SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

THE CORROSION PERFORMANCE OF COUPLED ZINC ANODE-MILD STEEL ATTACHMENT METHODS IN MALAYSIAN SEAWATER

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled: "**The Corrosion Performance of Coupled Zinc Anode-Mild Steel Attachment Methods in Malaysian Seawater**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

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TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF ABBREVIATIONS

ICCP	Impressed Current Cathodic Protection
EIS	Electrochemical Impedance Spectroscopy
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
I_{corr}	Corrosion current density
mm	Millimeter
XRF	X-ray fluorescence
XRD	X-ray Diffraction
SACP	Sacrificial Anode Cathodic Protection
SEM	Scanning Electron Microscope
EDX	Energy Dispersive X-ray spectroscopy
F	Farad
DOE	Design of Experiment
Rs	Solution resistance
rpm	Revolutions per minute
mg	Milligram
OCP	Open Circuit Potential
A	Ampere
V	Volt

LIST OF SYMBOLS

Wt%	Weight Percent
Z	Impedance (ohm)
ºC	Degree Celcius
E	Potential
I	Current
e^-	Electron
µ	Micro
%	Percentage
Ɵ	Theta

PRESTASI KAKISAN BAGI PASANGAN ZINC ANOD KORBAN DAN BESI MELALUI CARA PEMASANGAN DI DALAM AIR LAUT MALAYSIA

ABSTRAK

Kakisan air laut mengundangkan masalah serius kepada Tentera Laut Diraja Malaysia, di mana badan kapal dikakis dan menyebabkan kapal dalam keadaan rehat dan tidak dapat beroperasi. Budjet yang tinggi diperlukan untuk menjaga dan membaiki badan kapal yang rosak disebabkan kakisan. Kajian ini membantu mengurangkan masalah kakisan badan kapal dengan penyelidikan pasangan zink anod korban dengan besi. Dalam kerja kajian ini, prestasi kakisan dengan pasangan zink anod dan besi dikaji. Apabila zink dijadikan pasangan dengan besi, ia akan menjadi lebih anodik daripada besi dan menghadapi kakisan. Dengan ini, badan besi kapal dapat dielakkan daripada kakisan. Dalam kajian ini, cara untuk mengabungkan zink anod dan besi dikaji untuk mengetahui corak mereka dalam melindungi besi daripada kakisan dari segi tahap kakisan dan keupayaan untuk elak polarisasi. Selain itu, mekanisme kakisan untuk pasangan zinc anod dan besi juga dikaji. Kerja experimentasi dijalankan dengan teknik electo-kimia, Selain cara pengabungan, faktor alam sekitar dalam air laut seperti suhu air laut dan kelajuan juga dikaji untuk mengetahui kesan merekan terhadap kakisan zinc anod korban dan besi. Cara penggabungan zink anod dan besi melalui skru mempunyai kadar kakisan paling tinggi dalam suhu 45 ºC; kelajuan 200 rpm iaitu 1.202×10^{-2} mm/tahun dibandingkan dengan cara tuangan dalam suhu 45 ºC; kelajuan 0 rpm dengan bacaan 1.061×10^{-4} mm/tahun.

THE CORROSION PERFORMANCE OF COUPLED ZINC ANODE-MILD STEEL ATTACHMENT METHODS IN MALAYSIAN SEAWATER

ABSTRACT

Marine corrosion is causing severe problem to the Royal Navy Malaysia, where the navy ship hull is corroded and causing the navy ship to idle from operations. High budget is required to maintain and repair the ship hull. With this, study of this paper is to help to minimise the corrosion rate of ship hull by introducing the sacrificial anode cathodic protection. In this paper of study, corrosion performance of zinc anode coupled with mild carbon steel, which represents the ship hull is studied. Zinc which is more anodic compared to carbon steel tends to corrode when coupled. This is preventing the steel ship hull from corroding and lower down the corrosion rate. In this study, the method of attaching zinc anode to the ship hull is studied to find out the performance of them in protecting the carbon steel in term of corrosion rate and polarization resistance. Besides that, the corrosion mechanism of zinc anode coupled with steel is also one of the studies. The experimental work performed involved the technique of electrochemical analysis. Besides the attachment method, environmental effect in seawater such as temperature and velocity of seawater is studied to know the effect of these factors towards the corrosion performance of coupled zinc anode and mild carbon steel. The results of experimental shows that coupled zinc and carbon steel through attachment method of bolting at 45 ºC; 200 rpm has highest corrosion rate of 1.202×10^{-2} mm/year compared to the lowest corrosion rate of 1.061×10^{-4} mm/year from method of casting; 45 ºC; 0 rpm.

CHAPTER 1

INTRODUCTION

1.0 Background

Corrosion is the destructive attack and gradual deterioration of a material or its properties by electrochemical reaction with its environment. Corrosion damage costs a lot of money for repair. Thus, any research which can prevent corrosion are greatly important.

An electrical method known as cathodic protection (CP) is used to protect steel structures buried in soil, or immersed in water from corrosion. There are two main techniques in achieving cathodic protection, which are the impressed current cathodic protection (ICCP) and sacrificial anodes cathodic protection (SACP) system.

The earliest use of cathodic protection system in naval ships is in 1824 by Sir Humphry Davy. Sir Davy protected copper immersed in seawater by attaching a small amount of iron or zinc, which performed as a sacrificial metal (Tezdogan and Demirel, 2014). The cathodic protection system is the most widely used method of protecting a material from corrosion aside from coatings in a marine environment. For ships of older age with only short in-service lifetimes left, installing ICCP system involves high initial cost of installing. So, SACP is more conventional in protecting older ship.

For SACP system, the basis is that there is potential difference between the steel to be protected and second metal in the same environment causes the driving voltage. The steel will begin to interact with electrolytes and oxygen dissolved in the seawater, eventually undergoes corrosion if there is no anodes are attached to the ship’s hull. Sacrificial anodes are installed to ships to prevent ship hull from corroding.

About 15% - 20% of the sacrificial anodes should be installed to the to the stern and rudder area of the ship due to the water current flow and possible of high corrosion rate (Taylan, 2009).

1.1 Problem Statement

Seawater corrosion has caused unwanted ship hull corrosion to the navy ship of TLDM. Although SACP cathodic protection is applied to the ship to protect the steel ship hull from corrosion by shifting the potential of the steel to the least probable range for corrosion, but the corrosion behaviour of the ship hull is varying with the changing location of sea. With this, it is important to study the corrosion performance of coupled zinc anode and mild steel attachment methods in Malaysian seawater to identify whether the SACP method has the potential to protect the ship hull from corrosion under some circumstances.

There is a need to identify how well the cathodic protection can prevent corrosion when the anode is attached to the ship hull. Firstly, it is to study and identify which method of attachment of the zinc anode and mild steel cathode is the most suitable to prevent the corrosion by promoting the lowest rate of zinc consumption.

Besides that, research on different variables that may affect the corrosion rate is important. The variables that have the significant effects on the corrosion rate must be identified so that proper solutions can be done to prevent or slow down the corrosion rate. The two variables that can be changing when the ship is sailing in different seawater are the temperature and velocity. These two variables can affect the corrosion rate significantly. Experimental work is to be carried out to simulate the ship hull under cathodic protection and obtain the results of CP performance under variations of parameters.

1.2 Objectives:

The objectives of this research are:

a) To study the corrosion rate of zinc sacrificial anode coupled with mild carbon steel in Malaysian seawater
b) To determine the most ideal method of attaching zinc anode to mild steel (ship hull) in cathodic protection in term of corrosion protection performance
c) To study the environmental factors in seawater and mechanism of corrosion that affects the zinc anode SACP corrosion performance

1.3 Scope of Work

In this final year project, suitable methods of attaching zinc anode to mild carbon steel are identified. Raw materials of zinc anode, mild carbon steel and seawater are characterised to determine the factors that may affect the corrosion rate. Besides that, the environmental factors such as temperature and velocity are studied to know the effect and mechanism of them to the corrosion rate.

The experimental method used to study the corrosion performance of the coupled mild carbon steel and zinc anode are immersion testing, electrochemical testing of linear polarization and electrochemical impedance spectroscopy (EIS).

1.4 Outline of Chapters

This thesis consists of five chapters. Chapter 1 discusses on the introduction, objectives, problem statement and scope of work of the title. While, chapter 2 focuses on the literature review. Chapter 3 consists of the methodology in conducting the final year project. Chapter 4 discusses the results of the experimental work.

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

Literature review focuses on the literature studies done on sacrificial anode cathodic protection. It covers the topics of attachment method of coupled zinc anode and carbon steel. Besides that, literature study on the effect of environment factors such as temperature and velocity to corrosion rate is done. Furthermore, literature study on experimental setup and method of testing such as EIS and linear polarization are referred with data analysis and possible results to be obtained.

2.1 Sacrificial Anode Cathodic Protection

Cathodic protection is the electrochemical corrosion technique and is accomplished by applying a direct cathodic protection current to a structure. This will affecting a change in potential from the natural corrosion potential (E_{corr}) to a potential in the immunity region (Shashi et al., 2012).

For ship SACP protection installation, the anodes are either clamped or welded to the steel to ensure a permanent contact between two different metals. The attachment methods will further discussed in the section 2.2.

2.1.1 Galvanic Corrosion

Sacrificial anode cathodic protection (SACP) mechanism relates to galvanic corrosion. Galvanic corrosion occurs when two dissimilar metals are in electrical and ionic contact. Figure 2.1 shows the galvanic series of zinc and low carbon steel in seawater.

The more negative the potential value of the metal, the more the metal tends to undergo galvanic corrosion. Galvanic corrosion is usually not a desired occurrence but is used to advantage in sacrificial anode of zinc in seawater.

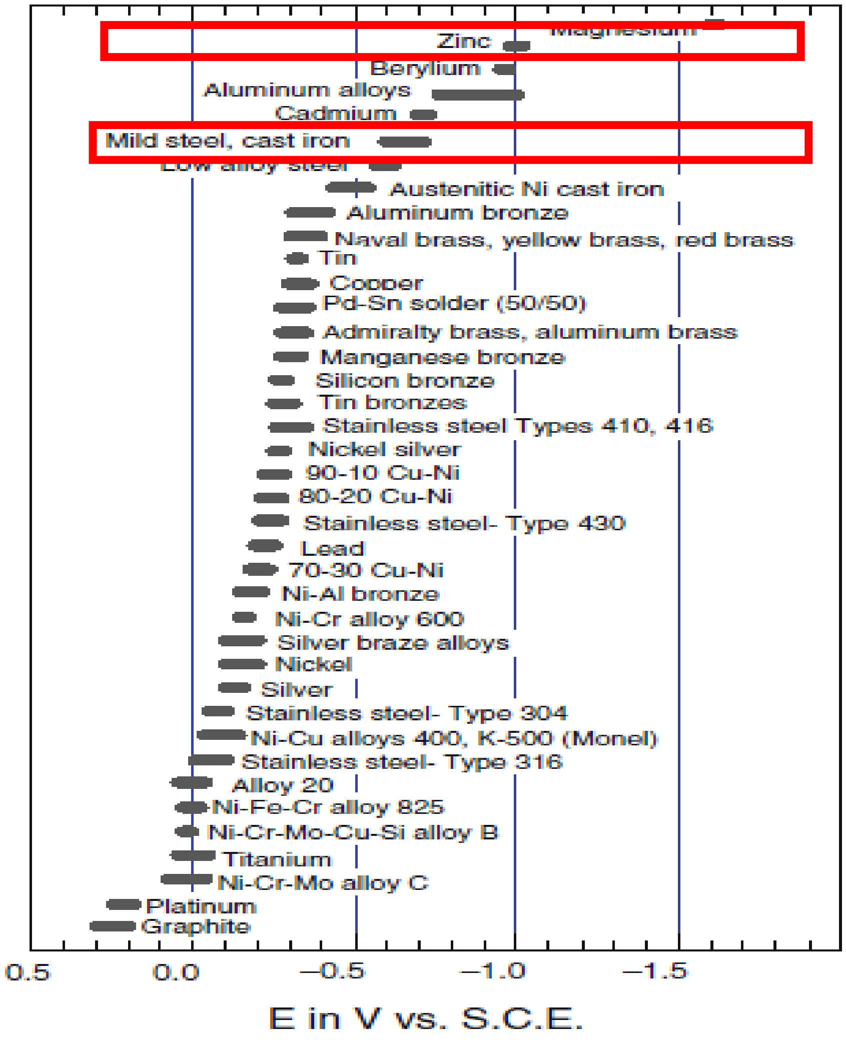


Figure 2.1: The galvanic series in seawater (McCafferty, 2010)

The two types of metals will have different electrochemical potentials and galvanic cell is generated between them due to their difference in voltage. In this case, the steel of ship hull will acts as a cathode and its partner as sacrificial anode.

A redox reaction can occur between the two metals with electron transfer occurring from the anode to the cathode which is dictated by their difference in electrochemical potentials. Figure 2.2 shows the electrochemical reactions that happen when zinc anode is attached to the protected steel.

2.1.2 Electrochemical Reactions

Figure 2.2 shows the anodic and cathodic reactions happen when zinc anode is coupled with mild carbon steel.

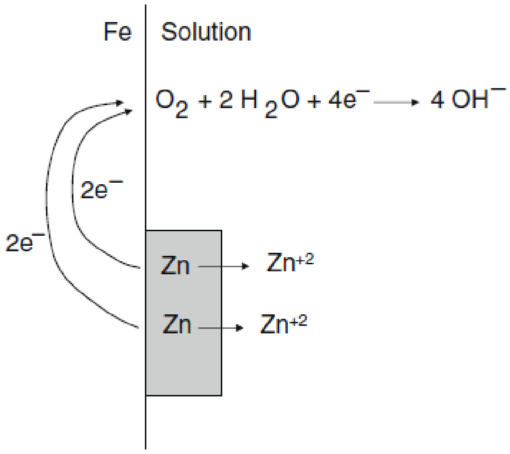


Figure 2.2: Schematic diagram of the cathodic protection of iron by zinc (McCafferty, 2010)

At Anodic Site (Reaction)

$Zn \rightarrow Zn^{2+} + 2e^-$ ....(2.1)

At Cathodic Site (Reaction)

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

The cathodic site, in Equation 2.2 undergoes reduction and becoming more negatively-charges due to electron donation from the anode and the anode will undergoes oxidation. At the anodic site in Equation 2.1, positively-charged metal ions which is cations will form at its surface. The cations will react with dissolved oxygen in seawater and leads to the formation of metal oxides at the surface of the anode (Tezdogan and Demirel, 2014).

Figure 2.3 shows a simple SACP system in which the protected structure is being protected by the positive current flow from sacrificial anode.

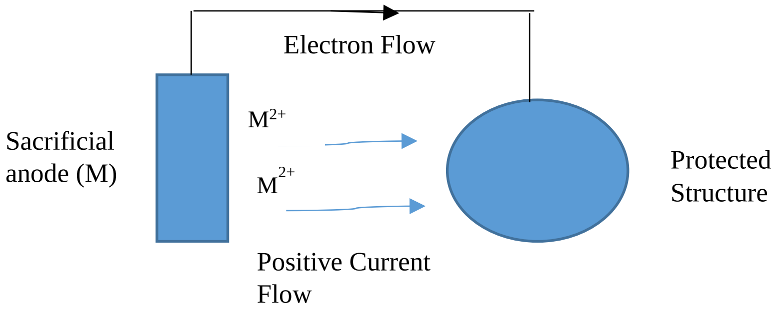


Figure 2.3: The electron flow diagram in SACP system

2.1.3 The Corrosion Rate of Zinc Galvanized Steel

Table 2.1 shows the corrosion rate of zinc-coated steel in different seawater. The coupled system is studied as the fabrication of samples in this experiment is similar to it. The corrosion rate of the zinc coated steel as shown in Table 2.1 is about 0.009 mm/year to 0.023 mm/year.

Table 2.1: Corrosion rate of zinc-coated steel in different seawater (Porter, 1994)

Location and Water	Type of Zinc-Coated Steel	Type of Test	Years	Agitation	Corrosion Rate (µm/year)
Gosport and Emsworth Seawater	Hot-Dipped	Immersion	6	Flowing	9
Kure Beach, North Carolina Seawater	Galvanized	Immersion	5	Flowing	13
Kure Beach, North Carolina Seawater	Galvanized	Immersion	3.5	Flowing	15
Kure Beach, North Carolina Seawater	Galvanized	Immersion	1	Flowing	23

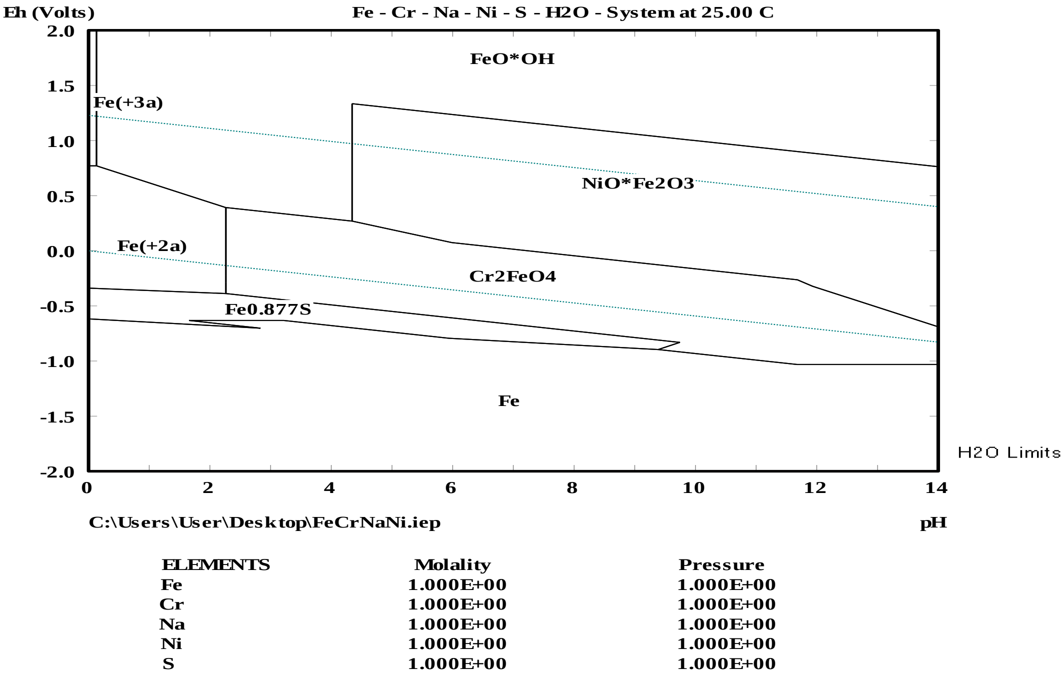
2.2 Methods of Attachment

2.2.1 Bolting

It has been customary to simply attach the anodes to the ship by bolting the anode elements in position. But, such bolting methods is not satisfied as good electrical contact between anode and the cathode. Undesirable factor arising with bolting the anodes into the position is that faying surfaces as well as the bolt holes of the anode must be carefully prepared with a waterproof material to prevent the anode material from dissipating and accumulating adjacent to the faying surfaces and bolt joints. This action causes loosening and later detachment of the anode from the bolting support (Preiser, 1965).

Besides that, during electrochemical action, the sacrificial anode is slowly dissipated and causes the securing bolts which hold the anodes protrude above the anodes which are dissipated. Problem arises when the protruding bolts which attached to the vessel of ship under the seawater to increase water resistance and turbulence. This will reduce the efficiency and speed of the vessel.

The bolt used in bolting attachment method should not be corroding during immersion and application in seawater. Figure 2.4 shows the pourbaix diagram of stainless steel. It shows that high potential and low pH value are required for stainless steel to corrode. Besides that, the formation of protective oxide layer on chromium has prevented further oxidation to happen.



ELEMENTS	Molality	Pressure
Fe	1.000E+00	1.000E+00
Cr	1.000E+00	1.000E+00
Na	1.000E+00	1.000E+00
Ni	1.000E+00	1.000E+00
S	1.000E+00	1.000E+00

Figure 2.4: Pourbaix diagram of stainless steel at room temperature

2.2.1.1 Crevice Corrosion

In the bolting system, crevice corrosion can occur. Crevice corrosion is localized corrosion that occur within narrow clearances or under shielded metal surfaces.

Crevice corrosion initiates due to the presence and operation of a differential oxygen cell. Figure 2.5 shows the condition for crevice corrosion to happen. Oxygen reduction occurs on both the metal surface which is exposed to the bulk electrolyte and also on the portion of the metal surface which is contained within the crevice as shown in Figure 2.5.

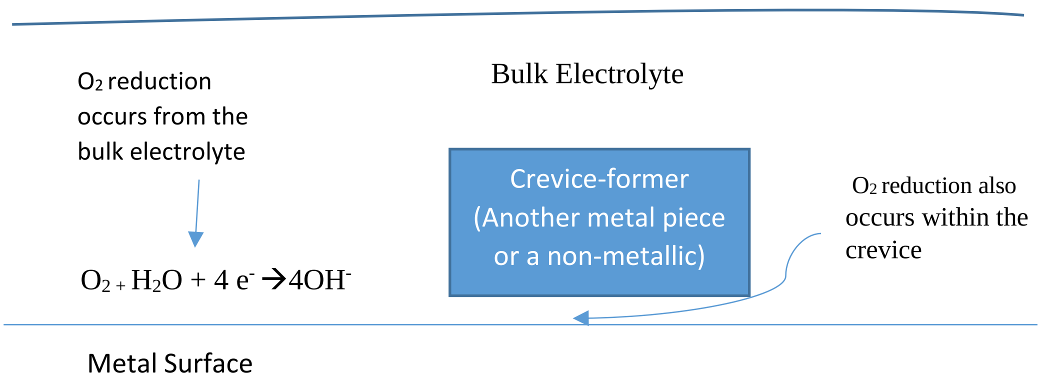


Figure 2.5: Schematic diagram of oxygen concentration cell of crevice on metal surface (McCafferty, 2010)

When the metal exposed to the bulk electrolyte is in contact with an open supply of oxygen from the atmosphere, O_2 is consumed near the external metal surface and steady-state concentration of O_2 is maintained near the surface of the external metal. But, when O_2 molecules are consumed within narrow clearance of the crevice, they are not easily replaced due to the long narrow diffusion path formed by the crevice and oxygen becomes depleted within the crevice as shown in Figure 2.6.

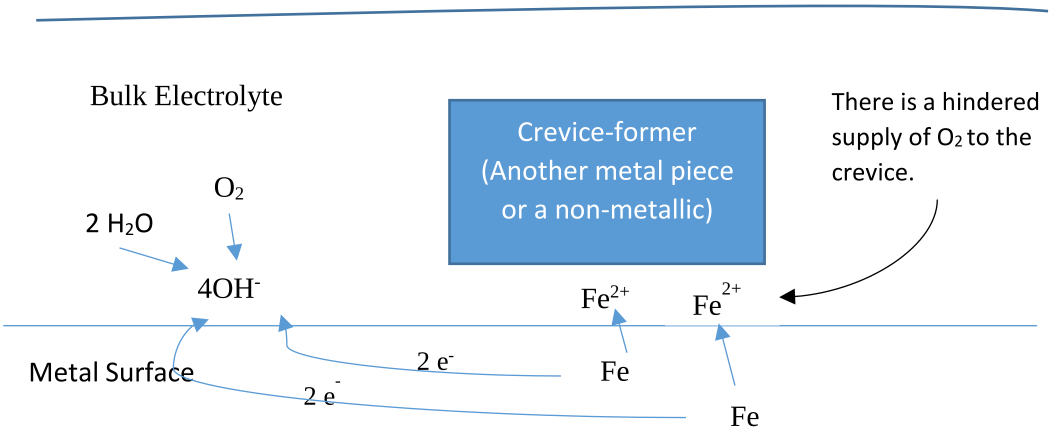


Figure 2.6: Mechanism of corrosion formation by crevice

With this, an oxygen concentration cell is formed between the metal surface outside the crevice and the metal surface within the crevice. The difference in O_2 concentration between the bulk solution and the sheltered crevice has two effects:

First, the metal exposed to the lower concentration of oxygen has a more negative potential for oxygen reduction than the metal exposed to a higher concentration of oxygen. Figure 2.7 shows that the concentration of dissolved oxygen varies with the gap size of the crevice and with time (Ulanovski and Korovin, 1962).

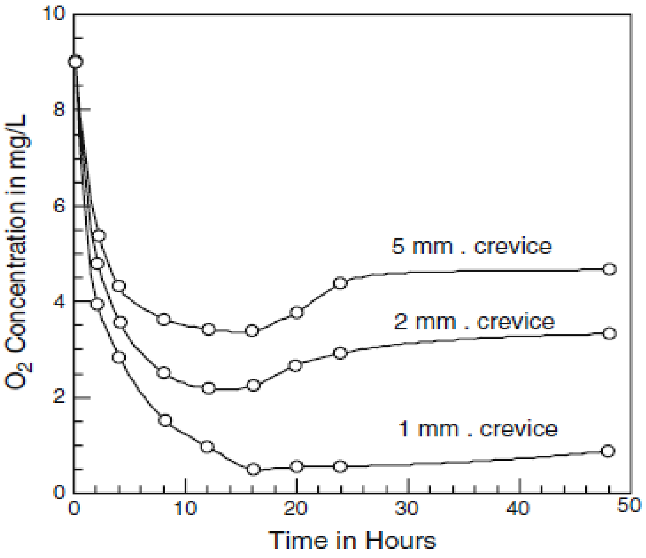


Figure 2.7: Variation of the oxygen concentration within crevices on a Cr-containing stainless steel (Ulanovski and Korovin, 1962)

The second effect is the limiting current density (i_L) for O_2 reduction within the crevice is decreased relatively to that for the bulk solution. This is caused by the concentration of dissolved O_2 decreases within the crevice. The corrosion potential for creviced metal becomes more positive with time as oxygen is depleted within the crevice.

The differences in electrode potential between open and crevice metal amount to only tens of millivolts but these differences is enough to initiate corrosion within crevice. Figure 2.8 shows that there is only a 25 mV difference in the electrode potential (McCafferty, 1974).

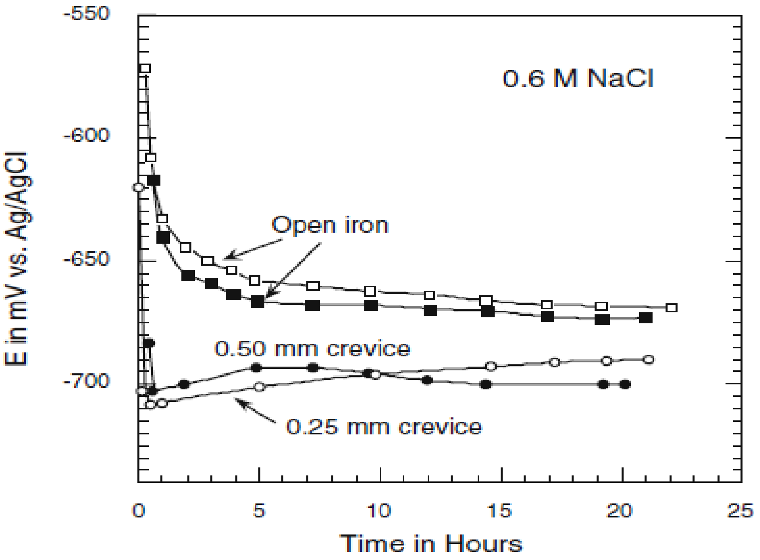


Figure 2.8: Establishment of steady-state potentials for open iron and iron within crevices in 0.6 M NaCl (McCafferty, 1974)

2.2.2 Welding

2.2.2.1 Weldability of Low Carbon Steels

Low carbon steels contain up to 0.30 wt% C and about 1.65 wt% of Mn. At low carbon levels which is less than 0.15 wt% of C, the steels are non-hardening and weldability is excellent. In the range of 0.15% to 0.30 wt% of C, also termed mild steel, the steels are commonly easily to be welded. But hardening is possible in this case (Davis, 2006). Preheating may be required at higher manganese levels, in thicker sections, or at high levels of joint restraint.

2.2.2.2 Welding Processes

All of the arc welding processes are suitable for welding carbon steels. The welding processes considerations depends on the materials characteristics, joint design, welding position and weld position (Davis, 2006).

2.2.2.3 Corrosion of Carbon Steel Weldments

The corrosion behaviour of carbon steel weldments through fusion welding depends on a number of factors. It is difficult to predict whether corrosion attack will be concentrated on the HAZ, weld metal or both areas in susceptible conditions (Davis, 2006).

2.2.2.4 Residual Stress of Weldments

The base metal, HAZ and underlying weld (see Figure 2.9) experience stresses due to thermal expansion and contraction during welding. High levels of residual stress which is often close to the material yield stress will remain as a result of weld shrinkage. Crevice corrosion and fatigue cracking will happen as a result of geometrical discontinuities such as weld reinforcement (excess weld metal) and lack of full weld penetration (Davis, 2006).

2.2.2.5 Preferential Heat Affected Zone (HAZ) Corrosion

Heat-Affected Zone is the portion of the weld joint which experience peak temperature high enough to produce solid state microstructural changes but not melting. Figure 2.9 shows the region of HAZ of a weld. Every position in HAZ experiences unique thermal experience during welding in terms of both maximum temperature and cooling rate, thus they has their own microstructural and corrosion susceptibility.

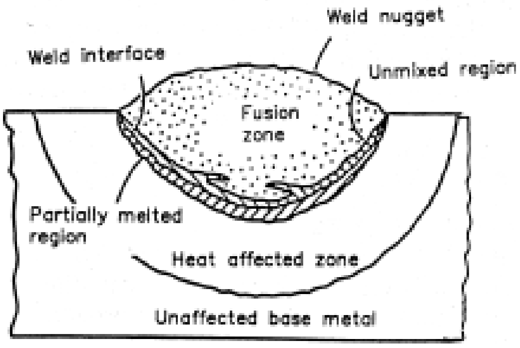


Figure 2.9: Region of a heterogeneous weld (Davis, 2006)

Preferential HAZ corrosion in seawater is attributed to the presence of low-temperature transformation products such as martensite, lower bainite or retained austenite.

Hardened steel corrode more rapidly in acid conditions than fully tempered material. This is because the local microcathodes on the hardened surface can stimulate the cathodic hydrogen evolution reaction and the rate of corrosion is usually controlled by the cathodic or reduction rate if other limiting factor are not affecting. Figure 2.10 shows the microstructure of preferential corrosion in the HAZ of a carbon steel weldment.

Although it is a factor in acidic environments but less in neutral or alkaline conditions. But even at a pH near 8, hydrogen ion (H^+) reduction can account for approximately 20% of the total corrosion current. Post weld heat treatment at 590 °C is useful to relieve stress and reduces HAZ attack but it is usually impractical (Gooch, 1986).

Figure 2.10: Preferential corrosion in the HAZ of a carbon steel weldment after service in an aqueous environment (Davis, 2006)

Figure 2.11 shows the average calculated electrochemical impedance spectroscopy (EIS) corrosion rates between 5 and 10 days from a low chloride (0.35 g/L NaCl) test. The results shows that the welds area are more susceptible to corrosion.

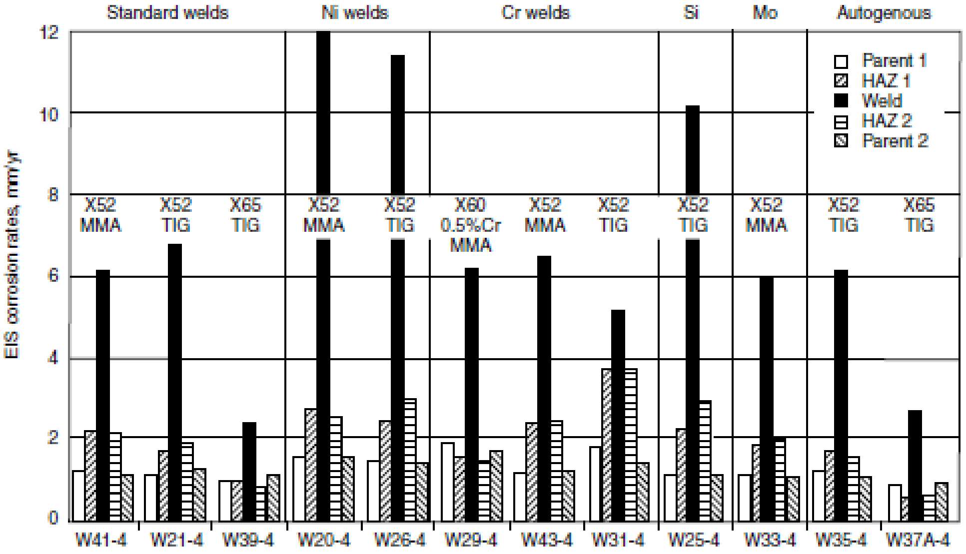


Figure 2.11: Average EIS calculated corrosion rate during the period of 5-10 days tests conducted in low chloride solution at 60ºC (Davis, 2006)

2.3 Thermodynamic Modelling of Corrosion

2.3.1 Pourbaix Diagram

Pourbaix diagram are plots of (reversible) potential vs pH for elements in pure water. It indicates certain regions of potential and pH where the metal undergoes corrosion and other regions of potential and pH where the metal is protected from corrosion.

2.3.2 Pourbaix Diagram of Carbon Steel

Thermodynamic modelling of pourbaix diagram of carbon steel and zinc is done using the HSC Chemistry 6 software before electrochemical analysis is carried out. This is done to maps out and study the possible stable state of a system at different potential and pH value.

Figure 2.12 shows the pourbaix diagram of carbon steel. From the diagram, it can be recognised that at which range of pH and potential the carbon steel is protected from corrosion (immunity) or vice versa.

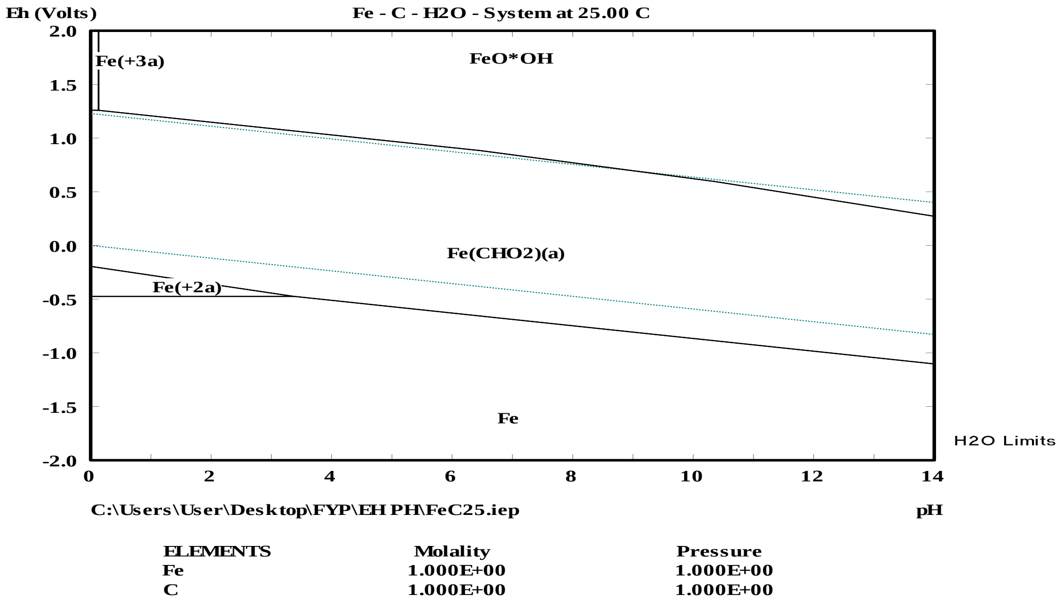


Figure 2.12: Pourbaix diagram of Fe-C-H$_2$0 system at room temperature

2.3.3 Pourbaix Diagram of Zinc

Figure 2.13 shows the pourbaix diagram of zinc at room temperature.

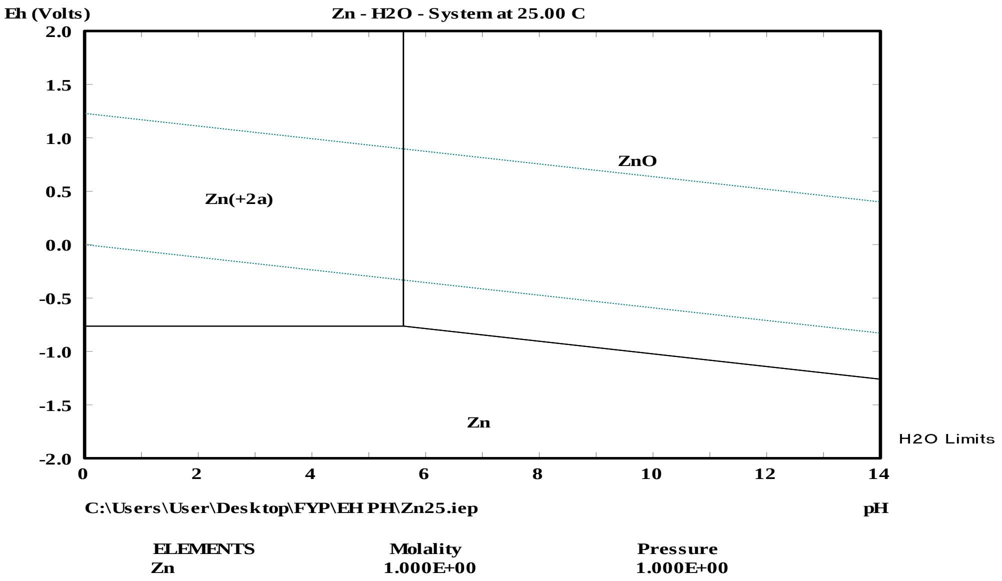


Figure 2.13: Pourbaix diagram of zinc at room temperature

2.4 Raw materials

2.4.1 Sacrificial Anode - Zinc Anode

Zinc has been in use for sacrificial anode cathodic protection in seawater in 1824. Zinc anode itself has low self-corrosion rate. In fresh cold water, zinc has corrosion rate of 25 µm a^{-1} or amounts to weight loss about 0.002 g m^{-2} h^{-1}. In stagnant cold seawater, the corrosion rate is 50% higher and greater in flowing water significantly (Baeckmann et al., 1997). Zinc anode is not recommended and not practically used in warm water or temperature higher than 50°C because it tends to passivate (Baeckmann et al., 1997).

Zinc anode will became passive if the purity of zinc is not high. Super high grade zinc which consists of 99.995% Zn and less than 0.0014% Fe without any additions has the least problems of passivation. But super high grade zinc is mostly coarse grained. This has led to non-uniform removal or dissolution of zinc due to its columnar crystal structure.

With this, alloy additions of up to 0.15% Cd and 0.5% Al are made for grain refinement (Baeckmann et al., 1997) and compensate the detrimental influence of higher Fe content up to 0.005% (Morgan, 1959).

Magnesium anode is not used in seawater because it can release a large volume of hydrogen gas due to a self-corrosion process (Taylan, 2009).

The consumption rate of aluminium is 1/3 of the weight of an equivalent zinc anode but Al is more expensive than Zn in terms of kilo price (Taylan, 2009). So, it can be said that Al anodes are advantageous over Zn anodes based on overall costs. On the other hand, there are restrictions in the use of aluminium anodes inside and adjacent to cargo tanks carrying cargoes with low flash point. This is because it will be danger of generating sparks if the anodes loosen and fallen down (Tezdogan and Demirel, 2014).

2.4.2 Mild-Steel or Low carbon steel

The average corrosion rate of carbon-steel which is total immersed in seawater is estimated to be 0.1mm per annum while 0.4-0.5mm per annum in splash zone (Baeckmann et al., 1997).

2.4.3 Seawater

The seawater through the ships travel are categorized by their salt content. The salt content of the world's ocean is almost the same and is 1.8 times the chloride ion content. The salt content determines the specific electrical conductivity of the water. Following are the approximate value for: seawater, 3.0 to 4.0% salt; coastal brackish water, 1.0 to 3.0% salt; river brackish water, 0.5 to 1.8%; salty river water, 0.05to 0.5%; river water, <0.05% (Baeckmann et al., 1997).

Conductivity increased with dissolved salts but do not take part in the corrosion process. Corrosion rate of carbon steel in salt solution is influenced by oxygen content but is not affected by salt concentration.

Dissolved salts have strong indirect influence on many local corrosion processes. Chloride ions in seawater accumulate at local anodes can stimulate dissolution of iron and prevent the formation of a film (Schwenk, 1977).

2.5 Effect of Environmental Factors on Corrosion Rate

2.5.1 The Influence of Mass Transport on Electrochemical Processes

Electrochemical reaction rate is controlled by rate of charge transfer or by mass transport. Velocity or agitation of solution strongly affect mass transport controlled processes but not the charge transport. Figure 2.14 summarizes the effects of solution velocity on various mass transport controlled corrosion situations.

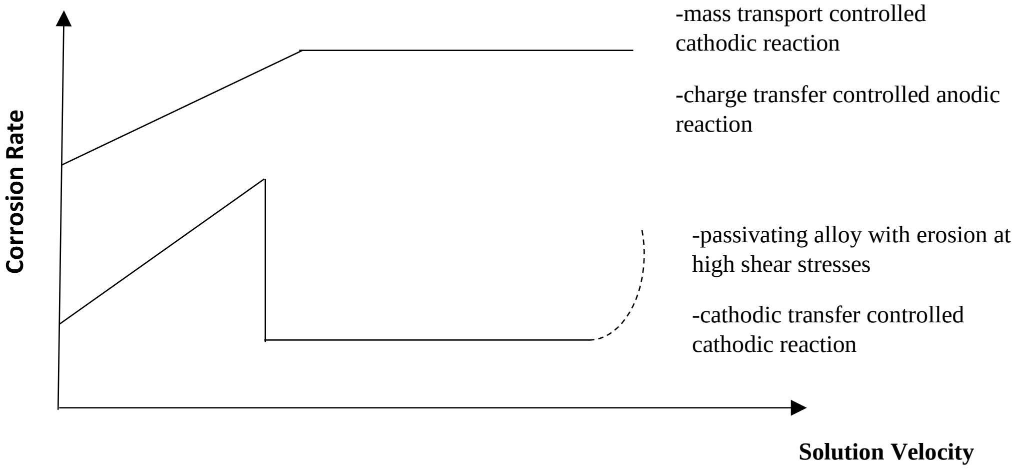


Figure 2.14: Phenomenological observations concerning the influence of solution velocity on metal corrosion rates (Robert G. Kelly, 2003)

The corrosion rate of bare metals is often observed to increase with solution velocity but becomes fixed at high solution velocities. This is a situation where the cathodic reaction is under mass transport control until high solution velocities are reached while the anodic reaction is charge transfer controlled.

At fixed intermediate cathodic potentials, the mass transport controlled reaction rate will continue to increase with increasing flow rate until charge transfer control is established. The transition to a velocity-independent cathodic reaction rate signifies the change from mass to charge transfer control (Robert G. Kelly, 2003). At high velocity, both anodic and cathodic reactions are charge transfer controlled.

Figure 2.15 shows that the effect of solution velocity on the corrosion rate of carbon steel in the water containing various amount of dissolved Cl^-. It can be seen that corrosion rate increases with increasing velocity.

But, the further increase in solution velocity will decreases the corrosion rate. This may due to an increased supply of O_2 and passivation happen to the metal surface which slow down the corrosion rate.

In more aggressive environment, which is the natural seawater, where passivation does not occur and the corrosion rate of steel increases with increasing velocity (Que, 1975).

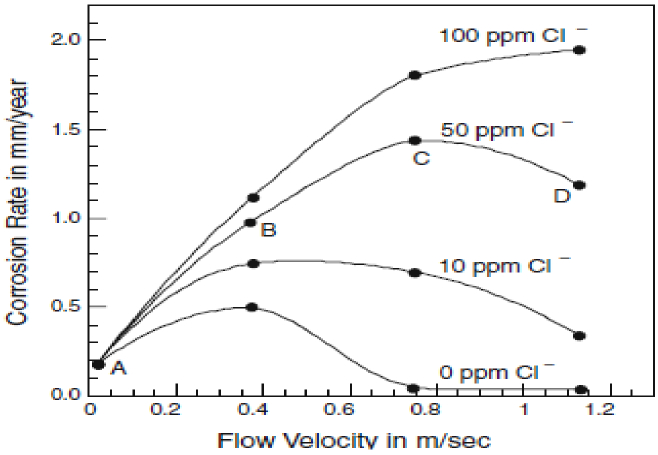


Figure 2.15: Effect of solution velocity on the corrosion (McCafferty, 2010)

2.5.2 Temperature

2.5.2.1 Temperature Effect on Aeration and Oxygen Content

In systems where the corrosion rate is under the control of the oxygen reduction reaction, oxygen is important component in the cathodic partial reaction. In the case of different aeration, heterogeneous film formed alongside with local corrosion. Local corrosion occurs on ships in splash zone due to differential aeration, particularly at welded joint.

The solubility of oxygen in water with a salt content up to 1 mol L^{-1} is only dependent on temperature. The depth of water has no effect to the concentration of oxygen in the case of ships. In the open sea, constant values of oxygen concentration are found at depths up to 20 m and decreases with increasing depth with low flow rates (Baeckmann et al., 1997).

With increasing temperature, the translational motion of molecules in the solution becomes more rapid. This causes the dissolved O_2 molecules more likely to enter the interface where it can escape back into the gaseous phase. Figure 2.16 shows the decrease in solubility of oxygen with the increase of temperature.

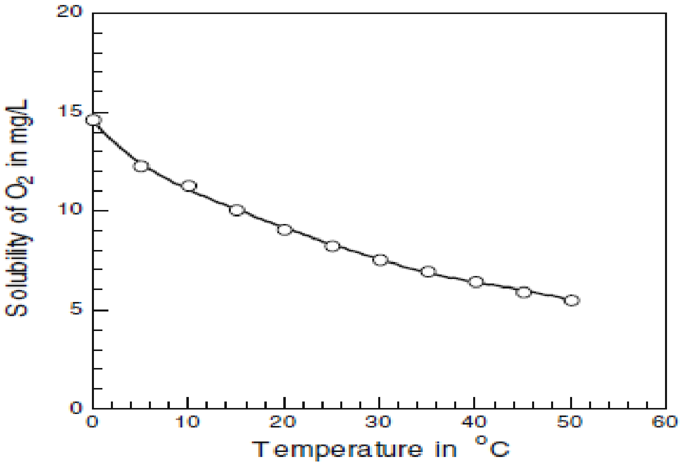


Figure 2.16: Solubility of O_2 in water as a function at 1 atm pressure (Droste, 1997)

Uglig et al. (Uhlig and Revie, 1985) has observed and stated that for the corrosion of mild steel in water containing small amounts of $CaCl_2$, the corrosion rate increases with increasing O_2 concentration as shown in Figure 2.17. So, solubility of O_2 is a factor to be considered to study the corrosion rate.

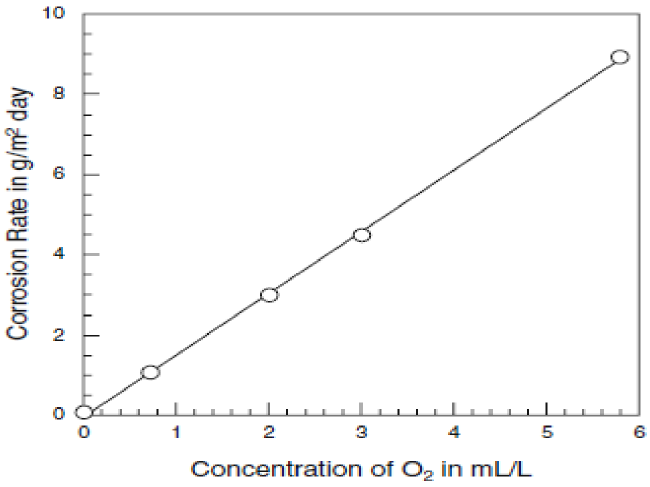


Figure 2.17: Effect of oxygen concentration on the corrosion of mild steel in water containing 165 ppm $CaCl_2$ (McCafferty, 2010)

Figure 2.18 shows the effect of temperature on the corrosion rate of iron in water open to the atmosphere and containing dissolved oxygen (Butler and Ison, 1966). The corrosion rate increases with increasing temperature up to about 80 ºC and decreases with further increase in temperature.

In this case, there are two effects which are competing. First, it is the diffusion coefficient D increases with temperature. The increase in diffusion coefficient also will increase the limiting diffusion current density i_L and thus the corrosion rate increases. This effect is predominant in the portion of the curve in Figure 2.18 where the corrosion rate increases with temperature (McCafferty, 2010).

Second temperature effect is the concentration of dissolved O_2 decreases with increasing temperature. As the O_2 concentration decreases, the limiting current density also decreases. This causes the corrosion rate to decrease. This effect can be seen when the corrosion rate decreases with increasing temperature from Figure 2.18.

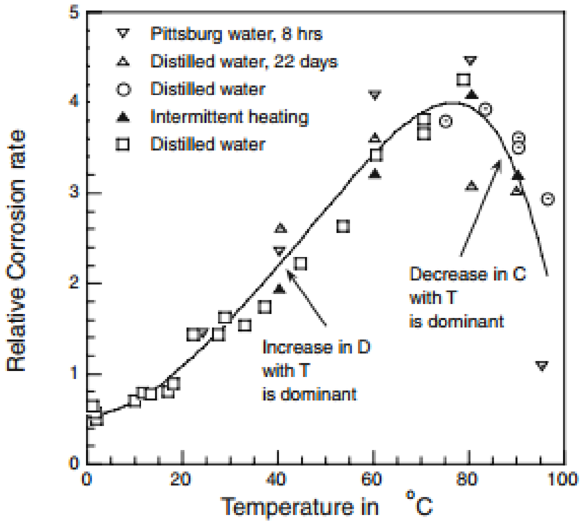


Figure 2.18: Corrosion rate as a function of temperature of iron in water open to the atmosphere (McCafferty, 2010)

2.5.2.2 Effect of pH on Corrosion Rate

A study done by S.Atashin, (2013) provides that in stagnant condition, corrosion rate increases by increasing pH up to 9. This can be explained that the increment of pH provides suitable media for localized corrosion. (Atashin et al., 2013) pH increment provides a favourable condition for localized attack and an increase in the rate of corrosion. As the pH increases to 10.5, corrosion rate decreases caused by the reduction in passive potential of metal and easier formation of protective layer.

Figure 2.19 shows the study of corrosion rate of carbon steel over the changing of pH by (Mardhiah Ismail, 2014). Results shows that the corrosion rate increases with the increase of pH from pH 7.5 to pH 9.5.

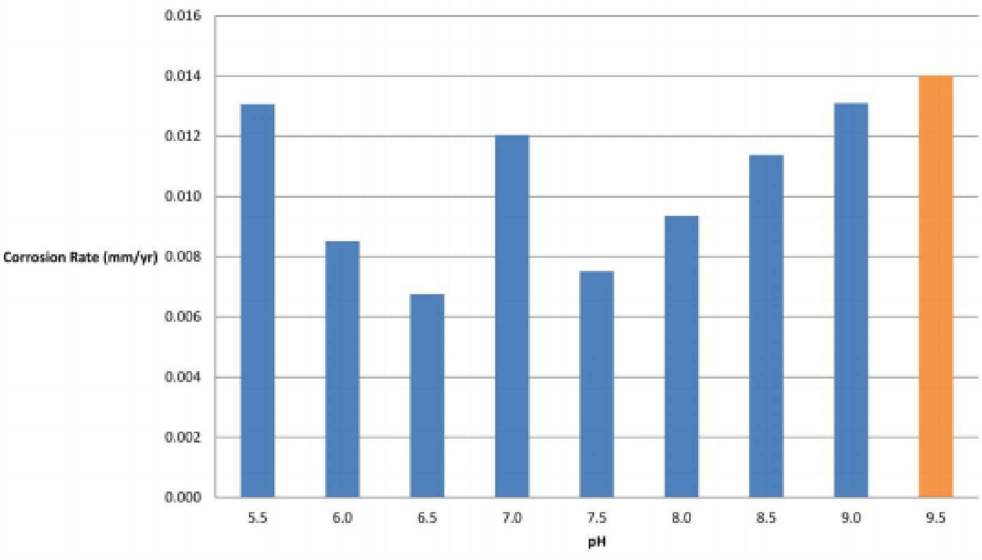
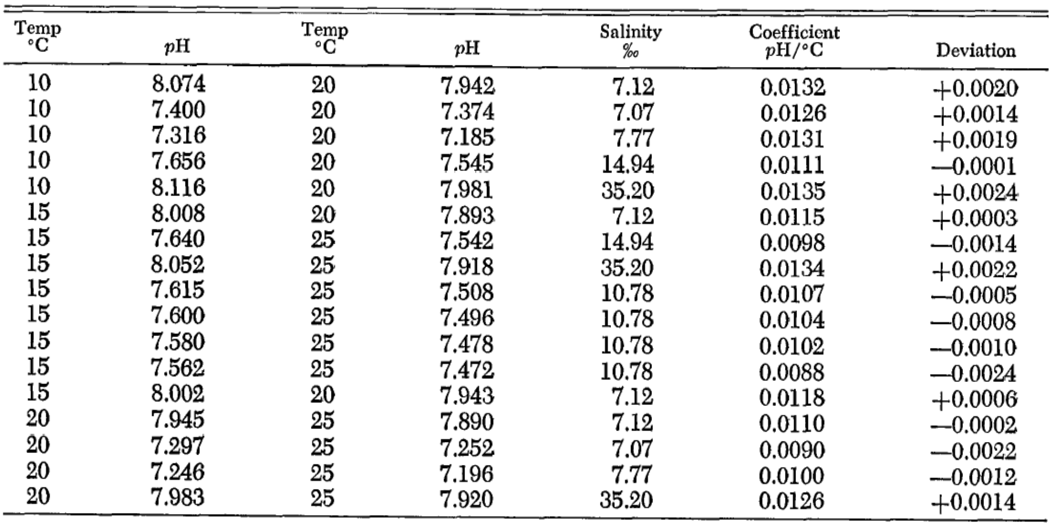


Figure 2.19: Corrosion rate of carbon steel with pH changes (Mardhiah Ismail, 2014)

2.5.2.3 Effect of Temperature on pH Value

pH value of seawater changes with temperature at fixed salinity. Increasing in temperature decreases the pH of the seawater. Table 2.2 shows the temperature coefficients for seawater at different salinity.

Table 2.2: Temperature coefficients for seawater ranging in salinity from 7.12% to 35.20% (Giekes, September 1969)



Temp °C	*p*H	Temp °C	*p*H	Salinity ‰	Coefficient *p*H/°C	Deviation
10	8.074	20	7.942	7.12	0.0132	+0.0020
10	7.400	20	7.374	7.07	0.0126	+0.0014
10	7.316	20	7.185	7.77	0.0131	+0.0019
10	7.656	20	7.545	14.94	0.0111	—0.0001
10	8.116	20	7.981	35.20	0.0135	+0.0024
15	8.008	20	7.893	7.12	0.0115	+0.0003
15	7.640	25	7.542	14.94	0.0098	—0.0014
15	8.052	25	7.918	35.20	0.0134	+0.0022
15	7.615	25	7.508	10.78	0.0107	—0.0005
15	7.600	25	7.496	10.78	0.0104	—0.0008
15	7.580	25	7.478	10.78	0.0102	—0.0010
15	7.562	25	7.472	10.78	0.0088	—0.0024
15	8.002	20	7.943	7.12	0.0118	+0.0006
20	7.945	25	7.890	7.12	0.0110	—0.0002
20	7.297	25	7.252	7.07	0.0090	—0.0022
20	7.246	25	7.196	7.77	0.0100	—0.0012
20	7.983	25	7.920	35.20	0.0126	+0.0014