely spaced pitting is formed due to electron receptors more efficient than oxygen. Closely spaced pitting is also associated with microbiologically influenced immersion corrosion under immersion conditions. The mechanisms involved in pitting for splash zone and immersion zone are complex. Hence, there is considerable scope for further research.

4.4.4 Statistical Variation of Corrosion Coupon Weight Loss.

Discussions in this section are based on the data presented in section 4.3.4.

4.4.4.1 Differences in weight loss at different levels – and with time

The direction effect is different for each of the coupon exposed. Surface seawater currents are mainly wind- drive. Surface seawater currents are deflected to the right in the Northern Hemisphere and to the left in the Southern Hemisphere due to "Coriolis Effect." The earth is spinning thus "Coriolis Effect" holds and the surface seawaters move in a clockwise direction in the Northern Hemisphere and in a counterclockwise direction in the Southern Hemisphere. The density differences caused by changes in temperature and salinity affect the vertical and seawater bottom currents. Currents help to move food and nutrients for marine life allowing photosynthesis, metabolic requirement and consumption to take place. Thus, each of the coupons subjected to various shadow effect and different impacts since the placement for each coupons are different. These and the natural variability of the samples regarding the small differences in composition and surface area have created the differences in weight loss.

4.4.4.2 Differences in standard deviation at Different Levels - and with time

Table 4.5 indicates the standard deviation of weight loss in atmospheric samples is generally low (at 3, 6, 21 months) where it is higher at 9, 12, 15 and 18 months in sample 1. The standard deviation of weight loss in splash zone (3.05-30.72) coupons was higher than atmospheric coupons (between 0.01-1.02) whereas for immersed coupon the standard deviation varied from 4.79-19.29. Table 4.6 shows the standard deviation of weight loss in atmospheric zone is low. The standard deviation for splash zone and immersion zone is high. In this case, a high standard deviation does not mean the data is not in good fit. Each coupon subjected to various impacts since the placement for each coupon is different. Thus the naturally variability of the samples created the difference in weight loss percentage.

4.4.5 Percentage Weight Reduction, Corrosion Loss with time and Corrosion Rate.

Discussions in this section are based on Figure 4.12- 4.18 presented in section 4.3.5.

4.4.5.1 Percentage Weight Loss

Figure 4.12 and 4.13 indicates that over the period of observation the weight loss is negligible for atmospheric zone and that the corrosion in the immersion zone is more than in the splash zone until month 18 where the rate of corrosion in splash zone increases tremendously. This indicates that corrosion rate at the immersion zone due to Sulphate Reducing Bacteria (SRB) is predominant. The curves (splash zone and immersed zone) exhibit similar trends as proposed by Melcher in Figure 2.4. However, the curve for immersion zone takes a shorter period (at month 9) to move from phase 2 to phase 3. It takes 12 months for coupons at splash zone to move from phase 2 to phase 3. This indicates the time taken for the rust layer and fouling load covered the surface of the coupon is shorter compare to splash zone. This probably due to the slow build-up of fouling at splash zone and higher oxygen, availability thus delayed the development of completely anaerobic at the sample 1 surface. The curves in Figure 4.13 did not exhibit similar trends as shown in Figure 4.12. This may be due to the dissimilar chemical composition of the samples. The copper and nickel content are higher in sample 2 and it helps in increasing corrosion resistance because its electrode potential is adjusted to be neutral with regard to seawater. Thus, it takes longer period to exhibit the curve shown in Figure 2.4 and Figure 4.12. A longer period of study may generate a similar trend of curve. Hence, further study is necessary to verify this hypothesis before it can be accepted.

4.4.5.2 Corrosion Loss (mm)

From figure 4.14 and 4.15, it is seen that the corrosion loss for the immersion zone is higher than that for the splash zone for both samples. For sample 1, the splash zone shows an increase towards the second year over the immersion zone. For atmospheric zone, the corrosion losses are very small compared to the other two zones.

4.4.5.3 Corrosion Rate (mm/year)

From the Figure 4.16-4.18 the following observations are made for the atmospheric, splash and immersed zone respectively.

Atmospheric Zone:

The corrosion rate for sample 1 is 0.0279 mm/side/year as shown in Figure 4.16. This is less than the upper limit of 0.10 recommended by BS 6349-1-2000 [49] for temperate climate referring to Table 2.5. Comparing with Table 2.3, the corrosion rate is less than the values for wet tropical region (0.08 – 0.70 mm/year) [46]. The values of corrosion rate in mils per year (mpy) in column 11 of Table 4.7 and Table 4.8 can be compared with the values in ISO [47], where the range of 3 – 8 mpy is classified as "high corrosion category". The mass loss (g/m^2/year) in column 13 can be checked with the classification in EN 12500 [48]. The atmospheric corrosion falls under "low category" (10 – 200 g/m^2/year) provided in Table 2.4.

Splash and immersion zones:

During the exposure period, fouling was mainly caused by algae and barnacles. Figure 4.18 shows that for sample 1 corrosion rates ranged from 0.32 to 0.7 mm/year at the immersion zone. Figure 4.18 shows that for sample 2 the corrosion rates ranged from 0.5 to 0.7 mm/ year at the immersion zone during the study period of 22 months. These are higher than the upper limits in BS 6349-1-2000 given in Table 2.5 [49] for immersion zone in temperate climates (0.13 mm/side/year) which is to be expected for a tropical zone. Figure 4.17 and Figure 4.18 for sample 1 show the distinctive change in corrosion behavior at the theoretical time, t_a as marked in Figure 2.4. In this case t_a is around 6 months exposure for both immersion and splash zones. This is shown much later for sample 2 in Figure 4.17 and Figure 4.18 for both immersion and splash zones for which t_a is estimated at around 15 to 18 months. The parameter C_a is around 0.422 mm/ year. This is slightly greater than the corresponding value for tidal corrosion 0.346 mm/ year for sample 1.

In Figure 4.14, the corrosion rate increases a little during the first 3 months for both splash and fully immersed zone due to moderate dissolved oxygen levels and salinity (35ppt) of the water. As corrosion continues, the corrosion products (rust) form on the corroding surface and the rate of oxygen diffusion through it will control the corrosion rate.

The corrosion rate declines slightly from 3 to 6 months implying the protective nature of corrosion products and biomass during exposure. A dense coverage is created by organisms over the substrate which reduces the diffusion of oxygen, thus reducing corrosion rate. The decrease in the cumulative corrosion rate is attributed to the bio-fouling acting as a barrier between metal and the seawater, thereby reducing the oxygen diffusion to the metal surface. As the dense coverage is built up, it becomes increasingly difficult for oxygen to reach the corroding surface. It is possible at this stage, aerobic and anaerobic condition co-exists in close proximity. This condition will expedite marine growth and by inference, it triggers the development of anaerobic conditions. This provides conditions under which sulphate-reducing bacteria (SRB) can flourish under the right nutrient conditions. SRB attacked the coupons through their waste products, principally H_2S producing FeS in the process. As a result, the rate of corrosion now depends on the rate of metabolism, which in turn depends on the rate of supply of nutrient. This constitutes phase 3. The photographs of the coupons at immersion zone clearly show that they were badly attacked by SRB.

Figure 4.14 shows the corrosion rate increasing linearly up to 9 months of exposure. The coupons exposed at the sea, is invaded by a complex mix of bacteria and nutrients. The corrosion process takes some time to become fully established and the rate of corrosion is controlled by the rate of arrival of oxygen at the corroding surface. Then there is a thin build up of corrosion products on the corroding surface as corrosion continues. Oxidation takes place therefore the corrosion rate increases. Figure 4.14 show that t_a is approximately 15 to 18 months and C_a is around 5.7mm/year. Evidently, t_a indicates that it takes more time to establish corrosion conditions similar to sample 1. Sample 1 only took 6 months for phase 3 to commence. This relationship does not appear to exist for sample 2. There may also be other influences involved such as the surface rust being more permeable for sample 2.

Comparing the corrosion rate of sample 2 conducted by this experiment and another experiment by Wan Nik et al.[18] at Kuala Terengganu, it showed that the weight loss after 25 days of exposure for sample 2 is 2.57% (by interpolation) while the weight loss after 25 days of exposure for mild steel at Kuala Terengganu is around 4%. The reason being comparing sample 2 only instead of sample 1 is because the chemical composition of sample 2 is similar to the mild steel used at Kuala Terengganu. The experiment conducted by Wan Nik et al. did not include the seawater quality and the duration of the field experiment is only 2 months which is insufficient to obtain accurate results. Wan Nik et al [18] does not mention nor measure the marine growth (fouling). Such experiments need to be conducted over longer periods to provide valid predictions as evident from earlier research discussed in Table 2.23. The variability in the corrosion losses or the parameters known to be involved was not considered in this research.

4.4.6 Comparison of Corrosion Rates

The minimum and maximum corrosion rate in mm per year for the different zones are compared with values recommended in BS 6349-1-2000 provided in Table 2.5 and those reported by Tidblad J et al, [46] in Table 4.18.

Table 4-18 Comparison of corrosion rates (mmpy)

Zones	Experimental Corrosion rate			Comparison with	
		Sample 1	Sample 2	BS 6349-1 (from Table 2.5)	
Atmospheric	Min	0.0008	0.0010	low	low
	Max	0.0279	0.012		
Splash	Min	0.2503	0.2821	Higher	Rates compare with sub tropical and wet tropical
	Max	0.6769	0.4210		
Immersion	Min	0.3401	0.4855	higher	
	Max	0.7173	0.6948		

The corrosion rates in mils per year (mpy) for the different zones are compared with values recommended in Table 4.19.

Table 4-19 Comparison of corrosion rates (mpy)

Zones	Experimental Corrosion rate (mpy)			Comparison with Table 2.3
		Sample 1	Sample 2	
Atmospheric	Min	0.03	0.04	Low
	Max	1.10	0.47	
Splash	Min	9.86	11.11	Very severe
	Max	26.65	16.57	
Immersion	Min	13.39	28.24	Very severe
	Max	19.12	27.36	

The corrosion rates in mass loss per year (g/m^2/year) for the different zones are compared with values recommended in Table 4.20 by EN12500 [48].

Table 4-20 Comparison of corrosion rates (g/m^2/year).

Zones	Experimental Corrosion rate (g/m^2/year)			Comparison with Table 2.4
		Sample 1	Sample 2	
Atmospheric	Min	6.1	8.2	Low to Medium
	Max	219.7	94.6	
Splash	Min	1969.8	2219.7	Very high
	Max	5326.6	3312.6	
Immersion	Min	2676.2	3820.3	Very high
	Max	5467.7		

In conclusion, Table 4.18 shows that the corrosion rates at the atmospheric zone were low compared to BS 6349 and Tidblad et al (2000). The rates for immersion and splash zone are higher. Table 4.19 shows that the corrosion values observed are low for atmospheric zone whereas they are very severe for splash and immersion zones. The corrosion rates are comparable to those given for sub- tropic and wet tropical zone. On comparison with EN 12500 values in Table 4.20, the experimental values indicate that the atmospheric zone falls in low to medium class; the splash and immersion zone falls in very high corrosion class.

4.4.7 Chemical Composition Analysis

Discussion in this section is based on Table 4.9 presented in section 4.3.6. Figure 4.16 through 4.18 showed the corrosion rate of the samples used at different type of exposure under different exposure time. The corrosion rate of samples at the atmospheric and splash zone showed different behaviours compared with the submerged location of the same sample. The results showed that sample 1 has the higher corrosion rate at atmospheric zone and splash zone compared to sample 2 whilst the sample 2 showed a higher corrosion rate at fully submerged zone compared to sample 1. The major factors such as oxygen, biological activities, pollution, temperature, salinity and velocity affect the corrosion behaviour of materials in the fully submerged zone [38]. Under atmospheric zone, there is a decrease in corrosion rates with increasing exposure time for all the test samples. This may vary from alloy to alloy mainly depending on chemical composition of the exposed alloy.

Structural steels usually have carbon content between 0.15 to 0.30%. The carbon content in Sample 1 is 0.088% and it is higher than Sample 2 (0.058%). Carbon increases the steel's strength and hardness but tends to decrease its ductility and toughness. There is no correlation between percentage of steel and on corrosion resistance.

Chromium, copper, nickel and silicon all serve to increase the corrosion resistance of the steel; manganese likewise had a beneficial effect on the corrosion resistance. The amount of manganese in structural steel grades ranged from about 0.50 to 1.70%. Manganese is included for the process of hot rolling of steel with the combination with oxygen and sulphur. Sample 1 contains 1.324% of manganese whilst Sample 2 contains three times lower, 0.424% of manganese. However, comparing the curve in Figure 4.16-4.18, the higher manganese content in Sample 1 found to be less resistant in splash zone.

The Ni content in Sample 2 is 0.035% and Cu is 0.140% whilst the Ni content in Sample 1 is 0.004% and Cu is 0.019% which is much lower than Sample 2. The higher content of Ni and Cu in Sample 2 were found to be much more resistant than Sample 1 in splash zone and atmospheric zone. This shows that the higher Ni and Cu content increase the corrosion resistance in splash zone and atmospheric. This could be related to fouling organism activities. However, further examination is needed to prove this hypothesis before it can be accepted.

The corrosion rate and pitting potential of samples in seawater are the function of Cr and Ni content. The chromium content in Sample 2 is 0.071% and it is slightly higher than that in Sample 1(0.063%). Silicon may also be present as deoxidizers. The silicon content in Sample 1 is 0.369%, which is double the silicon content in Sample 2.

Phosphorus and sulphur are considered to be impurities and should be minimized if possible because it reduces the ductility of the material. Sulphur triggers internal segregation in the steel matrix. Thus in all steel grade specification, the percentage of P and S allowed is less than 0.04 to 0.05. Intergranular embrittlement can appear in steel containing phosphorus in the normal range of 0.008 to 0.025% [139]. In this context, the phosphorus content is about 0.007% for both the samples and the sulphur content is about 0.002-0.003% for both the samples. It is less than the allowable value.

4.4.8 Fouling Load Analysis

The discussions in this section are based on Figure 4.20- 4.23. The corrosion rate seemed to be modified and regulated by the action of marine fouling macro organisms and marine bacteria. The corrosion coupons continuously immersed in seawater corroded very quickly on the first 9 months but they developed a fouling cover, which then provided appreciable protection to the corrosion coupons. The corrosion rate curve in Figure 4.20, 4.22 and 4.23 is practically linear after 9 months of exposure.

The linear relation would not be formed if the corrosion were being controlled by the diffusion of oxygen though a continually thickening corrosion scale and fouling cover; another explanation was therefore sought. The corrosion scale and fouling cover reached sufficient thickness to form an effective barrier against oxygen diffusion to the corroding surface after sometimes. The impermeability of the fouling cover is not the only reason that prohibits the oxygen diffusion into the corrosion coupons but it is possible that the aerobic bacteria present in the outer fouling layer helps to intercept some or all of the inward moving oxygen. Thus when this condition is created, the corrosion rate should drop to low value. This was shown at the 12 months of exposure where the fouling load is 0.218g/cm^2. The low corrosion rate did not continue due to the continuous activity of anaerobic sulphate reducing bacteria. The inward diffusion of oxygen to the sample 1 surface combines with the hydrogen to form water. This reaction is transferred to the sulphate reducing bacteria (SRB) which utilize the hydrogen to reduce sulphate to sulphide. This component then reacts with ferrous ions to form ferrous sulphides. The accumulated ferrous sulphide within the biofilm relates closely to the corrosion rate. There is a general agreement that for appreciable corrosion to occur from sulphate reducing bacteria, the following items must be present: (a) an absence of oxygen, (b) a source of sulphate, (c) source of organic nutrients and (d) the presence of ferrous ions. In this context, these environment conditions are established namely: (a) the seawater at Lumut (b) the presence of ferrous ions from the sample 1 (c) sulphate from the water, (d) a nutrient supply from the decomposing fouling organisms. The corrosion rate which drop after 12 months exposure start to increase until 18 months of exposure and approaches a constant rate which remains independent of further thickening of the cover. The fouling loads range from 0.096 – 0.103 g/cm^2 on 15 to 18 months of exposure.

When the corrosion losses were plotted against time for the fully immersed zone for sample 1, some interesting results were revealed which seemed to be against the biological control theory of marine corrosion. Figure 4.21 presents the curve for these fully immersed data. It can be seen that corrosion rate was very high on the third month of exposure (0.717 mm/year)- almost triple of that found for splash zone. However the corrosion rate for sample 1 at the fully immersed zone dropped tremendously on the 7 months of exposure. The fouling load is about 0.0999 – 0.106 g/cm^2 starting from 9 - 21 months of exposure. Comparing curve shown in Figure 4.20 and Figure 4.21, the biological control theory started 3 months (on the 7 months of exposure) earlier for sample 1 located at fully immersed zone whereas sample 1 located at splash zone started 5 months (on the 12 months of exposure) later. This probably due to the slow build-up of fouling at the splash zone and higher oxygen availability thus delayed the development of completely anaerobic conditions at the sample 1 surface.

The fouling load for sample 2 at the splash zone is 0.160 g/cm^2 after 9 months of exposure and the corrosion rate is the highest at this point. The fouling load and corrosion rate dropped on the 15 months of exposure with 0.079 g/cm^2 fouling load. The behaviour of the fouling load for sample 2 located at the splash zone and the fully immersed zone is similar. However, the fouling load discovered in sample 2 is completely different compare to fouling load obtained in sample 1. The difference on sample 1 and sample 2 is their chemical composition. The fouling might react differently towards the chemical composition of the sample thus the fouling load varies. Besides that, the coupons are subjected to various impacts such as different direction of the wave and different shadow effect. This may alter the distribution of the fouling on the coupons. However, further examination is still required to verify this hypothesis before it can be accepted.

4.4.9 Time Based Corrosion Model

Time based corrosion loss model for sample 1 was developed using Microsoft Excel spreadsheet(Figure 4.24) for splash zone and is given by $y = 1.0455t^{1.4165}$ and for immersion zone is $y = 5.8096t^{0.7971}$.

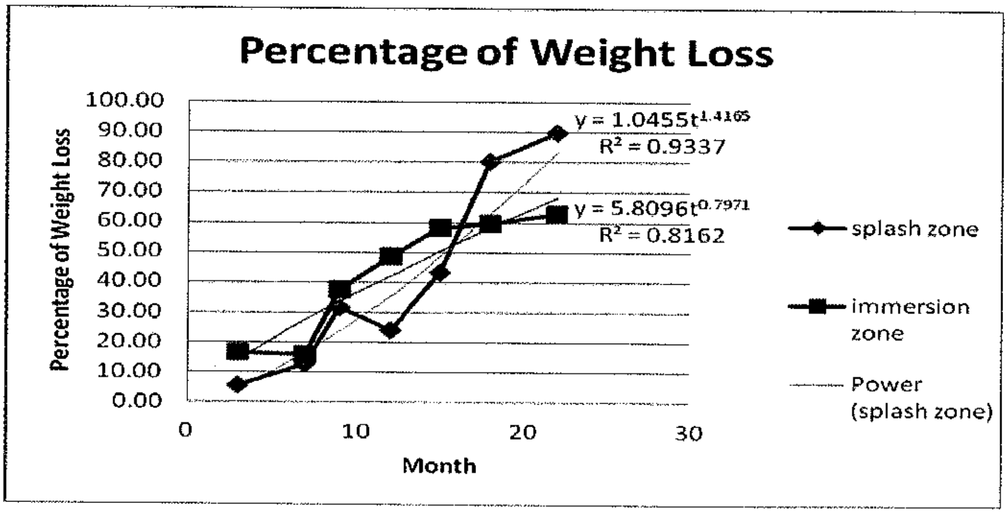


Figure 4.24: Time based Corrosion Model.

4.4.10 Analysis of the results of the Multiple Linear Regression by SPSS

The discussions in this section are on the results of the MLR presented in section 4.3.8. The research has attempted to explain the variation of the dependent variable (the corrosion rate) based on a combination of different independent variables (time in months, temperature, pH, salinity and fouling load). An attempt was made to understand the statistical significance of the predictors (time in months, temperature, pH, salinity and fouling load) on the dependent variable. The results were presented in Table 4.10-4.17.

The statistical significance of the explanatory variables, adjusted R square, and the coefficient of determination are explained in Chapter 2 section 2.12.1. The coefficient of determination, R^2 is shown in Table 4.11 and Table 4.12. The closer the value is to one hundred, the more variability of the dependent variable is explained by the variability of the independent variables. It is apparent from Table 4.11 and 4.12 that for both the results obtained from Microsoft Excel and SPSS, the values are almost the same. The R-squared shown in Table 4.11 is 0.945 meaning that 94.5% of the variability of corrosion rate is accounted for by the variables in the model.

The total, residual and regression sum of squares is shown in table 4.13 (SPSS analysis) and table 4.14 (Excel analysis). In table 4.13, the total, residual and regression sum of squares values are 0.211, 0.02267 and 0.188 respectively. This agrees closely with the values from the EXCEL analysis in which the total, residual and regression sum of squares values are 0.211, 0.0211 and 0.1899 respectively. The mean square, F-value and significance value also match.

The coefficients for each of the variables were presented in Table 4.15 and Table 4.16. The slopes and the y-intercept as seen in Table 4.13 should be substituted in the following linear equation to predict the corrosion rate.

$$y_i = b_0 + b_i x_{i,1} + b_2 x_{i,2} + \ldots + b_K x_{i,K} + e_i \qquad (4.1)$$

In this case, the values of x_{ik}, b_0, b_k and y_i will be as follows referring to the Table 4.13.

b_0 = -1.187; b_1 =(0.02151); b_2 =-0.08066; b_3 =(0.269); b_4 =(0.04943); b_5=(-2.533)

$x_{i,1}$ = months; $x_{i,2}$ = Temperature; $x_{i,3}$ = pH; $x_{i,4}$ = Salinity; $x_{i,5}$= Fouling Load

y_i= Corrosion Rate

As indicated in the output table (Table 4.13), the coefficient for month is (0.02151), the coefficient for temperature is (-0.08066), the coefficient for pH is (0.269), the coefficient for salinity is (0.04943) and the coefficient for fouling load is (-2.533). To predict the corrosion rate, the values x_{ik}, b_0, b_k and y_i should be substituted in the linear equation as shown below:

y_i= (-1.187) + (0.02151) * Months + (-0.0866)* Temperature + (0.269) * pH + (0.04943)*Salinity + (-2.533)* Fouling Load (4.2)

Another linear equation on corrosion rate is generated with the help of the Microsoft Excel software as shown in Table 4.14 is tabulated below:

y_i= (-1.128) + (0.0224) * Months + (-0.0771)* Temperature + (0.2718) * pH + (0.0437)*Salinity + (-2.468)* Fouling Load (4.3)

It is to be noted that the equations obtained from Regression analysis using SPSS and Microsoft EXCEL are very similar. The following section explains each of the parameter in the above regression equation.

The F-ratio and its exceedance probability provide a test of the significance of all the independent variables (other than the constant term) taken together. In a multiple regression model, the exceedance probability for F will generally be smaller than the lowest exceedance probability of the t-statistics of the independent variables (other than the constant). Hence, if at least one variable is known to be significant in the model, as judged by its t-statistic, then there is really no need to look at the F-ratio. The F-ratio is useful primarily in cases where each of the independent variables is only marginally significant by itself (e.g., has a t-statistic between 1 and 2 in absolute value, and an exceedance probability greater than .05), and there is a doubt that the model should be discarded or not.

The “p” value of the F-test (given in Table 4.13 and table 4.14) indicates whether the overall model is significant. Since the value is 0.527, the model is statistically not significant. Referring to table 4.13, and assuming an alpha of 0.1, the coefficient for months, temperature, pH, salinity and fouling loads are not significant because the p-value (sig) is larger than 0.1. However, the significance level of the test is not determined by the p-value. The significance level of a test is a value that should be decided upon interpreting the data before the data are viewed, and is compared against the p-value or any other statistic calculated after the test has been performed.

The regression constant in the above equations (-1.187 in SPSS and -1.128 in EXCEL) are very close.

Most multiple regression models include a constant term, since this ensures that the model will be "unbiased"--i.e., the mean of the residuals will be exactly zero. (The coefficients in a regression model are estimated by "least squares"--i.e., minimizing the mean squared error. The mean squared error is equal to the variance of the errors plus the square of their mean: this is a mathematical identity. Changing the value of the constant in the model changes the mean of the errors but doesn't affect the variance. Hence, if the sum of squared errors is to be minimized, the constant must be chosen such that the mean of the errors is zero.)

In a simple regression model, the constant represents the Y-intercept of the regression line, in unstandardized form. In a multiple regression model, the constant represents the value that would be predicted for the dependent variable if all the independent variables were simultaneously equal to zero - a situation which may not physically or economically meaningful. If one is not particularly interested in what would happen if all the independent variables were simultaneously zero, then the constant can be left in the model regardless of its statistical significance. In addition to ensuring that the in-sample errors are unbiased, the presence of the constant allows the regression line to "seek its own level" and provide the best fit to data which may only be "locally" linear.

The second term in the regression model is the month, the coefficients for which are very close (0.02151 for SPSS and 0.0224 for EXCEL). The coefficient indicates the increase in corrosion rate for unit change in month. In table 4.15, the row for month also gives values for standard error (0.01), Beta (0.78), t (2.088) and "sig" (0.284). The standard error is determined as the square root of the sum of the squares of the residuals divided by the degrees of freedom. It gives an idea regarding how well the fitted equation fits the data. But this depends on the context. The standard error is sensitive to the units of measurement of the dependent variable.

The beta coefficients are used to compare the relative strength of the various predictors within the model. Because the beta coefficients are all measured in standard deviations, instead of the units of the variables, they can be compared to one another. In other words, the beta coefficients are the coefficients obtained by transforming the outcome and predictor variables to standard scores, also called z-scores, before running the regression.

For the corrosion rate MLR model, "months" has the largest Beta coefficient, 0.780, and pH has the smallest Beta, 0.193. Thus, a one standard deviation increase in "months" leads to a 0.780 standard deviation increase in predicted corrosion rate, with the other variables held constant. And, a one standard deviation increase in pH, in turn, leads to a 0.193 standard deviation increase corrosion rate with the other variables in the model held constant.

As shown in Figure 4.14, the corrosion rate increases as time goes by even though the corrosion rate reduced in between for sample 1.

The t-statistics for the independent variables are equal to their coefficient estimates divided by their respective standard errors. If we want to identify variables that could be removed without seriously affecting the standard error of the estimate (SEE), a low t-statistic (or equivalently, a moderate-to-large exceedance probability) for a variable suggests that the SEE would not be adversely affected by its removal.

The commonest rule-of-thumb in this regard is to remove the least important variable if its t-statistic is less than 2 in absolute value, and/or the exceedance probability is greater than 0.05. However, the variable with a low t-statistic has to be removed and checked whether this leads to an undesirable increase in the standard error. In the MLR for corrosion rate, the "t" values are 2.088 (for months), 0.726 (for temperature), 0.254 (pH), 0.401 (salinity) and 0.949 (FL). This indicates that the variables temperature, pH, salinity and FL could be in turn removed and inspection done to see whether the standard error value is affected.

Generally variables are added or removed one at a time, in "stepwise" fashion, since when one variable is added or removed, the other variables may increase or decrease in significance or may remain insignificant. If one variable remains insignificant it may also be removed. The t-statistic is usually not used as a basis for deciding whether or not to include the constant term. Usually the decision to include or exclude the constant is based on a priori reasoning, as mentioned earlier. If it is included, it may not have direct economic significance, and its t-statistic is not inspected too closely.

Referring to the MLR equation using SPSS, for every unit increase in fouling load, a -2.533 unit change in the corrosion rate occurs, assuming that all other variables in the model are held constant which is expected. Fouling load has the largest Beta coefficient, 0.791 Thus, one standard deviation increase in fouling load leads to 0.791 standard deviation decreases in predicted corrosion rate with the other variables held constant. As explained in the literature studies (Chapter 2) and fouling analysis (4.4.7), the corrosion rate increases at the beginning but as time goes by, the corrosion rate reduced because denser fouling load covered the coupons and protection is formed.

The correlations among the variables in the regression model were shown in Table 4.15 and are reproduced as the correlation matrix in Table 4.21.

The correlation matrix provides an a posteriori indication of the relative independence of the variables in the fitted model. It shows the extent to which pairs of variables provide independent information for purposes of predicting the dependent variable, given the presence of other variables in the model. Extremely high values here (say, much above 0.9 in absolute value) suggest that some pairs of variables are not providing independent information.

In this case, either (i) both variables are providing the same information (i.e. they are redundant) or (ii) there is some linear function of the two variables (e.g., their sum or difference) that summarizes the information they carry.

In case (i), it is usually desirable to try removing one of the variables. The estimated coefficients of redundant variables are often extremely large and utterly lacking in economic interpretation. This condition is referred to as multicollinearity.

In the most extreme cases of multicollinearity--e.g., when one of the independent variables is an exact linear combination of some of the others--the regression calculation will fail. (Statgraphics usually detects this condition and tells you which variable is found to be a linear combination of the others.). In case (ii), it may be possible to replace the two variables by the appropriate linear function (e.g., their sum or difference).

The correlation is expressed as a "coefficient". The Correlation Coefficient (r) ranges between -1 and 1. A value of 1 indicates perfect positive correlation - as one variable increases, the second increases in a linear fashion. Likewise, a value of -1 indicates perfect negative correlation - as one variable increases, the second decreases. A value of zero indicates zero correlation. A scatter diagram plotted in any spreadsheets, including Excel, will give a broad understanding of the correlation. The correlation coefficient (further as the CC) is scaled so that its value is independent from the units in which the four measurement variables are expressed as shown in Table 2.21.

Referring to the table below, the correlation between corrosion rate (CR) and month is 0.734 with a p-value of 0.060 whereas the correlation between corrosion rate

(CR) and salinity is 0.326 with a p-value of 0.476. The first is statistically more significant.

Table 4-21 Correlation matrix of the estimated coefficients with the corresponding their 2 tailed significance.

	CR	Months	Temp	PH	Salinity	FL
CR	1					
Months	0.734 0.060	1				
Temp	-0.484 0.271	-0.239 0.605	1			
PH	-0.322 0.481	-0.115 0.807	0.9053 0.911	1		
Salinity	0.326 0.476	0.463 0.296	-0.449 0.312	-0.484 0.271	1	
FL	-0.126 0.787	0.365 0.421	-0.232 0.617	0.264 0.567	0.624 0.134	1

The corrosion rate has higher correlation with "months" whereas it has negative correlation with Temperature, PH and FL. It is important to keep in mind that by examining pairs of variables a better understanding of the data is obtained. The fact that the correlation of a particular explanatory variable with the response variable does not achieve statistical significance does not necessarily imply that it will not be a useful (and significant) predictor in a multiple regression.

Numerical summaries such as correlations are useful, but plots are generally more informative when seeking to understand data. Plots tell whether the numerical summary gives a fair representation of the data. For a multiple regression, each pair of variables should be plotted. For the six variables in the corrosion rate model, 15 plots should be examined. In general there are $p + 1$ variable in a multiple regression analysis with p explanatory variables, so that $p(p + 1)/2$ plots are required. Multiple regression is a complicated procedure. If the necessary preliminary work is not done, there is serious danger of producing useless or misleading results.

There will be a 0.269 increase in corrosion rate for every unit increase in pH holding all other variables constant. However a negative Pearson's r value (-0.322) shown in correlations (Table 4.17). This result was somewhat unexpected.

The coefficient for months (0.02151) is not statistically significantly different from 0 because its p-value is 0.284, which is larger than 0.1.

In addition, suppose that the relationship between y and x is basically linear, but is inexact: besides its determination by x, y has a random component,e_i, which we call the 'disturbance' or 'error'. R^2 =0.893,' shown in Table 4.11. As shown in Table 4.13, the sum of squared residuals or SSR is 0.02267. SSR and the R^2 value obtained are sufficient to judge that the best-fitting line does in fact fit the data to an adequate degree. Thus, the error term is not available in the equation.

There are 7 valid pairs of data for temperature and pH, so that the correlation of 0.053 is based on 7 observations. Table 4.17 (Correlation) shows that the strongest correlation with corrosion rate is month with a correlation of 0.734. This means that the corrosion rate increases as months increase. The second strongest correlation with corrosion rate is temperature. Knowing that these variables are strongly associated with corrosion rate, it predicts that these variables would be statistically significant predictor variables in the regression model.

There is a statistically significant correlation between corrosion rate and month as shown in the sig 2-tailed (0.06) in Table 4.17 that is less than 0.1. Note that the number of cases used for each correlation is determined on a "pair-wise" basis.

The variable fouling load is strongly correlated with corrosion rate with a correlation of -0.126 as shown in Table 4.17. The temperature and pH is not strongly correlated with corrosion rate with a correlation of -0.484 and -0.322. This correlation is negative meaning that as the value of one variable goes down; the value of the other variable tends to go up. The salinity is fairly correlated with corrosion rate with a correlation of 0.326. Since the Pearson's r is positive, the salinity increases, the corrosion rate increases. However, most of the variables (temperature, pH, salinity and fouling load) are not statistically significant correlated to corrosion rate since the sig (2-tailed) value is greater than 0.1.

It is concluded that while equations for the estimation of corrosion rate can be developed from these data. Correlation between two variables does not automatically imply that one causes the other (though correlation is necessary for linear causation in the absence of any third and countervailing causative variable, and can indicate possible causes or areas for further investigation; in other words, correlation is a hint). Overall, this master thesis introduced ways of searching for, visualizing and modelling relationships between the corrosion rate and its various parameters. If the data had been more complete and complex, the results would be more trustful, meaningful and predicative.

4.5 Methods of Increasing Effective Life of Marine Steel Structures

The effective life of unprotected steel piling depends upon the combined effects of imposed stresses and corrosion. Where possible, the structure should be designed so that low corrosion rates exist at positions of high imposed stresses. Measures for increasing the effective life of a structure, where necessary, are covered in BS 6349 [49]; these can be used separately or in combination and are outlined below:

(a) Use of a heavier section

(b) Use of high yield steel at mild steel stress levels

(c) Apply a protective organic coating

(d) Apply cathodic protection

(e) Use concrete encasement where practicable

CHAPTER 5

CONCLUSION

5.1 Summary

In this research, a time based corrosion model as well as a multiple parameter based corrosion model for steel structures under marine exposure is developed by conducting an experimental work and to extract other information related to corrosion behaviour. Parameters such as pH, salinity, seawater quality, temperature, fouling effect and chemical compositions of the samples were considered in this experiment to better understand the joint effects of these parameters on the corrosion behaviour. The study also includes a review of existing standards with the minimum and maximum corrosion rate for different zones. Furthermore, statistical variations of corrosion coupon weight loss have been studied. The objectives stated in Chapter 1 are achieved and summarized below:-

5.1.1 Development of time based and multi parameter corrosion rate model using regression analysis.

This study contributes to the current literature as the first piece of empirical endeavour in Malaysia to probe the relationship between corrosion rate and other variables such as time of coupons exposure, seawater temperature, pH, salinity and fouling load. To the researcher's knowledge, there has been no report to date of empirical study that explored the influence parameters on corrosion rate in Lumut, Malaysia. The time based corrosion loss model for sample 1 is stated below-

Splash zone : $y = 1.0455t^{1.4165}$

Immersion zone: $y = 5.8096t^{0.7971}$

where:

y= corrosion rate; t= time

The above model gives the average rate over the period of study. The evaluations performed in Chapter 4 indicate that for the marine fully immersed zone, the corrosion process is complex and non-linear at the initial stage. These characteristics have provided models for general corrosion and enabled data on marine corrosion to be interpreted and applied for calibration. The field data obtained for splash, fully immersed and atmospheric corrosion shows a trend that is consistent with the model proposed by Melchers [12] for marine immersion corrosion.

This proves that marine corrosion at site follows the standard corrosion processes which include oxidation in the early stages and anaerobic corrosion in the longer term. Finally the action of sulphate reducing bacteria causes severe corrosion. The patterns and trends of the corrosion rate obtained from the experimental work can be taken into consideration by corrosion engineers or maintenance engineers at Lumut during design stage or maintenance purposes. Information available can only be taken as guide as it is based on what is currently known.

A review of existing models in Malaysia for corrosion loss showed that mostly these are based on insufficient understanding of the corrosion process including that due to fouling effect, chemical composition of the steels, pH, salinity and temperature of the seawater. The data indicates the protective nature of fouling organisms. The fouling creates dense coverage over the sample and reduces the diffusion of oxygen. However, under long term exposure, the action of sulphate reducing bacteria causes severe corrosion. Thus, the adverse effect of localized fouling and corrosion products should not be overlooked.

Sample 1 and sample 2 exposed to a marine industrial site exhibit difference in corrosion behaviour. Sample 2 consists higher nickel and copper content compared to Sample 1, thus increases the corrosion resistance. However, the manganese content in

Sample 1 is higher than Sample 2. Therefore the corrosivity rate of the coupons is counter balanced. The limitations of the amount of different kinds of steels lead to unsatisfactory results, thus further research is needed to improve the results.

Comparison is made between the results obtained with the available codes. The corrosion in atmospheric zone for the sample 1 located at atmospheric zone is less than the upper limit set in BS6349 [49] and considered as low category in EN12500 [48] and categorized as high corrosion in ISO [47]. The corrosion rates obtained at splash zone and immersion zones exceeded the limit set by BS6349 [49]. Notional average and upper limit values of corrosion for exposed, unprotected samples (mild steels) in tropical climate provides as a guide to what could be expected. However, the existing codes are unclear on how to make decisions based on these limits. A sufficient method of establishing these acceptable safety levels is not included in the evaluated standards.

The predicted multi-parameter corrosion rate in the form of a linear equation using SPSS is shown below-

y_i= (-1.187) + (0.02151) * Months + (-0.0866)* Temperature + (0.269) * pH + (0.04943)*Salinity + (-2.533)* Fouling Load

Another linear equation on corrosion rate is generated with the help of the Microsoft Excel software is shown below:-

y_i= (-1.128) + (0.0224) * Months + (-0.0771)* Temperature + (0.2718) * pH + (0.0437)*Salinity + (-2.468)* Fouling Load.

The multiple linear regression equation can prove useful in establishing the basis for future corrosion rate for instance predicting corrosion allowance. Furthermore, planners may use the results in carrying out major construction projects at marine environment.

5.2 Recommendations for future work.

The current research has provided an outline of the time based corrosion model through focussing on corrosion science principles with microbiological consideration. The corrosion rate changes with time thus it is important to obtain estimates of parameter uncertainty for each of the significant parameters involved. The corrosion time based model needs to be extended by including other parameters such as seawater flow effect, dissolved oxygen in the seawater, orientation of the sample and deposition of SO_2 and Cl. It is also important to estimate the parameters influence in quantitative terms.

Selecting more samples with different chemical compositions to determine the effect of chemical composition towards corrosion rate would give in depth understanding on the localized corrosion resistance of the steels. Among the different types of offshore structure steels, only type 3 was examined.

Thicknesses and the size of the sample might also affect the rate of corrosion. A larger coupon evens out the local mass loss and gives better average weight loss. Thus, selecting different thicknesses and size of the sample might give different results. Determining appropriate thickness and size is a topic for further exploration.

The samples obtained from the field experiment (splash zone and fully immersed zone) show pitting corrosion. Samples located at atmospheric zone show uniform corrosion. Pits initiate at metallurgical heterogeneities including non-metallic which includes the grain boundaries and phase variations and as a result initiation sites will vary depending on matrix composition and heterogeneities present. Thus the correlation between the pitting formation and fouling effect is an interesting topic to explore in the future.

In practice, corrosion is not an independent issue for risk and remaining life assessments. Corrosion relates with applied stress, fatigue, mechanical damage and coating. Therefore it is vital to take this interaction into consideration when assessing corrosion.

The field experiment also can be conducted at other sites located at East and West Malaysia to compare the corrosion rate obtained from Lumut.

In future, this corrosion research work can be extended for the development of steel structure elements specification that can be standardized for use in marine structures in Malaysia.

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1. Ong Shiou Ting, Narayanan Sambu Potty, M. Shahir Liew, 2011, Prediction of Corrosion Rates in Marine and Offshore Structures, NPC 2011
2. Narayanan Sambu Potty and Ong Shiou Ting, 2011, Prediction of Corrosion rates in Marine Structures, International Conference on Modelling and Simulation in Civil Engineering, India, 8-10 December.
3. Ong Shiou Ting, Narayanan Sambu Potty, Mohd. Shahir Liew, 2012, Marine Corrosion Of Mild Steel at Lumut, Perak, International Conference on Fundamental and Applied Science, Universiti Teknologi Petronas.

JOURNAL PAPERS

1. Narayanan Sambu Potty, Ong Shiou Ting and M.S. Liew, 2012, Study of Marine Structural Corrosion Using Corrosion Coupons In Lumut Area, Malaysian Journal of Science. Accepted for publication.

PRESENTATIONS / PAPER PRESENTATION CONTEST

1. Ong Shiou Ting, 2011, Prediction of Corrosion Rates in Marine and Offshore Structures, Shell Intervarsity Student Paper Presentation Contest, SPE-UTM Student Chapter.

APPENDIX A

Process on the fabrication and installation of corrosion coupons and frames displayed in pictures.

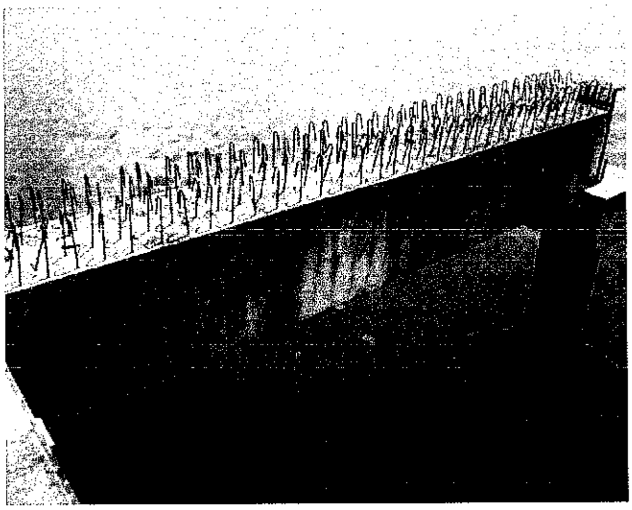

Figure A.1: The beam dimension was measured before fabricating the frames.

Figure A.2: The first set of frame attached with corrosion coupons (as the control of the experiment) were installed on 24 March 2010 to ensure the dimension of the frames fit the beam.

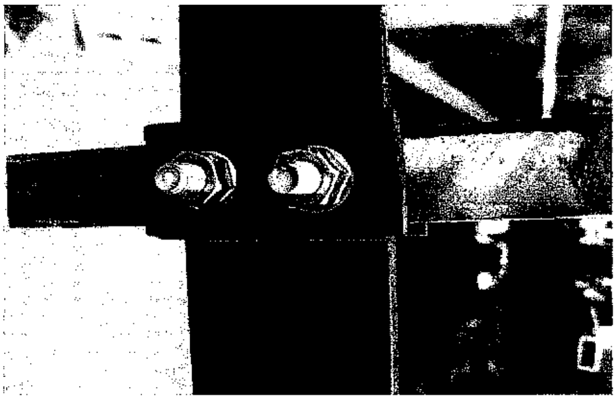

Figure A.3: The rubber pads were used to separate the bolt and washes from the corrosion coupons to avoid galvanic corrosion.

Figure A.4: The remaining 18 set of frames was installed on 29th March 2010.

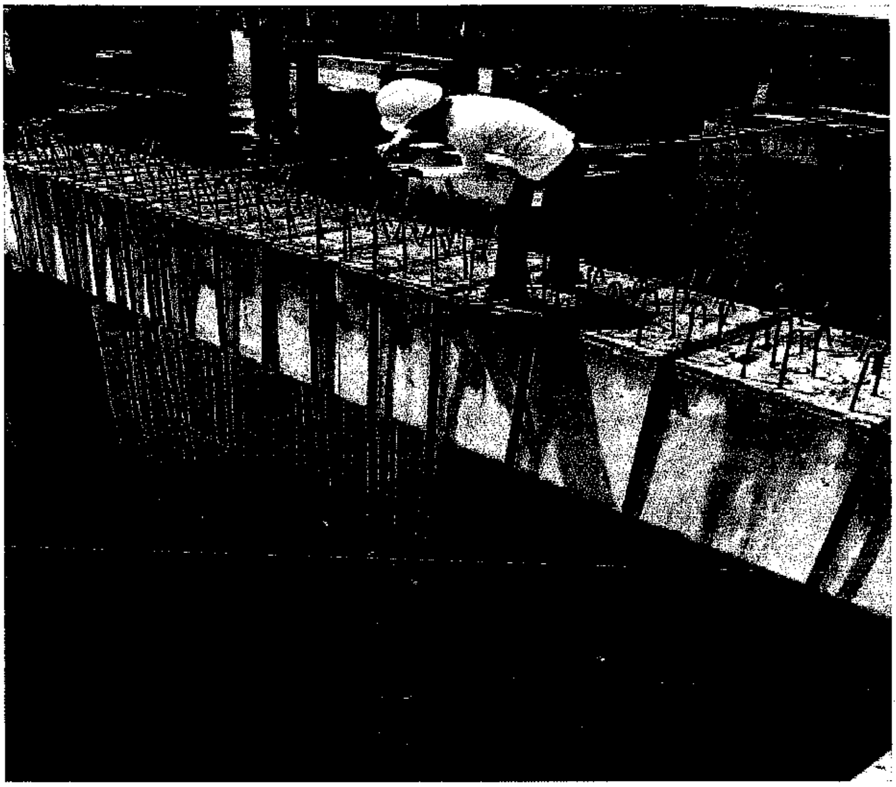

Figure A5: The experimental set up is completed.

APPENDIX B

Appendix B illustrates the step-by-step flow chart of the fabrication and set up of the experiment for determination of marine corrosion rates of type 3 steel at Lumut.

Fabrication of Coupons and Frames

1. Two sets of corrosion coupons of Type 3 with different sources (namely Japan and China) are fabricated.
2. Four coupons are placed on each zone; atmospheric (73 x 22x 3.8mm), semi-submerged((152 x 22x 3.8mm)) and totally submerged zones(73 x 22x 3.8mm).
3. The corrosion coupons are then removed every 3 months and sent to University Teknologi Petronas laboratory.

⇩

Laboratory Studies on Corrosion Coupons

a)Manual Cleaning

1. The corrosion coupons with fouling load are kept in the oven at 100°C to remove the water content.
2. The corrosion coupons are weighed using the weighing scale and the fouling loads are then removed by light brushing.

⇩

b) Chemical Cleaning according to ASTM G1

1. The corrosion coupons are cleaned in a mixture of 1000 mL hydrochloric acid (HCl), 20g antimony trioxide (Sb2O3),50g stannous chloride (SnCl2) and at the same time the mixture are stirred vigorously for 25 min at 23°C. Longer times may be required in certain instances.
2. The reagent water is mixed with 50g sodium chloride (NaOH) and 200g granulated zinc to make a mixture of 1000mL at 90°C. Corrosion coupons are submerged in the mixture for 40 minutes. Caution should be exercised in the use of any zinc dust since spontaneous ignition upon exposure to air can occur.
3. The reagent water is mixed with 200g sodium hydroxide (NaOH), 20 g granulated zinc to make another 1000 mL mixture. The temperature of the mixture should also be 90°C. The corrosion coupons are cleaned in the mixture for 30 to 40 minutes.
4. 200g diammonium citrate ((NH4)2HC6H5O7)is added into the reagent water to make a 1000mL mixture. The corrosion coupons are neutralized in the mixture for 20 min at 75 to 90°C. Depending upon the composition of the corrosion product, attack of base metal may occur. 500mL of hydrochloric acid (HCl, sp gr1.19), 3.5 g hexamethylene tetramine are mixed with the reagent water to make1000mL mixture. Coupons are neutralized in the mixture for another 10 min at 20-25°C. Longer time may be required in certain instances.
5. Lastly, the corrosion coupons are cleaned in the molten caustic soda (NaOH) with 1.5-2.0 % sodium hydride (NaH) for 1-20 min at 370°C.