

**CORROSION BEHAVIOR OF EPOXY (SIGMALINE) COATED X65 STEEL
IN SOME SELECTED CORROSIVE MEDIA**



A

THESIS

PRESENTED TO THE DEPARTMENT OF MATERIAL SCIENCE AND ENGINEERING
AFRICAN UNIVERSITY OF SCIENCE AND TECHNOLOGY, AUST, ABUJA, NIGERIA

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR A DEGREE OF

MASTER OF SCIENCE

BY

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ABUJA, NIGERIA

DECEMBER, 2014

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ABSTRACT

Like any industry, the economic success of the oil and gas industry can be no swifter than its success in corrosion control/prevention. Some oil and gas industries operate in hostile offshore environment that harbors significantly quite substantially different corrosive agents including ions of chloride, Cl^- , bicarbonate (HCO_3^-), hydrogen sulfide (HS^-), sulfide (S^-), etc., coupled with gases such as oxygen (O_2), carbon dioxide (CO_2), just to name a few. Oil and gas structural materials and pipeline steels are made of metals. The interaction amongst these metals and between the metals and the aforementioned corrosive agents in seawater water environment causes metallurgy in-reverse (corrosion) with time. The result of the corrosion process leads to rusting and subsequently, failure of the materials. Understanding the effects different corrosive environments have on materials deterioration doesn't only drive a better understanding of corrosion control methods and mitigation techniques but also play a pivotal role in preventing oil and gas offshore platform from corrosion attacks. The protection and safety such understanding offers to human and marine lives cannot be overemphasized. Billions of dollars can also be lost by poor corrosion management strategies. Although "corrosion prevention" is an overstatement as this research is concern, "corrosion control" is the diction of choose. Different corrosion control methods including cathodic protection, coating, etc., are possible but epoxy coating was considered for the purpose of this research. An analysis of the corrosion behavior of X65 steel samples coated with epoxy (sigmaline), was carried out in some selected corrosive media of different concentrations. Weight loss measurement was obtained at different time intervals. The corrosion rate of the steel samples were characterized based on weight loss measurements obtained from weighing balance and pH change calculations from corrosion reactions.

ACKNOWLEDGEMENT

My heartfelt thanks appreciation God Almighty, my **strength**, without whom this academic sojourn wouldn't have been a success. My gratitude goes to Prof. Winston O. Soboyejo, my supervisor and head of Department for his mentorship. I also want to recognize the DTCA/AfDB for funding my scholarship. Let me also appreciate Dr. Shola O. Odusanya for his guidance and provision of some research materials that made this work a success. My special thanks and appreciation goes to Dr. Conteh, Ambassador of the Republic Liberia accredited to the Federal Republic of Nigeria for his supports and efforts in the negotiation of my scholarship with the DTCA and AUST. Let me also salute the Civil Servant Agency and the Government of the Republic of Liberia for affording me the opportunity as one of the beneficiaries of her bilateral scholarship. I would also want to recognize the SCC Steel Company, Abuja, Nigeria, for her assistance in the provision of some research materials. My gratitude to the entire AUST faculty, staff, and students for the support which made this research a success. I am grateful to my family and friends whose prayer to God Almighty kept me focused through the course of my research.

DEDICATION

This thesis is dedicated to God Almighty for his guardian and my mother (late) who was always there with me and for me in the difficult times of my academic sojourn.

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CHAPTER ONE: INTRODUCTION

1.1 BACKGROUND

The demand for energy has continue to drive enhanced recovery and technological sources[1,2] including solar panels, organic light emitting devices, petrochemical products, etc., with petroleum being demanded the most World-wide[3] according to figure 1.1. Being the major demand of energy source, petroleum recovery, its transportation, and storage still remain a serious challenge through metal pipelines subject to failure in corrosive environments[4,5] However, this demand has not only driven lucrative investments in new pipeline designs, but has also challenged scientists and engineers involved with both researching and providing pipeline coatings to address protection requirements in corrosive environments that traditional coatings technologies cannot provide [6].

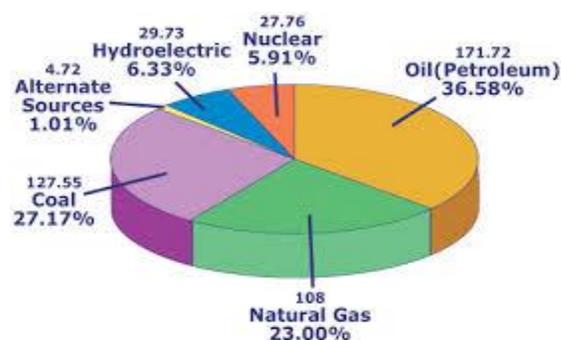


Figure 1.1: World major energy sources and consumption (Adapted from www.triplehelixblog.com)

Most of oil and gas pipelines, valves, bolts, and other structural materials are made of metals that once existed in nature as stable ores, carbonates, or sulfides [1]. During metallurgical extraction process of ores, the refined metal absorbs a tremendous quantity of energy (unstable state), and corrosion is the natural means of releasing the high energy, thus reversing the metal to its initial low energy stable state [7]. Thus, preventing this reversible process, and hence, preventing oil and gas pipeline structures from corroding is very crucial to the petroleum industries whose products power a vast majority of the World's manufacturing industries, transportation, and also serve as energy source in homes. Although hydrocarbon fluids are not corrosive, pipelines carrying these fluids are not immune to corrosion [5]

In this research, X65 steel is coated with fusion-bonded epoxy and studied in different corrosive environments (NaCl, Na₂CO₃, and HCl), and the rate of corrosion is analyzed by means of the following characterization techniques:

1. Weight loss
2. pH measurements

Good functions of a coating material rely on its strong metal surface adhesion and durability, extremely low porosity, high viscosity among others.

1.2 MOTIVATION AND PROBLEM STATEMENT

The fight against corrosion attacks on offshore oil and gas metallic structural materials have become a major area of research from metallurgical recovery and processing of metal, though, design stage up to the production, transportation, and storage environments [8]. The truth remains that no matter how carefully controlled the metallurgical and design processes are, metals are susceptible to corrosion attack by exposure to environments with time [1]. Thousands of human lives and billions of dollars are lost through structural deterioration by poor corrosion management and control strategies [9,10].

Like all other industries, the economic success of the oil and gas industry can be no swifter than its success in maintaining its metallic structures from corrosion attacks. The fact is that most oil and gas production includes co-produced water that makes corrosion a pervasive issue across the industry [1].

Although a lot of research has been devoted to corrosion mitigation and control methods, some of which though not environmentally friendly, cause millions of dollars, yet, corrosion still remain a major threat to the structural integrity of oil and gas platform[11].

1.3 OBJECTIVE AND SCOPE OF THE RESEARCH

1.3.1 OBJECTIVES

1. To investigate the effect/rate of corrosion on coated (with FBE) X65 steel use in oil and gas pipelines when the steel sample is immersed in the following corrosive media with time:

- i. 3.5% aqueous sodium chloride, $\text{NaCl}_{(\text{aq})}$
- ii. Aqueous sodium carbonate, $\text{Na}_2\text{CO}_{3(\text{aq})}$, with pH 8.16
- iii. Dilute hydrochloric acid, $\text{HCl}_{(\text{aq})}$, with pH 2.71

2. To study the discrepancy, if any, between weight loss values obtained from weighing balance and pH calculations during metal dissolution in the aforementioned corrosive media

1.3.2 SCOPE OF THE RESEARCH

The research will involve:

1. Preparation of steel sample
 - i. Cutting of samples in a regular shapes as to easily determine the their area geometries
 - ii. Grinding using silicon carbide (SiC) with roughness of 60 micron
2. Mixing of epoxy (the base material) with activator (the hardener), in an appropriate volume ratio as recommended by SIGMALINE

3. Application of the mixture (epoxy-activator) on the surfaces of grinded samples – coating of the prepared X65 steel samples
4. Immersion of the coated X65 steels in the different corrosive environments as mentioned in the objective and observing their corrosion behavior with time

1.3.3 ORGANIZATION OF THESIS

This thesis consists of five chapters. Chapter one gives background introduction of the thesis, defines the problem, and states the objective and scope of work. Chapter two discusses the literature review. The thesis experimental approach is presented in chapter three before presenting results and discussion in chapter four. Conclusions, and future works arising from this study are summarized in chapter five.

CHAPTER TWO: LITERATURE REVIEW

2.1 THE BASIS OF CORROSION THEORY

Corrosion can simply be defined as the deterioration of a material (metals, ceramics, or polymers) due to an interaction of its environment [12,7]. However, for the purpose of this research, the definition is only restricted to metals. To be realistic, all environments are corrosive to some degree [12,9]. Environment as mentioned in this context refers to the corrosive media, basically air, water, solution (of acid, base or salt), temperature as well as industrial atmosphere [13]. The steel pipelines used in oil and gas industries are always under constant attacks at every stage by corrosion from casing strings to production platform; from drilling to refinery up to storage [1]. The time interval between the interaction of the material with its environment and subsequently the metal's deterioration determines the corrosion rate. The corrosion process of sensitized 18-8 stainless steel may take just few hours in polythionic acid but several years are required for the corrosion process of a railroad track [12].

The corrosion of metals is a reversed process of extractive metallurgy as illustrated by figure 2.1. Most metals exist in nature as stable ores of oxide, carbonates, or sulfides [12]. However, extractive metallurgical processes involved in obtaining metals from their ores require high energy absorption and hence, resulting in an unstable metallic state – the metal must be maintained at this high energy state. Corrosion is nature's way of reversing the refined metals back to their once low energy stable state [12,7]. For instance, most iron ores contain oxides of iron. The formation of hydrated iron oxide results in a process of metallurgy in reverse (lower energy stable ore state) when steel (which contains iron) becomes rust (steel and iron corrosion) by its interactions with water and oxygen [Fontana].

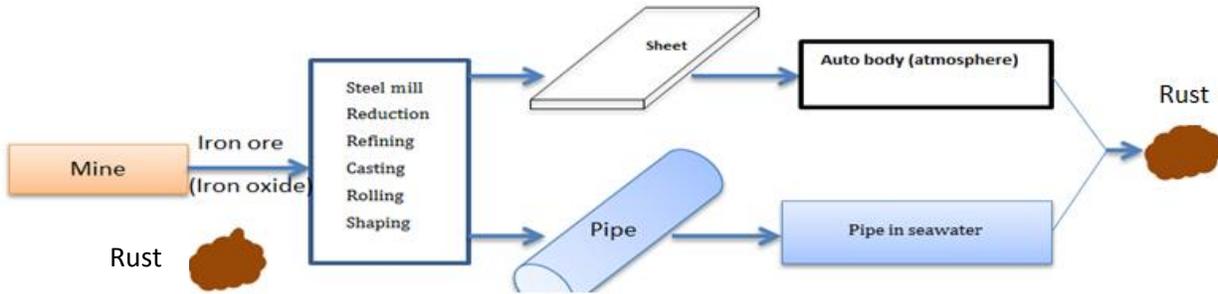


Figure 2.1 Metallurgy in Reverse

(Adapted from Mars G. Fontana; Corrosion Engineering, Third Edition)

Basically, corrosion of metallic materials can be categorized into three main groups [1,10]:

1. Wet corrosion: this occurs in environments where water/liquid solution with dissolved species (Cl^- , H_2S , OH^- , CO_2 , etc) serve as the corrosive media and it accounts for most corrosion [12,1]. The liquid is an electrolyte and the process is typically electrochemical.
2. Corrosion in other fluids such as fused salts and molten metals.
3. Dry corrosion: the corrosive environment is a dry gas. Dry corrosion is also frequently called chemical corrosion and the best known example is high temperature corrosion [12]. However, the focus of the research is wet corrosion.

2.1.1 WET CORROSION: CHARACTERISTICS; THE IMPORTANCE OF CORROSION PREVENTION; AND CORROSION RATE

2.1.2 CHARACTERISTIC DESCRIPTION

Figure 2.2 describes a schematic of the main feature of wet corrosion of a divalent metal M, in aqueous environment - electrolyte containing oxygen which accounts for the greatest amount of

corrosion by far [12]. Two reaction processes namely: (1) anodic reaction involving an oxidation process (loss of electron(s), thus increase in oxidation number) and a subsequently, the gradual dissolving and transferring of ions from metal surface into the solution as M^{2+} ions; and (2) the cathodic reaction which involves oxygen reduction (i.e. the gaining of the lost electron(s) of the metal by another species in the solution) [14]. This process is supported by aqueous solution in contact with the metal (forming an electrolyte) and the electrochemical process is closed by ion conduction through the electrolyte [15]. In accordance with the conditions as described by the anodic and cathodic processes, the dissolution process is referred to as wet corrosion and the mechanism is typically electrochemical [10].

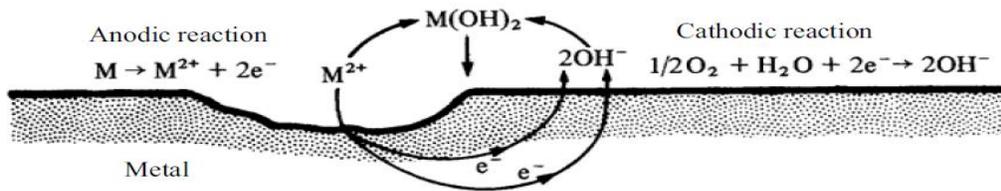


Figure 2.2: Wet corrosion of a divalent metal M in an electrolyte containing oxygen.

(Adapted from *Corrosion and Protection (Engineering Materials and Processes 2004; by E. Bardal)*

In natural environments like seawater, fresh water, soil and the atmosphere, oxygen reduction is the most dominant cathodic reaction[16,10]. However, under certain conditions there are also other important cathodic reactions: the hydrogen evolution reaction, reduction of carbonic acid (H_2CO_3) (in oil and gas production), reduction of metal ions etc. The driving force for the

electrochemical process (the corrosion) is the cell voltage, or in other words the potential difference between the anode and the cathode[10].

2.1.3 CRUCIAL MECHANISM THAT DETERMINE CORROSION RATES

The deposition of corrosion products - hydroxide $M(OH)_2$, on the metal surface may reduce/limit the oxygen supply because oxygen, the absence of which the corrosion process may not occur, has to diffuse through a deposits of continuous layer of oxide film (the hydroxides) on the metal surface[17]. A limited oxygen supply to the metal surface caused by the protection of oxide film results in a limited reduction rate of oxygen and a subsequent reduction of the corrosion rate since the rate of metal dissolution equals the rate of oxygen reduction [18,10]. This reduction in corrosion rate is under cathodic control – a widespread mechanism for corrosion limitation by nature. Agitating the solution at high velocity and the corresponding fluid dynamical forces can increase the rate of oxygen reduction and even remove the corrosion product from the metal surface thereby increasing the corrosion rate (erosion corrosion) [19].

If the agitation is not vigorous enough, the continuous oxide films of corrosion products form at metal surface. These films prevent the conduction of metal ions from the metal-oxide interface to the oxide liquid interface, thus resulting to a very low corrosion rate (anodic control) [19]. The phenomenon is referred to as passivation [12] and typical to materials like stainless steel and aluminum in many natural environments [18]. Structural steels are also passivated in alkaline waters. Upon its nucleation, the growth of the passivation is accelerated by ample access of oxygen on the metal surface, which is obtained by high oxygen concentration in the solution and

by efficient transport of oxygen as a result of strong convection (high flow rates provided the energy associated with such high flow rate doesn't exceed the energy that binds the film to the metal surface) [20.]. Conversely, passivation may be retarded or a passive film may be broken down by the lack of oxygen. This often happens underneath deposits and in narrow crevices that obstruct the oxygen [18]. Aggressive species like chloride ions are other major causes of the local breakdown of passive films that occurs in crevice corrosion, pitting and other forms of corrosion [10].

When a noble metal with large surface area is brought in contact with a less noble metal of small surface area, the noble material offers an extra area for the cathodic reaction [21]. Therefore the total rate of the cathodic reaction is increased, and this is balanced with an increased anodic reaction, i.e. increased dissolution of the less noble material (galvanic corrosion) [18].

2.2 CLASSIFICATIONS OF STEELS TYPES:

Steels are generally classified into two broad categories of carbon steels and alloy steels.

2.2.1 CARBON STEELS

- i) Low carbon steels containing about 0.05 – 0.15% C. Due to their very low carbon content, these steels have the basic structure of ferrite thus making them ductile and low strength. They have the ability to mildly respond to strength hardening by cold working and not hardenable by quenching and have low corrosion resistance[22]

- ii) Mild steels contain about 0.15 – 0.30% C with ferrite structure in which pearlite is scattered and are ductile and strong with low corrosion resistance compared to low carbon steels[22]
- iii) Medium carbon steels contain about 0.30 – 0.70% C with essentially pearlite structure and can be used in quenched and tempered conditions, but can also be normalized occasionally. These steels have lower corrosion resistance than mild steels[22]
- iv) Hard carbon steels fall in the range of about 0.65 -2.0% C. They can be used in the quenched and tempered conditions of hardening for hard strength applications like springs, hammers, wood saws, high elasticity steels, etc.

2.2.2 ALLOY STEELS

- i) Low Alloy steels – these are carbon steels that contain fewer percentage of alloying elements of chromium, nickel, copper, molybdenum, phosphorus, and vanadium. They have better corrosion resistance than plain carbon steels[22]
- ii) Medium Alloy steels – chromium and silicon are added to these steels to improve their oxidation and corrosion resistance and help improve their creep and high temperature resistance properties which allow the steels in applications such as in engine valves, boiler tubes, furnace materials, etc.[22]
- iii) High Alloy Steels – these steels have better strength, and a significant wear and corrosion resistance. The mechanical hardenability properties are improved by high alloy addition. High alloy steels are used for ultra-high strength and tool steels [12]

- iv) Stainless Steels – the formation of adherent chromium oxide film on the steel surface prevents chemical attacks. Their applications are found in resisting heat and harsh chemical corrosion. To improve their protection ability, >12%Cr is required[22]

2.3 FORMS OF CORROSION

Corrosion forms can be classified on the basis of how the corrosion manifests itself in terms of the appearance of the metal through visual observation by means of naked eye or sometimes with aided magnifications [12, 23]. The damage caused by each of the different forms of corrosion results in the deterioration and failure of the susceptible material with a subsequent loss of physical and/or chemical properties such as strength, ductility, composition, etc.[24] .

These corrosion forms include:

1. General or uniform corrosion – probably the most common form of corrosion and can be characterized by chemical or electrochemical interaction between a metal and its environment with equivalent intensity over the entire exposed surface or over a large area. When handling chemical media in correlation with uniform corrosion, the metals involved can be classified into three groups in accordance with the rate of corrosion and the intended application as follows[24]:
 - A. < 0.15 mm/y (< 0.005 ipy) — Metals in this category have good corrosion resistance to the extent that they are suitable for critical parts, for example, valve seats, pump shafts and impellers, springs.
 - B. 0.15 to 1.5 mm/y (0.005 to 0.05 ipy) — Metals in this group are satisfactory

if a higher rate of corrosion can be tolerated, for example, for tanks, piping, valve bodies, and bolt heads.

C. > 1.5 mm/y (> 0.05 ipy) — Usually not satisfactory.

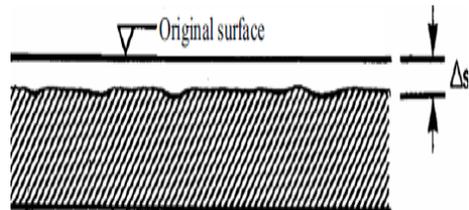


Figure 2.3: Uniform corrosion (a) On metal surface (b) Material reduction at metal surface

(a) *Uniform corrosion on metal surface (Adapted from WWW.METROHM-AUTOLAB.COM)*

(b) *Reduction in material at surface (Adapted from E. Bardal Corrosion and Protection(Engineering Materials and Processes)*

2. Galvanic corrosion – results when two dissimilar metals are electrically connected or brought in contact in a corrosive electrolyte [12]. The driving force for this form of corrosion is the potential different that results from electron flow from the more active metal to the less active or noble metal [24].

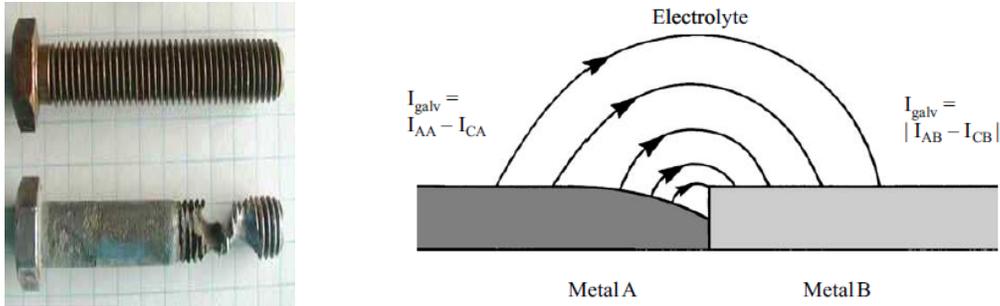


Figure 2.4 (a) contacts between two dissimilar metals (b) transfer of electrons from Metal A to Metal B

(a) Corrosion as a result of contacts between two dissimilar metals (Adapted from Corrosion_kinetics) and (b) transfer of electrons from Metal A to Metal B (Adapted from E. Bardal, Corrosion And Protection(Engineering Material and Processes)

3. Crevice corrosion – a localized corrosion concentrated between a gap of screw heads of metals which is wide enough to allow penetrate and at the same time narrow enough to allow stagnation of liquid. It also occurs beneath flange gaskets, paint coating edges, in overlap joint, etc, caused by differences in the concentration of dissolved ions and gases such as oxygen that develops beneath deposits of corrosion products, dirt, and sand. The metals must be passive beforehand, or should be easily passivated [12,24].

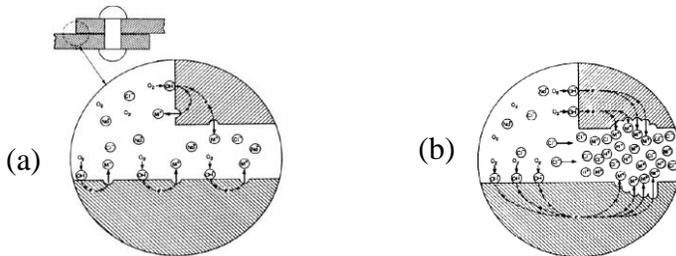


Figure 2.5: (a) crevice initiation (b) Crevice corrosion – late stage (Adapted from Fontana)

4. Pitting corrosion - another form of very localized corrosion attack in which small pits or holes form that eventually penetrate from the top of a horizontal surface downward in a vertical direction with very little material loss; extremely insidious in nature and considerably difficult to predict[12]. It occurs on passivated metals and alloy in environments containing chloride, bromide, iodide, or perchlorate ions when the electrode potential exceeds the critical value of the pit with similar mechanism of initiation and growth as crevice corrosion [24].



Figure 2.6: Different shapes of corrosion pits

(Adapted from E. Bardal, Corrosion and Protection (Engineering Materials and processes))

5. Intergranular corrosion – preferentially, this form of corrosion occurs along grain boundaries for some alloys and in specific environments resulting in disintegration of macroscopic specimen. It is mainly prevalent in stainless steels when heated to temperatures between 500 – 950 °C for sufficiently long periods of time, thus permitting the formation of small sensitized precipitate particles of chromium carbide, Cr_{23}C_6 , due to reaction between chromium and carbon in the steel [24]. This occurs along grain boundaries leaving chromium-depleted zone adjacent the grain boundary susceptible to corrosion [24].

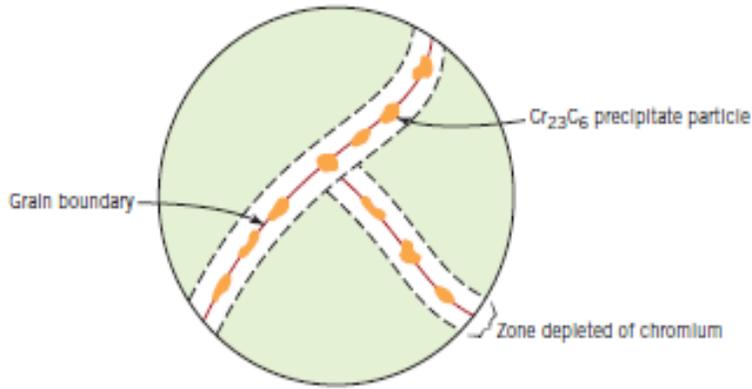
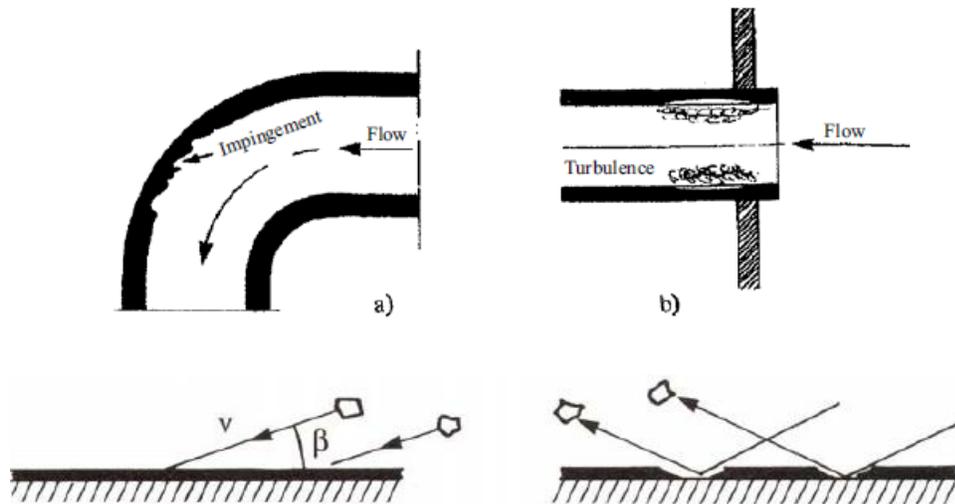


Figure 2.7: Intergranular corrosion

(Adapted from Callister)

6. Erosion corrosion – results from the combined actions chemical attack and mechanical abrasion or wear along metal surface by eroding motion of fluid and/or its containing particles which is more detrimental to alloys that passivate by forming protective surface film. It is commonly found in piping, especially at bends, elbows, and abrupt changes in pipe diameter—positions where the fluid changes direction or flow suddenly becomes turbulent [23,12].



(c)

Figure 2.8: (a) impingement (b) turbulence corrosion (c) Impacts from solid particles in a liquid flow causing removal of corrosion products from the surface (erosion corrosion)

(Adapted from Corrosion And Protection(Engineering Materials and Processes);By: E. Bardal).

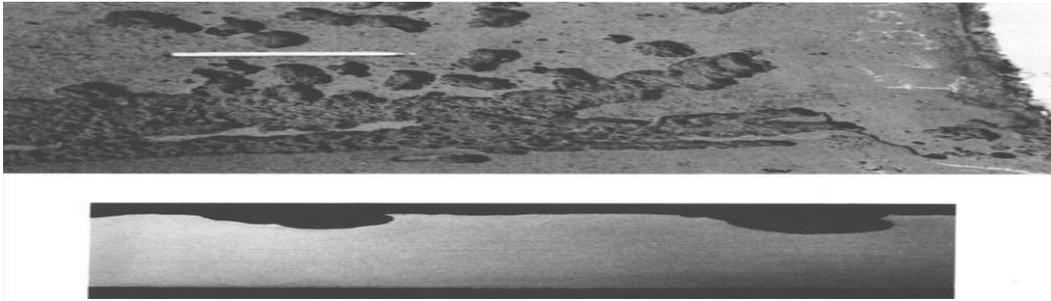


Figure 2.9: Flow-affected corrosion in a flowline for oil and gas in a field in the North Sea.

A view of the pipe bottom and Cross-section of typical pits (2.5 x). (Photo:J.M. Drugli, SINTEF Corrosion Centre). (Adapted from Corrosion And Protection (Engineering Materials and Processes);By: E. Bardal)

7. Stress corrosion/stress corrosion cracking - influenced by the combined action of an applied tensile stress and a corrosive environment. This form of corrosion also attacks some materials that are virtually inert in a particular corrosive medium thus making the material susceptible corrosion [24,23].



Figure 2.10: Impingement failure of an elbow that was part of a steam condensate line

Adapted from Callister: (Photograph courtesy of Mars G. Fontana. From M. G. Fontana, Corrosion Engineering, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)

8. Corrosion fatigue – this form of corrosion is influenced by cyclic stresses combined with corrosive environment. The corrosion splash zone of oil and gas platform is an example [23].
9. Fretting corrosion – occurs at contact areas between loaded materials under vibration and slip [12].
10. Hydrogen damage – a mechanical damage of material in contact with hydrogen. E.g. hydrogen embrittlement and decarburization, etc. [12].

2.4 SELECTED CORROSIVE MEDIA

Corrosive media are solutions whose interaction with materials (metals) causes the metal to become oxidized/corrode [25]. Corrosive media basically include: acid, base, solution of salts, gases, etc.

2.4.1 SODIUM CHLORIDE SOLUTION

Sodium chloride is a binary neutral salt whose cation comes from a strong base (NaOH), and whose anion comes from strong acid (HCl), [52]. Seawater contains about 3.5% sodium chloride, NaCl. When in aqueous form, the dissolved chloride ions attack the protective passive film and cause metals to corrode under pitting [10].

2.4.2 HYDROCHLORIC ACID SOLUTION

This is a strong binary acid that ionizes completely in a single step releasing hydrogen ion, H^+ , and chloride ion, Cl^- [52]. Its corrosion ability of metal is due to the presence of both hydrogen and chloride ions [1].

2.4.3 SODIUM CARBONATE SOLUTION

Sodium carbonate also referred to as soda ash is a basic salt with cation originating from a strong base (sodium hydroxide, NaOH), and cation from a weak acid (carbonic acid, H_2CO_3) and is used in a number of applications in industrial processes, involving treatment of water, soap, detergents, medicine, and food additive manufacturing[52]. Solution of this salt Na_2CO_3 has also been used to study rust formation and corrosion mitigation in aqueous medium [53]

2.5 THE ELECTROCHEMISTRY OF CORROSION

Most metal corrosion occurs via electrochemical reactions at the interface between the metal and an electrolyte solution [26, 27]. This reaction occurs through exchange of electrons in a process of oxidation (occurring at the anode) and reduction (occurring at the cathode); hence an oxidation-reduction or simply redox reaction [18]. The conductive characteristics of metals allows the flow of electron(s) from their surfaces at the anodic regions (which tend to develop at locations where the metal is stressed or protected from oxygen) to a suitable electron acceptor or depolarizer (commonly oxygen, acids, and cations of less active metals) at the cathodic region [24].

The surfaces of all metals (except for gold and platinum) in air are covered with oxide films which tend to dissolve when the metal is immersed in aqueous solution [28]. When the metal is immersed in acidic solution, there is a high tendency of the oxide film dissolving and leaving the bare metal surface expose to the corrosive acidic medium [18]. The solubility of the oxide film reduces in near-neutral solutions compared acidic solution and the extent of metal dissolution (hence rate of corrosion) tend to reduce simply because the metal is only initially exposed at localized points of discontinuity at grain boundaries [23] (where the oxide film may be thinner or more prone to dissolution than elsewhere) due to inclusions (foreign atoms/particles) [18].

A near-neutral solution of containing inhibiting anions, for instance hydroxide, OH^- , with relatively low hydrodynamic flow tends to reduce the dissolution of the oxide film which stabilizes to form a passivating oxide film thus retarding the corrosion rate of the metal in its passive state.[26]

Some metals can be resistant to corrosion for kinetic reasons [18]. For example, aluminum in soft-drink cans and airplanes is protected by a thin coating of metal oxide that forms on the surface of the metal and acts as an impenetrable barrier that prevents further destruction [18]. Chromium, magnesium, and nickel also form protective oxide films. Stainless steels are remarkably resistant to corrosion because they usually contain a significant proportion of chromium, nickel, or both (seawater environment is an exception due to presence of chloride ions) [30,1]

On the contrary, when iron corrodes, a reddish-brown hydrated metal oxide ($\text{Fe}_2\text{O}_3 \cdot \text{XH}_2\text{O}$), rust, forms which does not provide a tight protective film but continually breakdown thus making the fresh surface of the metal vulnerable to corrosion by interaction with oxygen and water according to figure 2.12 [18].

Because both oxygen and water are required for corrosion process, an iron nail immersed in deoxygenated water will not rust - even over a period of several weeks [18]. Similarly, a nail immersed in an organic solvent such as kerosene or mineral oil saturated with oxygen will not easily rust because of the absence of water [31].

2.5.1 THERMODYNAMICS OF CORROSION

Thermodynamics - the free energy change (ΔG), provides a direct measure of work capacity or maximum electric energy available from a system in corrosion process. The value of the free energy change determines whether a metal will corrode in a given environment. However, it does

tell how fast the corrosion process will proceed. [12]. The free energy associated with an electrochemical/corrosion process can be expressed as:

$$\Delta G = -(W_m - P\Delta V) = -nFE \dots\dots\dots 2.1$$

Where ΔG the free energy change as is mentioned earlier, W_m is the maximum work, $P\Delta V$ is used to reduce/stop the effect of the atmosphere by pressing it aside so that the maximum work is the difference between these two terms; n is the number of electrons involved in the electrochemical process, F is the Faraday constant, and E is the cell potential, the maximum electrical energy that can be achieved from the cell [24]

2.5.1.1 SIGN CONVENTION OF ΔG

1. For negative ΔG : spontaneous process – the system can carry out work and/or release energy and hence favors corrosion
2. When $\Delta G = 0$: the system is at equilibrium
3. For positive ΔG : energy must be supplied

Also the cell potential, E, of a system where the reactants are not at unity can be obtained from the famous Nernst equation expression [12]:

$$E = E_0 + 2.303 \frac{RT}{nF} \log \frac{a_{oxid}}{a_{red}} \dots\dots\dots 2.2$$

Where E_0 is the standard half-cell potential, R is the gas constant, T is the absolute temperature and n and F represent the parameters as mentioned earlier. As the half-cell potential becomes more positive, the amount of oxidizing species also increase making E more positive, and ΔG

more negative, thus favoring a spontaneous corrosion process. A negative E inhibits corrosion of metal [12]. It is important to note that as the potential reaches the reverse potential, no further dissolution of metal occurs.



However, the potential of a metal in a solution does not usually reach the reversible potential but remains more positive because electrons can be removed from the metal by alternative reactions. According to equation 2.3, the reaction in acidic solution permits the continual passage of equivalent amount of metal ions into the solution, thus leading to corrosion of the metal. This reaction is reversible and has reversible potential of the form [26]

$$E_{r,H^{+}/H_2} = E^{\circ}_{H^{+}/H_2} - \frac{RT}{F} \ln \frac{P_{H_2}^{\frac{1}{2}}}{a_{H^{+}}} \dots\dots\dots 2.4$$

Where P_{H_2} is the partial pressure (fugacity) of hydrogen gas, $a_{H^{+}}$ is the activity/concentration of hydrogen ions which is also proportional to metal ions in the solution, the first term represents metal dissolution and the second is the metal deposition term.

<i>Electrode reaction</i>	<i>E° /V</i>	<i>Electrode reaction</i>	<i>E° /V</i>
$Li^{+} + e^{-} \rightarrow Li$	- 3.045	$AgI + e^{-} \rightarrow Ag + I^{-}$	- 0.152 2
$K^{+} + e^{-} \rightarrow K$	- 2.925	$Sn^{2+} + 2e^{-} \rightarrow Sn$	- 0.136
$Rb^{+} + e^{-} \rightarrow Rb$	- 2.925	$Pb^{2+} + 2e^{-} \rightarrow Pb$	- 0.125 1
$Cs^{+} + e^{-} \rightarrow Cs$	- 2.923	$2H^{+} + 2e^{-} \rightarrow H_2$	0 exactly
$Ba^{2+} + 2e^{-} \rightarrow Ba$	- 2.92	$AgBr + e^{-} \rightarrow Ag + Br^{-}$	+ 0.071 1
$Sr^{2+} + 2e^{-} \rightarrow Sr$	- 2.89	$Sn^{4+} + 2e^{-} \rightarrow Sn^{2+}$	+ 0.15
$Ca^{2+} + 2e^{-} \rightarrow Ca$	- 2.84	$Cu^{2+} + e^{-} \rightarrow Cu^{+}$	+ 0.159
$Na^{+} + e^{-} \rightarrow Na$	- 2.714	$AgCl + e^{-} \rightarrow Ag + Cl^{-}$	+ 0.222 3
$La^{3+} + 3e^{-} \rightarrow La$	- 2.37	$Hg_2Cl_2 + 2e^{-} \rightarrow 2Hg + 2Cl^{-}$	+ 0.268 16
$Mg^{2+} + 2e^{-} \rightarrow Mg$	- 2.56	$Cu^{2+} + 2e^{-} \rightarrow Cu$	+ 0.340
$Sc^{3+} + 3e^{-} \rightarrow Sc$	- 2.03	$Fe(CN)_6^{3-} + e^{-} \rightarrow Fe(CN)_6^{4-}$	+ 0.361 0
$Be^{2+} + 2e^{-} \rightarrow Be$	- 1.97	$Cu^{+} + e^{-} \rightarrow Cu$	+ 0.520
$Th^{4+} + 4e^{-} \rightarrow Th$	- 1.85	$I_2 + 2e^{-} \rightarrow 2I^{-}$	+ 0.535 5
$Al^{3+} + 3e^{-} \rightarrow Al$	- 1.67	$I_3 + 2e^{-} \rightarrow 3I^{-}$	+ 0.536

$\text{Ti}^{2+} + 2\text{e}^- \rightarrow \text{Ti}$	-1.63	$\text{Hg}_2\text{SO}_4 + 2\text{e}^- \rightarrow 2\text{Hg} + \text{SO}_4^{2-}$	+0.613
$\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$	-1.18	$(\text{AuSCN})_4^- + 3\text{e}^- \rightarrow \text{Au} + 4\text{SCN}^-$	+0.636
$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.762 6	$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	+0.771
$\text{Ga}^{3+} + 3\text{e}^- \rightarrow \text{Ga}$	-0.529	$\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow 2\text{Hg}$	+0.796 0
$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.799 1
$\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$	-0.424	$\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}$	+0.911 0
$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	-0.042 5	$\text{Pd}^{2+} + 2\text{e}^- \rightarrow \text{Pd}$	+0.915
$\text{Ti}^{3+} + \text{e}^- \rightarrow \text{Ti}^{2+}$	-0.37	$\text{AuCl}_4^- + 3\text{e}^- \rightarrow \text{Au} + 4\text{Cl}^-$	+1.002
$\text{PbSO}_4 + 2\text{e}^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.350 5	$\text{Pu}^{4+} + \text{e}^- \rightarrow \text{Pu}^{3+}$	+1.01
$\text{In}^{3+} + 3\text{e}^- \rightarrow \text{In}$	-0.338 2	$\text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2\text{Br}^-$	+1.065
$\text{Tl}^+ + \text{e}^- \rightarrow \text{Tl}$	-0.336 3	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.229
$\text{Co}^{2+} + 2\text{e}^- \rightarrow \text{Co}$	-0.277	$\text{Tl}^{3+} + 2\text{e}^- \rightarrow \text{Tl}^+$	+1.25
$\text{V}^{3+} + \text{e}^- \rightarrow \text{V}^{2+}$	-0.255	$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	+1.358 3
$\text{Ni}^{2+} + \text{e}^- \rightarrow \text{Ni}$	-0.257	$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	+1.52

Table 2.1: Standard Oxidation-Reduction Potentials: 25°C volts vs. normal hydrogen electrode*

(Adapted from <http://www.kayelaby.npl.co.uk>)

Thermodynamic applications to electrochemical processes can be generalized by potential-pH plots referred to as Pourbaix diagram after Dr. M. Pourbaix who first suggested their use [24].

The Pourbaix diagrams are constructed from potential values calculated using the Nernst equation (i.e. equation 2.2) [12]

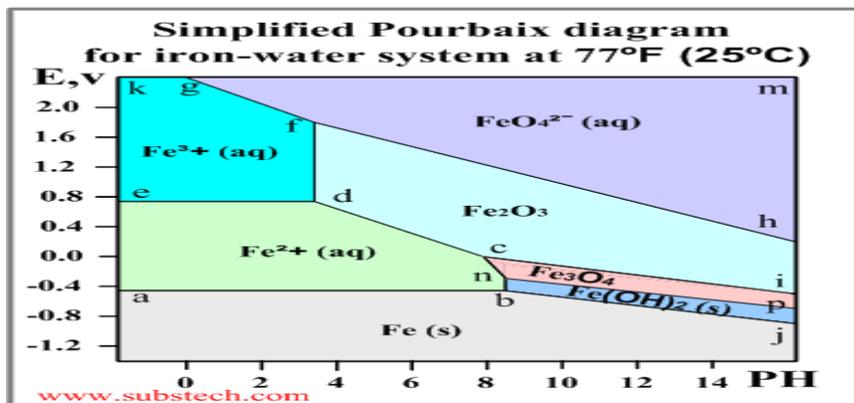
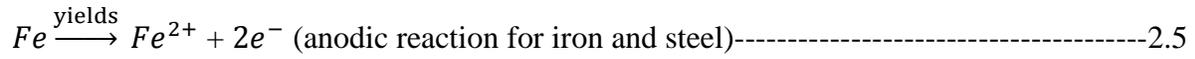
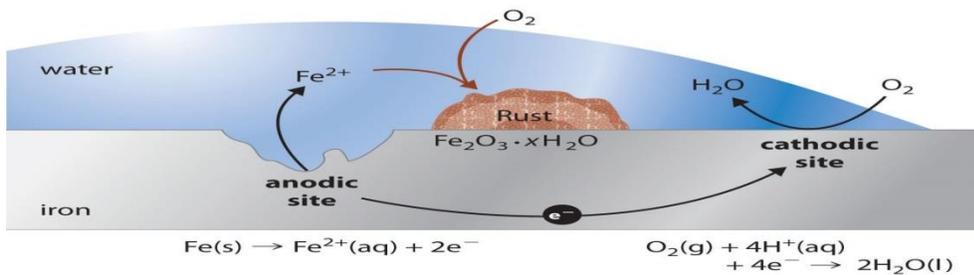
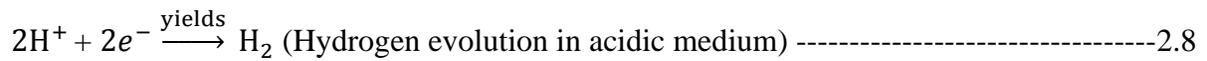
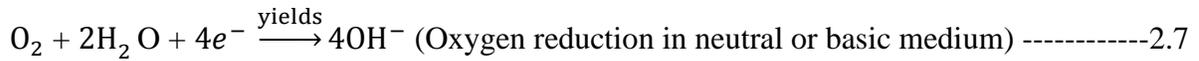
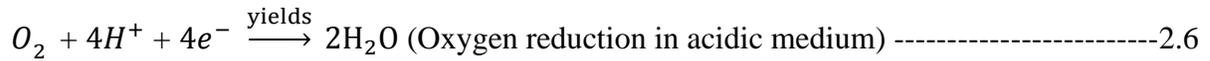


Figure 2.11: Pourbaix diagram of iron

The rusting (corrosion) of iron due to the couple reactions (anodic and cathodic) as mentioned follows the electrochemical reactions below:



After the metal atoms at the anodic site release electrons, there are four common cathodic reactions:



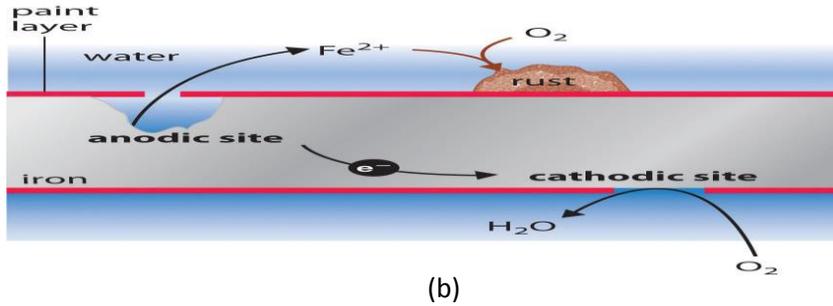
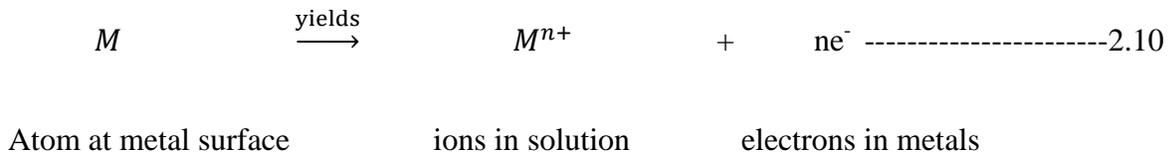


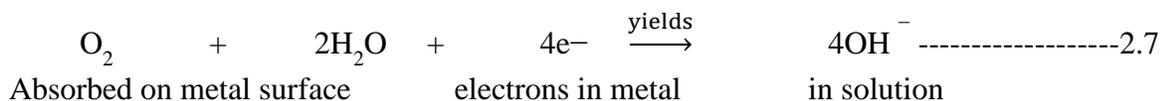
Figure 2.12: (a) Rust, the Result of Corrosion of Metallic Iron (b) Small Scratches in a Protective Paint Coating Can Lead to the Rapid Corrosion of Iron (b)

(Adapted from Corrosion control "Corrosion Control" NAVFAC MO-307 September 1992)

When the oxide-free surface of a metal becomes exposed to a solution, positive charged metal ions tend to pass from the metal into the solution, leaving electrons behind on the metal [31], i.e.



The accumulation of negative charge on the metal due to the residual electrons leads to an increase in the potential difference between the metal and the solution. This potential difference is called the electrode potential (or simply, the potential of the metal), which become more negative. The implication of the change in potential is a retardation of metal ions dissolution and a subsequent increase in the deposition of the metal ions from the solution onto the metal resulting to reverse reaction similar to equation 2.3 [26].



2.5.2 CORROSION KINETICS

When a metal is exposed to an electrolyte of particular pH value, the Pourbaix diagram only tells the ranges of potential that give immunity, corrosion, and passivity respectively but ignores how the potentials are determined and the rate of corrosion at each potential [10]. The rate of corrosion implies metal dissolution with time in corrosive environment(s) at specific potential [12]. Corrosion rates may be measured in weight loss per unit area per unit time, penetration rate, or electrochemical rate. There is no specific standard unit for measuring corrosion rate and various units have been used to expressed corrosion rate [32,54]. Most importantly, many of the tests are made to select materials for use in specific environments [12].

WEIGHT LOSS	PENETRATION RATE	ELECTRICHEMICAL RATE (Corrosion current density)
$\text{g/cm}^2\text{hour}$	ipy(inch per year)	$\mu\text{A/cm}^2$
$\text{g/cm}^2\text{ day}$	mpy(miles per year)	mA/cm^2
$\text{g/m}^2\text{hour}$	mm/year	A/cm^2
$\text{g/m}^2\text{day}$	$\mu\text{m/year}$	A/m^2
$\text{mg/m}^2\text{second}$		
$\text{mdd}(\text{mg/dm}^2\text{day})$		

Table 2. 2: Some units commonly used to express corrosion rates

2.5.3 POTENTIAL AND POLARIZATION

During corrosion reaction, there is a transfer of electrons and ions between the metal and the solution with rates equivalent to the electric current and depend on potential difference between the metal and solution, i.e. the potential of the metal.[19,26]. As the potential of the metal

becomes more positive, the rates of anodic reactions increase and the rates of cathodic reactions decrease. The converse effect on the reaction rates occurs as the potential of the metal becomes more negative [33]. The potential of the working electrode is measured against that of a reference electrode by means of a voltmeter. The reference electrode is chosen to give a stable and reproducible potential in the solution [26]

While in a solution, a corroding metal takes on a potential (corrosion potential), whereby the rate of anodic reaction of metal dissolution equals the rate of cathodic reactions of hydrogen evolution and/or oxygen reduction [34, 19,12]. The corrosion current, i_{corr} , can be related to the amount of metal corroded by Friday's law:

$$i_{corr} = \frac{nFW}{M} \text{-----2.12}$$

n= number of electrons involved in metal dissolution

F= Friday's constant with value 96,500 Coulomb per mole

W= mass of corroded metal in grams

M= molecular weight of metal in grams per mole

A slight displacement by the corroding metal from the corrosion potential, E_{corr} , either by galvanostatic or potentiostatic polarization shows that the potential was initially a linear function of the current density, i (current per unit area) [35,26]. It is however, important to also note that because the areas of the anodic regions, A_a , are generally different from the areas the cathodic

regions, A_c , the current densities are generally not equal. Hence, this linear relationship holds for a potential of up to 10mV [36,26]. The slope of the linear polarization curve, dE/di , termed the polarization resistance R_p , has an inverse relationship to the rate of corrosion expressed as the equivalent corrosion current density, i_{corr} , from the Stern-Geary equation

$$i_{corr} = \frac{B}{R_p} \text{-----2.13}$$

The proportionality constant, B , for a particular system can be determined empirically (calibrated from separate weight loss measurements) or, as shown by Stern and Geary, can be calculated from electrochemical data of b_a and b_c , the slopes of the anodic and cathodic curves in a Tafel plot. The relationship is:

$$B = \frac{b_a \cdot b_c}{2.303(b_a + b_c)} \text{-----2.14}$$

The instantaneous rate of corrosion of a metal is determined from measurements of the polarization resistance. [26].

When a cell is short-circuited, the net oxidation and reduction reactions occur at the electrode interfaces, where the potential of the electrodes can no longer be at equilibrium. [12]. The result of this phenomenon is a deviation of the electrochemical process from equilibrium due to an electric current passing through the galvanic cell and is referred to as polarization. It is the displacement of electrode potential resulting from a net current [37,54,12]. Polarization may occur either at the cathode (cathodic polarization) or at the anode (anodic polarization). However, cathodic polarization is common [54]. The magnitude of polarization is measured in terms of overvoltage/overpotential, η , which is a measure of polarization with respect to

equilibrium potential of an electrode [38]. The overpotential, η , defines the difference between the applied potential, E , and the corrosion potential, E_{corr} . [54]. That is, the equilibrium of the electrode is considered as zero, the overvoltage is stated in terms of volts or millivolts plus or minus with respect to this zero reference. [12].

There are two main types of polarization:

Activation polarization

Concentration polarization

2.5.3.1 ACTIVATION POLARIZATION

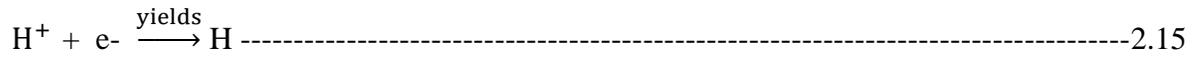
Activation polarization is the overpotential (change of the electrode potential) caused by overcoming the energy barrier of the slowest step of the electrochemical process that is controlled by a reaction sequence at the metal-electrode interface [12]. It is usually the controlling factor during corrosion process in media of concentrated acids as the active species. [12,55]

An electrochemical reaction proceeds through several successive steps where the reaction rate is controlled by the slowest step (rate-determining step) of the process [33]. The activation energy required for overcoming the barrier changes the electrode potential [12,54].

Common cause of cathodic activation polarization is the reaction of hydrogen formation and evolution at the cathode surface in the following steps: [54,12]

- First step: involves the absorption or attachment of the species, H^+ , to the metal surface
- Second step: electron transfer must occur resulting in reduction of the hydrogen ions thus

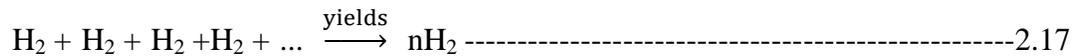
forming atomic hydrogen on the cathode surface.



- Third step: formation of molecules of gaseous hydrogen from two hydrogen atoms from the second step.



- Forth step: formation of more hydrogen bubbles.



The mechanisms involved in these reactions are much more complex than that shown and these steps can also be applied to the reduction of any species on a metal surface[12]

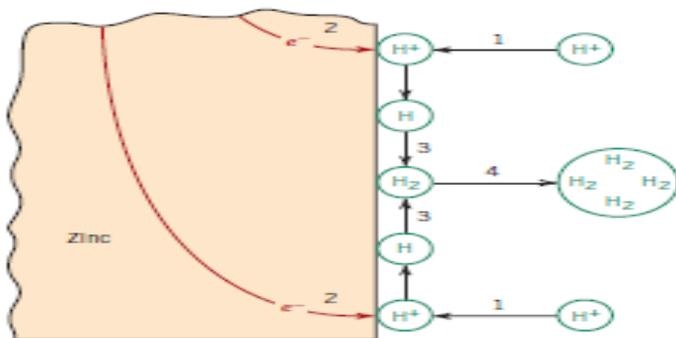


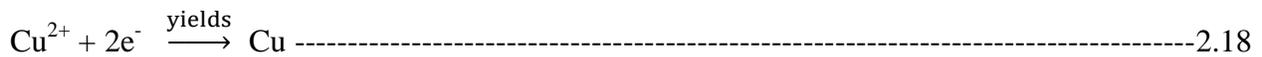
Figure 2.13: Cathodic Activation Polarization

(Adapted from Callister)

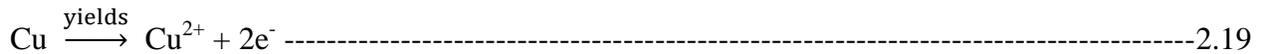
The polarization of the cathode by the hydrogen atoms produces a film covering the cathode surface. The film affects the process kinetic by slowing down the reaction between the electrons and hydrogen ions dissolved in the electrolyte [54].

At the equilibrium (non-polarized) state the rates of oxidation and reduction reactions proceeding at any electrode are equal. For example the ions of Cu are receiving electrons on the electrode surface and transfer from the electrolyte to the copper deposit. In parallel the same number of copper atoms give up their electrons and dissolve in the electrolyte [19,54].

Reduction:



Oxidation:



These processes produce two equal electric currents in opposite directions. The current passing through the electrode surface in the equilibrium (non-polarized) state at any direction is called **exchange current** [38]. The relationship between the exchange reaction rates and current density can also be directly derived from Friday's law as:[54]

$$r_{\text{oxid}} = r_{\text{red}} = \frac{i_0}{nF} \text{-----} 2.20$$

However, at equilibrium,

$$\eta = 0$$

$$E = E_e$$

$$i = 0$$

but $i_a = -i_c = i_o$ (i.e., the anodic and cathodic reactions are equal and the rate corresponds to the exchange current, i_o).

When an electrode is polarized, the magnitude of its current is controlled by the reaction kinetics and diffusion of reactants both toward and away from the electrode [54]. The expression that relates the overpotential, η , to the net current, i , is the Butthler-Volmer equation:

$$i = i_o \left\{ e \left(\beta \frac{nF}{RT} \eta \right) - e \left(-[1 - \beta] \frac{nF}{RT} \eta \right) \right\} \text{-----2.21}$$

Where R is the gas constant, T is the absolute temperature, and β is the symmetry coefficient (or simply the Tafel slope. For activation polarization $\beta = 2.303(RT/\alpha nF)$). The first term in $\{ \}$ in the Butthler-Vomer equation describes the anodic reaction (metal dissolution) while the second term in $\{ \}$ describes the cathodic reaction (metal deposition) [19,54].

The above Butthler-Vomer equation can also be simply expressed as:

$$i = i_{\text{corr}} \left(e^{\left(\frac{2.303 \eta}{b_a} \right)} - e^{\left(\frac{-2.303 \eta}{b_c} \right)} \right) \text{-----2.22}$$

Where the overpotential, η , is expressed as:

$$\eta = E - E_{\text{corr}} \text{-----2.23}$$

E is the applied potential and i the measured current density. The corrosion potential, E_{corr} is the open circuit potential of a corroding metal[39].The corrosion current, i_{corr} , and the Tafel constants b_a , and b_c can be measured from experimental data [54]

$$b_a = \frac{2.303(RT)}{\beta(nF)} \text{-----2.24}$$

and

$$b_c = \frac{2.303(RT)}{(1-\beta)nF} \text{-----2.25}$$

A polarization curve is obtained from a plot of Butthler-Vomer equation of metal dissolution/deposition reaction of the form:

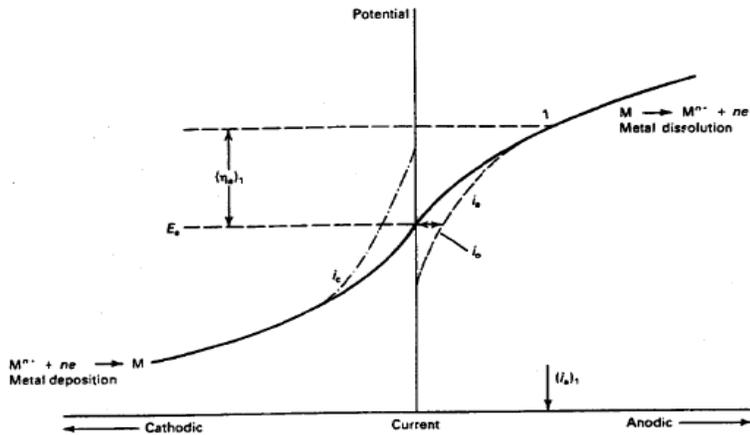


Figure 2.14: Current-potential relationship for metal dissolution ($M \longrightarrow M^{n+} + ne$)/deposition ($M^{n+} + ne \longrightarrow M$)

(Adapted from Dr. Derek H. Lister: *Kinetics of Aqueous Corrosion: (Alternative: Cook, William G., and Derek H. Lister. "Chemistry in CANDU Process Systems.")*)

If the symmetry coefficient, $\beta = 0.5$, the curve is a symmetrical ($i = 0, E_e$) and the Butthler-Vomer equation has a sinh form[19]

As the overpotentials get large and larger, the reactions of the electrode go all in one direction resulting to one of the terms in the Butthler-Vomer equation being neglected and dropped. Thus, anodic reaction (metal dissolution):[19]

$$i_a = i_o \exp\left(\frac{\beta \eta F \cdot \eta_a}{RT}\right) \text{-----} 2.26$$

Or

$$\eta_a = b_a \log \frac{i}{i_o} \text{-----} 2.27$$

For small η , i.e. for potentials close to corrosion potential, the above equation can be reduced to:[54]

$$i_{\text{corr}} = 2.303 \frac{b_a b_c}{b_a + b_c} \left(\frac{1}{R_p} \right) \text{-----} 2.28$$

Or

$$R_p = 2.303 \frac{b_a b_c}{b_a + b_c} \left(\frac{1}{i_{\text{corr}}} \right) \text{-----} 2.29$$

The relation becomes linear in the narrow region of small overpotential according to figure 2.15, and this linear region conforms to the equation[19]:

$$i = i_0 \frac{\eta F}{RT}$$

-----2.30

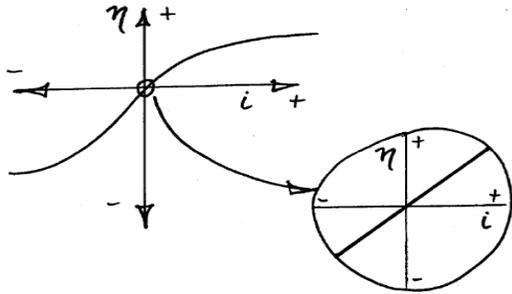


Figure 2.15: Low-overpotential or “low-field” approximation

(Adapted from Dr. Derek H. Lister: Kinetics of Aqueous Corrosion: (Alternative: Cook, William G., and Derek H. Lister. "Chemistry in CANDU Process Systems.")

The curve becomes shallow and large current is obtained for small overpotential if a reaction has a large exchange current, i_0 [40]. However, the reaction is not easily polarized (approaching non-polarizable point) as shown in figure 2.16

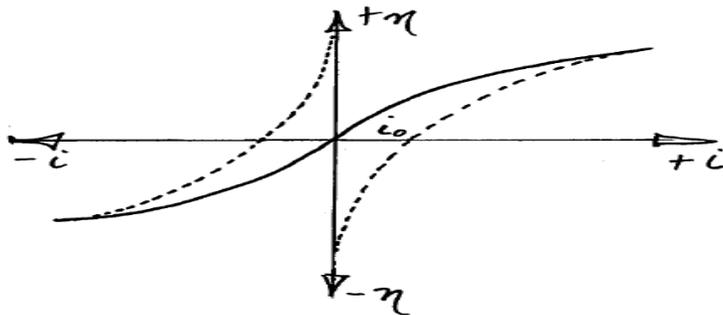


Figure 2.16: Nonpolarized curve exchange current

(Adapted from Dr. Derek H. Lister: Kinetics of Aqueous Corrosion: (Alternative: Cook, William G., and Derek H. Lister. "Chemistry in)

The activation polarization overpotential may be calculated by the **Tafel equation** of the form:

$$\eta_{act} = -(RT/\alpha nF) \ln (i/i_0) = -2.3(RT/\alpha nF)\log(i/i_0) \text{ for cathodic activation polarization} \text{-----} 2.31$$

$$\eta_{act} = (RT/\alpha nF) \ln (i/i_0) = 2.3(RT/\alpha nF)\log(i/i_0) \text{ for anodic activation polarization} \text{-----} 2.32$$

Where

R = gas constant = 8.3143 J/(mol*K);

T = absolute temperature, K;

n = number of electrons transferred by one ion;

F = Faraday constant F=96500 C/mol (C-coulombs);

α = electron transfer coefficient (0<α<1);

i = current density;

i₀ = current exchange density.

Equation 2.31 and 2.32 can be written in combined form as:

$$\eta_{act} = \pm \beta \log(i/i_0) \text{-----} 2.33$$

Where β also presents the parameter as discussed in equation 2.21.

2.5.3.2 CONCENTRATION POLARIZATION

Concentration polarization of an electrode is a result of formation of a diffusion layer adjacent to the electrode surface where there is a gradient of the ion concentration [12].

Diffusion of the ions through the layers controls the electrochemical reaction/corrosion. The electrode potential may be calculated according to the Nernst equation of the form:

$$E = E^0 - (RT/nF) \ln (C_{ion}) \text{-----2.34}$$

Where:

E^0 - Standard electrode potential, V;

R - gas constant $R=8.3143 \text{ J}/(\text{mol}\cdot\text{K})$;

T - temperature, K;

n - number of electrons transferred by one ion;

F - Faraday constant $F=96500 \text{ C}/\text{mol}$ (C-coulombs);

C_{ion} - molar activity (concentration) of ions.

The concentration within the diffusion layer changes from C_b (bulk concentration) to C_s (concentration at the electrode surface) [54]. Correspondingly, the electrode potential changes within the diffusion layer:

That is from

$$E_b = E^0 - (RT/nF) \ln (C_b) \text{-----2.35}$$

to

$$E_s = E^0 - (RT/nF) \ln C(s) \text{-----2.36}$$

The difference between E_s and E_b is called concentration overpotential, which is the measure of the concentration polarization:

$$\eta_c = E_s - E_b = (RT/nF)\ln(C_s/C_b) \text{ -----}2.37$$

2.6 CORROSION AND SOME CORROSIVE AGENTS IN SEAWATER

The oil and gas industries consume significant amount of iron and steel pipes, tubing, casings, pumps, valves, and sucker rods (the entire platform) which are not immune to corrosion [1]. As a result, oil and gas production pipelines are always attacked by either internal or external corrosion or even both at the same time [12,10]. Much corrosion control and prevention attention has been given to industries involved with offshore oil and gas production, simply because of the huge installation of non-corrosion resistant materials in contact with the highly corrosive seawater environment (containing NaCl, H₂S, CO₂, ect.), which poses a major challenge for inspection and control [10]. Although it is difficult and even almost impossible to prevent corrosion against metallic structures in industries (especially offshore oil and gas industry) due to different inherently corrosive media present figure 2.17; however, controlling the rate of corrosion is an economical solution [1]. Saline water and sulfides are often present including other corrosive agents. The surface equipment is exposed to air (atmospheric corrosion), and sulfate containing water can be pumped into wells to force up oil during secondary recovery. Corrosion is an inevitable problem in oil and gas/petroleum industries in at least three general areas [12]:

1. Production
2. Transportation and storage
3. Refinery operation

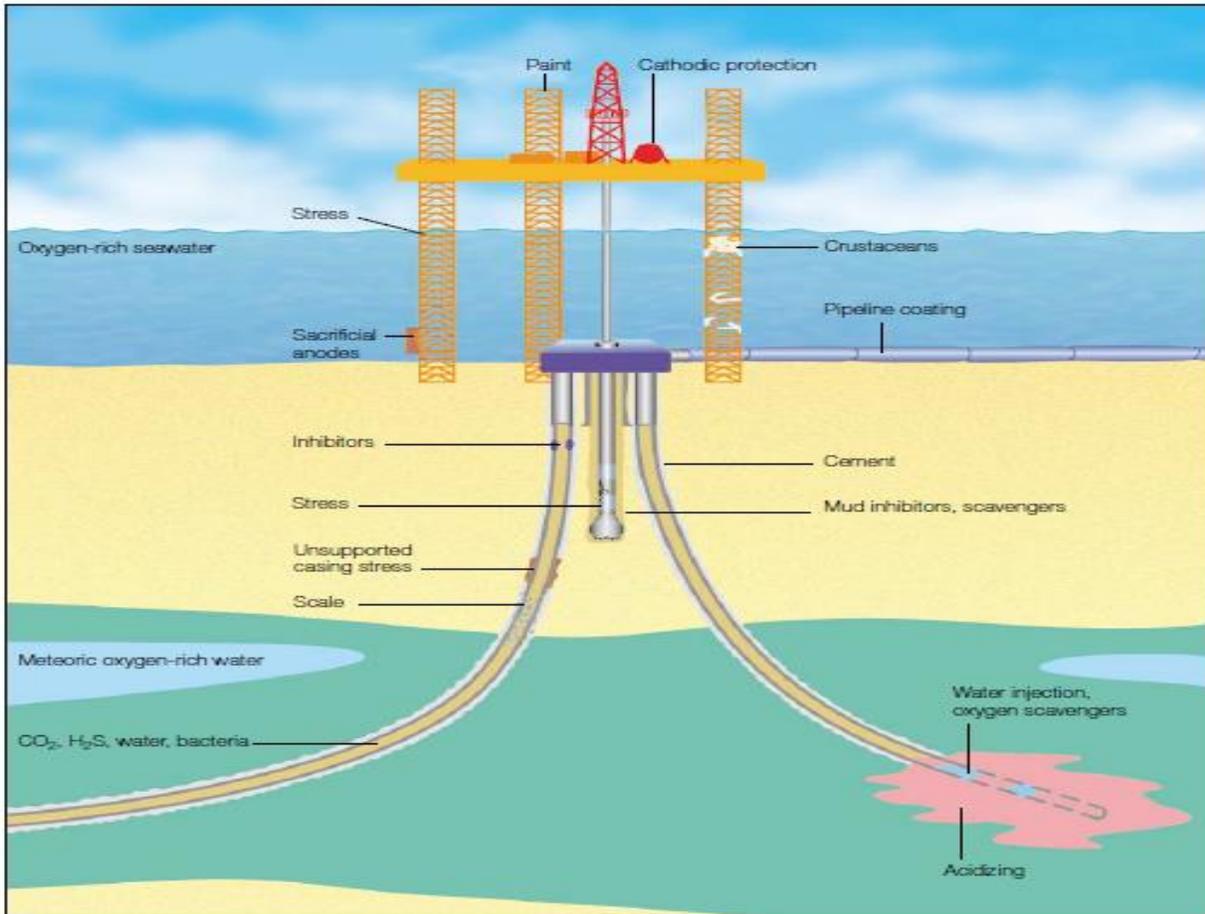


Figure 2.17: Offshore Oil and Gas Platform Subjected to different Corrosive Agents

(Adapted "Corrosion in the Oil Industry," pp. 4–18. By: D. Brondel, R. Edwards, A. Hayman, D. Hill, and T. Semerad)

2.6.1 SODIUM CHLORIDE

The salinity of seawater is about 3.5% [41]. Salinity generally referred to the amount of dissolved salts with sodium chloride (NaCl), constituting 90% of the salt content of the seawater

[42]. The high Chloride, Cl^- , ions in seawater causes corrosion of metallic structures subjected to this environment.

Chemical Contributing to Seawater Salinity	Ion Concentration in o/oo (parts per thousand) in average seawater	Proportion of Total Salinity (no matter what the salinity)
Chloride	19.345	55.03
Sodium	10.752	30.59
Sulfate	2.701	7.68
Magnesium	1.295	3.68
Calcium	0.416	1.18
Potassium	0.390	1.11
Bicarbonate	0.145	0.41
Bromide	0.066	0.19
Borate	0.027	0.08
Strontium	0.013	0.04
Fluoride	0.001	0.003
Other	less than 0.001	less than 0.001

Table 2.3: The Ion Contribution, Concentration, and Proportion of Total Salinity in Seawater from Castro and Huber's, Marine Biology textbook

(Adapted from <http://www.marinebio.net>)

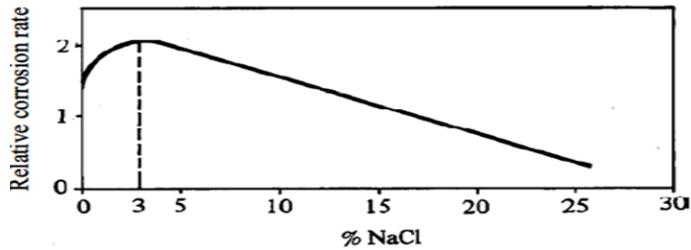


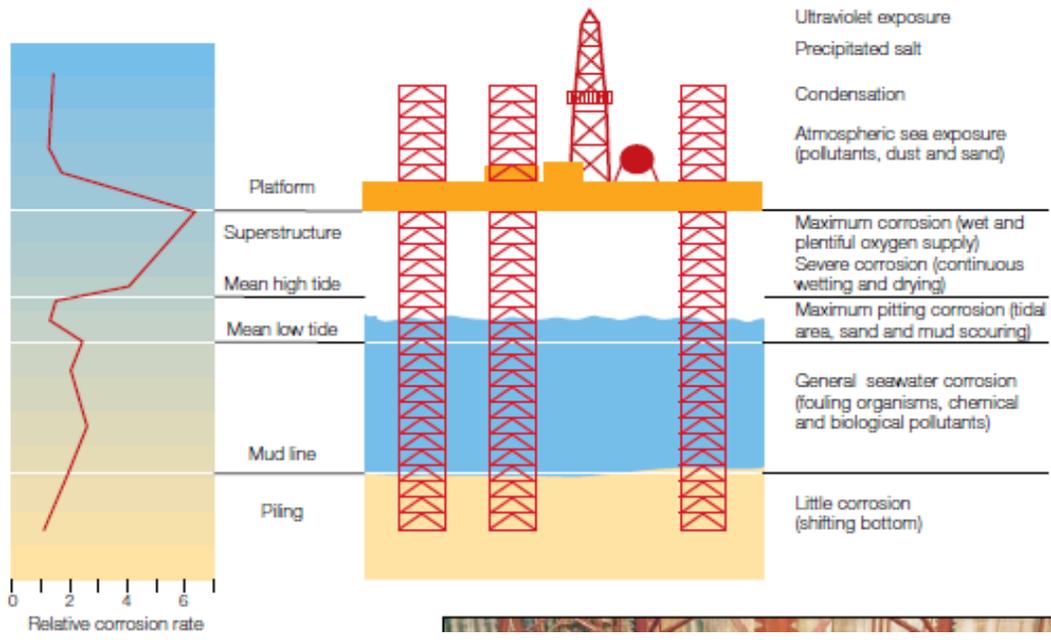
Figure 2.18: The effect of NaCl concentration on corrosion rate of steels in aerated solutions at room temperature

(Reproduced from Uhlig HH. Corrosion and Corrosion Control. 2nd Ed. New York: John Wiley & Sons, 1971- Adapted from E. Bardal: Corrosion and Protection (Engineering Materials and Processes)

The presence of other ions such as Ca^{2+} and Mg^{2+} play a pivotal role in reducing the corrosion rate of Cl^- . In seawater, the bulk pH is 8 to 8.3 [10]. However, this value may increase at the surface due to the cathodic production of hydroxide, OH^- ions, primarily for deposition of CaCO_3 and to a small extent by some $\text{Mg}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$. The formation of a surface layer by these deposits, inhibits the diffusion rate of oxygen and lowers the corrosion of the pipeline steel in seawater compared to equal amount of Cl^- ions in soft fresh water [10].

The part of the offshore platform exposed to atmosphere (oxygen) – the splash zone corrodes faster than any other part due to the following reasons [1,10]:

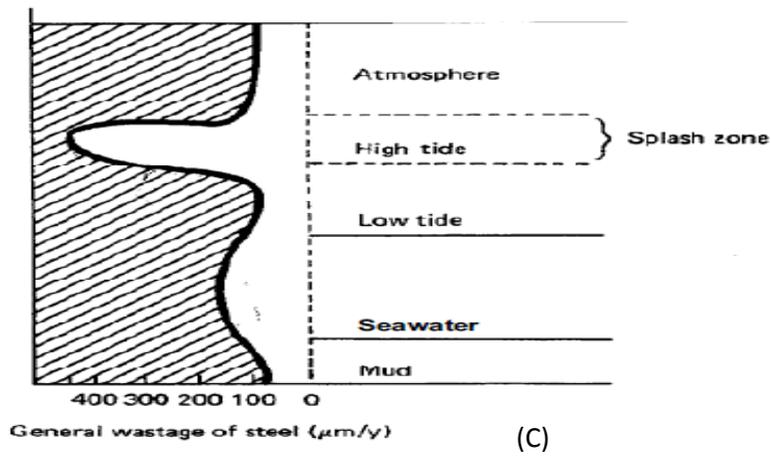
1. High atmospheric oxygen concentration
2. The cyclic wetting and drying processes the occur of this point



(a)



(b)



(c)

Figure 2 19:(a) corrosion rate at different regions of oil and gas offshore structure (b) Cathodic Protection at sea bottom (c) corrosion rate at different regions of oil and gas offshore structure with respect to general wastage of steel ($\mu\text{m}/\text{y}$)

(a) And (b)(Adapted “Corrosion in the Oil Industry,” pp. 4–18. By: D. Brondel, R. Edwards, A. Hayman, D. Hill, and T. Semerad)and (c) (Adapted from Corrosion and Protection (Engineering Materials and Processes; By: E. Bardal)

Normally, oxygen is not present during the producing formations. It only first introduced during the drilling stage by oxygen-contaminated fluids at the shifting bottom [43,10]. Thus, untreated drilling muds have high tendency to corrode not only well casing, but also drilling equipment, pipeline, and muds handling equipment [1]. The measure of the hydrogen ion concentration, pH, [52] is another key parameter whose effect on corrosion rate of steels in seawater is of vital importance. The higher the hydrogen ion concentration of a solution, the stronger the is the acid [52]. The lower the pH value, the higher the acidity thus the rate of corrosion [12]. Normally, pH values range from 0 – 14 on a scale referred to as pH scale shown in figure 2.20.

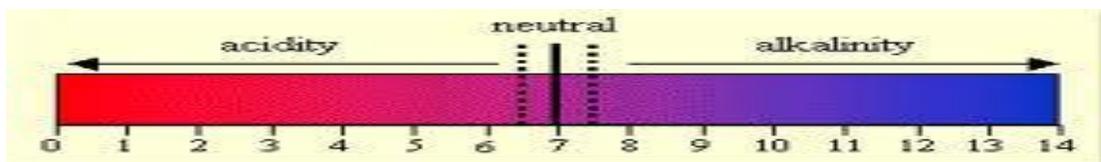


Figure 2.20: pH scale

(Adapted from www.panamenv.com)

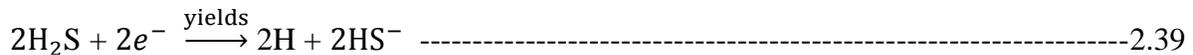
2.6.2 HYDROGEN SULFIDE

Hydrogen sulfide, H₂S, attacks the bottom of a jackup rig or production platform at the seabed after being produced by sulfide reducing bacteria (SRB) [44]. However, the corrosion rate of H₂S can be low initially due its low concentration including the presence of cathodic protection at the seabed, figure 2.19 (b), and the limited oxygen concentration present as a result restricted diffusion due to high concentration of sodium chloride[1,10]. The concentration of H₂S increased with time by the action SRB when seawater containing sulfate is injected into the well. This form of corrosion is referred to as sour corrosion when the partial pressure of H₂S exceeds 0.003 bar according to NACE standards [10].

Like oxygen and carbon dioxide, H₂S also dissolves in water forming weak acid according to the equation:



At higher pH (> 6) HS⁻ dissociates further to H⁺ + S²⁻ [10] . The most important cathodic reaction in a sulfide containing environment can be expressed by

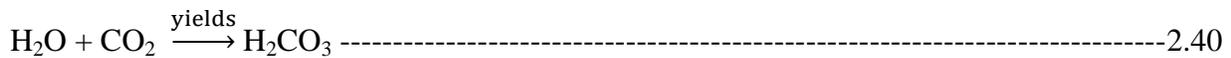


Although some H atoms combine to form hydrogen gas according to equation 2.16, other H atoms diffuse into the material leading to a phenomena referred to as hydrogen embrittlement, particularly in high strength steels resulting to hydrogen-induced cracking, a form of stress corrosion cracking[10].

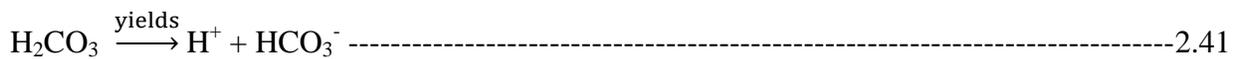
2.6.3 CARBON DIOXIDE

Secondary recovery of oil and gas involves the production of water and CO₂, whose presence cause severe corrosion of completion strings [1]. The precipitated water dissolves the gaseous CO₂ in the production tubing and pipeline system thus causing cathodic reactions on its own [10]. The solubility of CO₂ in seawater increases with decrease in temperature and increase in depth [56]. Its conductivity in the water phase also increase due to the presence of considerable quantities of dissolved salts [1,10]. If the total pressure is known, the partial pressure of CO₂ can be determined to equal the mole fraction of CO₂ in the gas times the total pressure – often in the order of 100 bar while the partial pressure of CO₂ may be 1 bar, which varies considerably with sites [10].

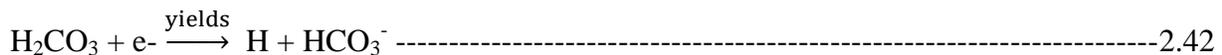
The process mechanisms:



H₂CO₃ is a weak acid and dissociates to a minor extent.



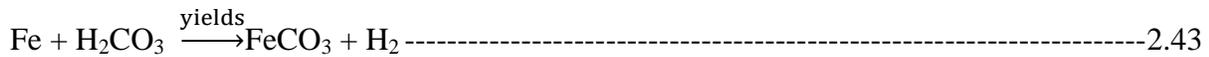
At higher pH values (> 6) HCO₃⁻ dissociates further to H⁺ + CO₃²⁻ [10]. The pH value is usually lower, so the latter dissociation occurs normally to a very small extent. The cathodic reaction is assumed primarily to follow the equation



The H atoms are absorbed on the metal surface and combined with hydrogen molecule to form hydrogen gas according to the reaction equation 2.16.

Although the reduction of H^+ at lower pH values (2–4) contribute to the corrosion rate to some extent, reduction of HCO_3^- is significant at $pH > 6$ [10]. The corrosion of carbon steel in water containing CO_2 , has similar anodic reaction as in equation 2.5 [10].

The overall reaction takes a form as:



$FeCO_3$ has a low solubility and decreases with temperature increase and deposits when the temperature exceeds $60 - 80^{\circ}C$, which is the temperature limit of CO_2 [44,10]. Based partly on both theoretical and experimental testing, the de Waard and Milliams mathematical model can be used to determined CO_2 corrosion rate on steels [10] from the expression:

$$\log V_{corr} = 5.8 - \frac{1710}{273+t} + 0.67 \log(pCO_2) \text{-----} 2.44$$

2.7 CORROSION CONTROL/PREVENTION OF OIL AND GAS PIPELINE SYSTEM

Corrosion of offshore oil and gas pipelines can lead to catastrophic failure causing the loss of life and billions of dollars to repair damaged structures if a proper management—from the design stage of the pipeline system through ongoing monitoring and maintenance is not considered[8]. Although corrosion prevention appears to be almost impossible, controlling the rate of corrosion

is the most economical means of corrosion prevention [1]. The process involves a cogent corporation between corrosion Engineers and pipeline designers collaborating a full understanding of the methods of corrosion mitigation in oil and gas pipeline systems [12]. With tremendous improvements being made in the various corrosion control/prevention methods over time, significant challenges remain in the difficult subsea environment, where assets can be located up to a mile deep or more [8].

A better knowledge and understanding of material properties and the technological applications of materials play a pivotal role in corrosion prevention which is vital to cost management. Corrosion control/prevention aims at the removal or reduction of one or more environmental conditions associated with corrosion initiation and growth through the following measures [2,10,46]:

1. Selecting a material that does not corrode in the actual environment
2. Changing the environment, e.g. removing the oxygen or adding anticorrosion chemicals
3. Using a design that will avoid corrosion, e.g. preventing the collection of water so that the metal surface can be kept dry
4. Changing the potential, most often by making the metal more negative and thus counteracting the natural tendency of the positive metal ions to be transferred from the metal to the environment, e.g. using a sacrificial anode
5. Applying coatings on the metal surface, usually in order to make a barrier between the metal and the corrosive environment [10]

2.7.1 INSPECTION AND MONITORING

In addition to application of the corrosion control and prevention strategies mentioned, a routine inspection and monitoring as to avoid a stoppage in production processes for periodic monitoring or an abrupt break in production due to corrosion failures of process equipment is of great necessity [10, 57]. The cost of periodic monitoring and abrupt failure repairs can be estimated as 20 -25% of the total maintenance cost, with the latter being in the same order as the capital cost [57]. Routine inspection and monitoring is important to track information of corrosion rate from the following data: cathodic protection (CP) surveys, intelligent pigging results, pipeline coating inspections, span length, corrosion probe & coupon data, visual, NDT inspection results and corrosion map data [48].

2.8 COST ASSOCIATED WITH CORROSION FAILURES

Research has shown that the cost of corrosion in industrial countries is estimated at 3-4 % of the gross national product and approximately about 20% of this cost can be saved if the requisite corrosion control/preventive measures are in place [49,10]. The corrosion cost of the United States industries has been estimated at \$170 billion per year [1].

According to analysis of oil pipeline failures in the oil and gas industries in the Niger Delta Area of Nigeria, (C.H. Achebe, Member, IAENG, U.C. Nneke, and O.E. Anisiji), twenty one pipeline failures between the periods 1999 to 2005 were reported: 42% of the failures were due to mechanical induced failure, 18% due to corrosion, 24% third party contribution, 10% operational

errors, and 6% natural hazard [47]. Although Achebe did not mention the estimate cost of repair, corrosion repair cost are generally high [57]. Besides the cost implication, it is also important to consider the safety risks and pollution of the human environment due to corrosion [1].

2.9 PROIR WORK OF CORROSION CONTROL/PREVENT

Two of the most commonly used corrosion control and prevention strategies in addition to metallurgical design are cathodic protection and coating. Both could be used separately or combined [58,1]

2.9.1 CATHODIC PROTECTION

Cathodic protection technique dates as far back as 1824, prior to its theoretical foundation, and is credited to Sir Humphrey Davy [9]. The technique is employed as a secondary corrosion control mechanism simply to minimize potential difference between the anode and cathode materials – reducing the corrosion rate by applying current from an external source to a structure, pipeline for instance [9]. The external source has a negative potential than the pipeline to be protected causing electron transfer to the pipeline steel [50]. The external electron donor than becomes the anode while the pipeline steel occupies the cathodic end, thus becoming protected and immune to oxidation [51,58]

Basically, cathodic protection falls into two different methods:

- a) Sacrificial (or galvanic) anode cathodic protection: This method of cathodic protection involves the use of material (an anode) with higher potential than the structure to be protected [52]. Zinc or magnesium can be used as sacrificial anode to protect steel structures

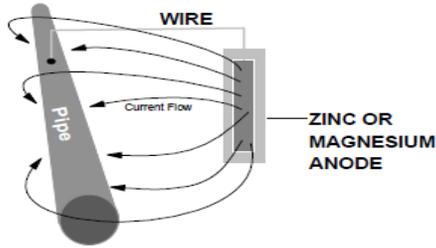


Figure 2.21 : Sacrificial anode cathodic protection

(Adapted from James B. Bushman P.E. Principal Corrosion Engineer Bushman & Associates, Inc Medina, Ohio USA. Corrosion and Cathodic Protection Theory)

- b) Impressed Current Cathodic Protection (ICCP): Uses an external power source wherein the materials providing the protection (the anodes installed in the electrolyte) are connected to a positive DC terminal power source and the protected structure is connected to the negative terminal.

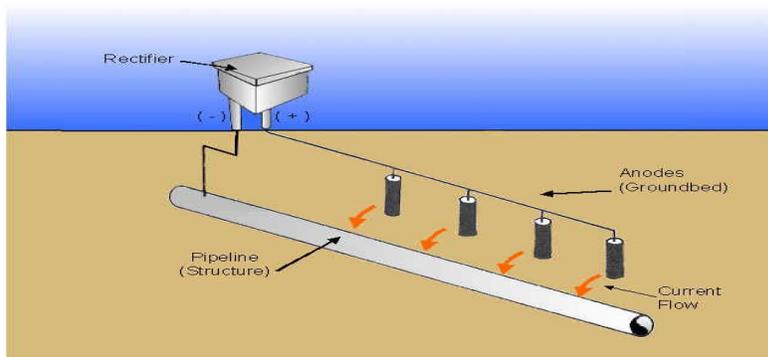


Figure 2.22: Impressed Current Cathodic protection

(Adapted from <https://www.faculty.kfupm.edu>)

2.9.2 COATING OF OIL AND GAS PIPELINE STEELS

Coating is one of the effective methods of preventing metals from corroding when exposed to a corrosive environment with time. It provides the first line of protection of pipeline steel against corrosion in seawater [2]. The adhesion of any coating material to pipe surface is very crucial in corrosion mitigation which is influenced by a well-defined surface preparation of the pipe. This involves the removal of any previous coating/paint or rust and subsequently blasting of pipe surface. Not only does coating mitigate corrosion, some poses serious human and environmental hazard as well [10].

A wide variety of coating materials have been used to coat oil and gas pipelines. Few of these include: coal tar or asphalt enamels, cement mortar, liquid epoxies, polyurethanes, polyolefin tapes, single or dual-layer fusion-bonded epoxy coatings and two- and three-layer polyolefin coatings [6,2]

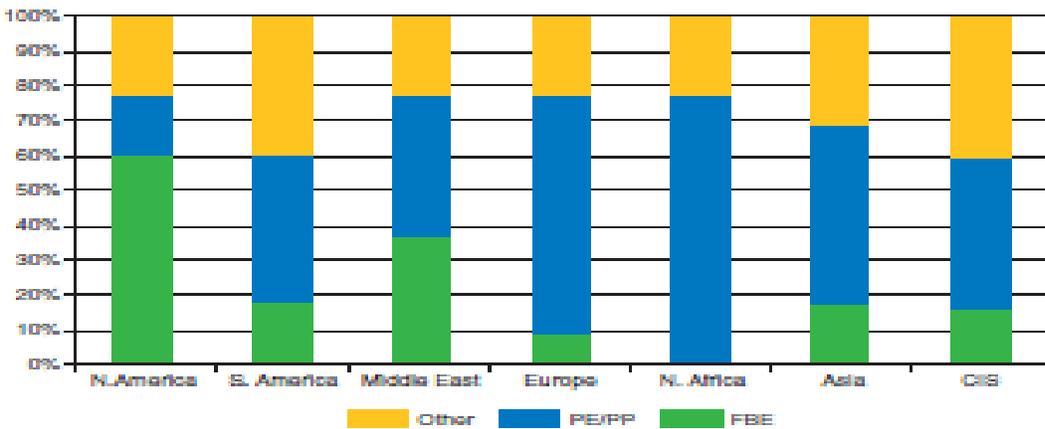


Figure 2.23 Shows Pipeline Coatings Dominant in Different Regions of the World

(Adapted from New Challenges and Developments in Pipeline Coatings. By Shiwei William Guan) New Challenges Coatings

Although many of these pipeline coating systems have satisfied different degrees of success in serving the oil and gas industry in its fight to mitigate corrosion, the need for improvement still remains of vital importance in terms of durability and biocompatibility amongst others.[6].

Fusion-bonded epoxy (FBE) and three-layer polyolefin (3LPO) — which uses polyethylene (PE) or polypropylene (PP) — are the most widely used external coating systems for newly constructed oil and gas pipelines but FBE can also be used internally [6].

Incidents of coating failures have strongly been linked with factors such as:

1. Changes in offshore temperatures which affect the adhesion property of the coating material. At low temperature, the coating contracts while at high temperatures, it expands. This fluctuation in temperature causes thermal fatigue which results in crack initiation and growth and/or disbandment/delamination of coating at the metal-coating-interface, thus exposing the pipe to a corrosive environment.[2, 45]
2. The zone of the platform above the high tide mark called the splash zone is always in a continuous wet and dry cyclic process. The protective coating and any other film at this zone are continually eroded by waves and there is an ample supply of oxygen and water. Corrosion can be controlled at this zone by further coating and also, increasing the metal thickness to compensate for the higher metal loss [1]

Of the coating failures associated with the aforementioned factors, massive disbandment of 3LPO coatings have been reported due to the lack of consistent quality and performance. The disbandment of 3LPO can cause shielding to cathodic protection current and further expose the pipeline to environmentally induced cracking [6,45].

2.9.2.1 FUSION BONDED EPOXY, FBE, COATING

FBE, (thermoset), is a high performance anti-corrosion coating that provides excellent protection for small and large diameter pipelines with moderate operating temperatures [59]. It is applied in the form of wet or a dry powder at thicknesses of 400-600 microns onto the heated surface of the steel pipe. Once applied and cured, the epoxy film exhibits an extremely hard surface with excellent adhesion to the steel surface. The FBE protective surface is homogeneous and offers an excellent resistance to chemical reaction [60]

The FBE coating systems provide protection at moderate temperatures (-40°C to 85°C) and come in two options [60]:

FBE Dual: recommended for sub-sea pipelines and flow lines operating in the toughest environments. It offers excellent impact resistance and abrasion properties which, combined with its good flexibility, provide suitable protection against coating damage during pipe transportation and construction

FBE Non-slip: this coating system provides a rough, non-slip surface for a pipeline that will subsequently be concrete-coated [60]

FBE coatings has become the most widely used one layer corrosion protection because of their excellent adhesion to steel surface, good chemical/corrosion and shrinkage resistance, including their ability to resist the shielding of the pipe from cathodic protection at the same time significantly reduced the rate stress corrosion cracking, SCC, under harsh environmental conditions (in deep sea, through rolling plains, rocky mountains, etc.) [59]

CAPABILITY/PROPERTY	FBE
Minimum Pipe Diameter	90 mm (3.5")
Maximum Pipe Diameter	1220 mm + (48"+)
Minimum Pipe Length	5.5 m (18')
Maximum Pipe Length	25 m (82')
Minimum Recommended Handling & Construction Temperature	-30°C (-22°F)**
Maximum Recommended Operating Temperature	110°C (230°F)*

Table 2. 4: Typical Plant Capabilities and Product Properties

(Adapted from www.brederoshaw.com/main/home.html © 2012- 2014 ShawCor Ltd. All rights reserved)

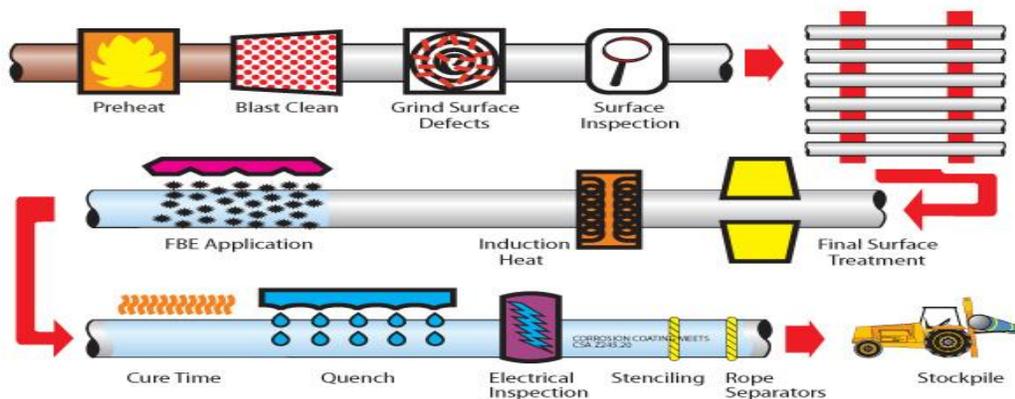


Figure 2.24: Describes the product application process; Surface preparation and coating procedures

(Adapted from www.brederoshaw.com/main/home.html)© 2012- 2014 ShawCor Ltd. All rights reserved.

CHAPTER THREE: EXPERIMENTAL APPROACH

3.1 MATERIAL SELECTION

The material used in the analysis was X65 steel obtained from SCC steel company in Abuja, Nigeria.

3.2 CHEMICAL ANALYSIS

The X65 steel sample was analyzed using Solaris CCD at SCC steel company, Abuja, Nigeria with elemental composition in table 3.1



Figure 3. 1: Solaris CCD Machine used for chemical Analysis

MAJOR ELEMENTAL COMPOSITIONS (wt. %) OF X65 STEEL: API STANDARD WITH YIELD STRENGTH OF 448 MPa AND UTS 517 MPa								
ELEMENT	C	Si	Mn	P	S	Mo	Ni	Al
%	0.068	0.156	1.616	0.015	<0.001	<0.002	0.312	0.023
ELEMENT	Fe	Cu	Ti	Cr	Nb	Mg	Zn	W
%	97.450	0.256	0.014	0.020	0.042	0.0013	<0.001	<0.005

Table 3. 1: Elemental Composition of X65 Steel from Chemical Analysis

3.3 SAMPLE PREPARATION

3.3.1 CUTTING OF SAMPLE

The samples were cut at Galadimawa, Abuja, Nigeria, with dimension of 13cm x13cm x 18cm (length, weight, and thickness respectively).

3.3.2 SURFACE PREPARATION

The surfaces of the samples were prepared by grinding using silicon carbide (SiC, 60 microns) paper mounted on the grinding machine, which also allowed the removal other corrosive materials that might have been present on the surfaces of the samples.



Figure 3.2: Grinding machine

3.3.3 WEIGHT MEASUREMENT

The weight of each sample was measured after preparing the surface (before coating, after curing, and with time after each sample was immersed in the selected corrosion medium).

3.4 COATING OF SAMPLE

4. The coating materials were mixed in a volume ratio of 2:1. That is the quantity of base to activator. The top of a La Voltic (mineral water bottle with volume capacity of 8ml) was filled twice with the base and once with the activator and thoroughly mixed. Four of the samples labeled 1-4 were coated by dipping the brush in the prepared base-activator mixture and passed over each of the six surfaces ones. Four other samples were obtained and labeled 5-8, then coated by passing the brush twice over each of the surfaces. All of

these were carried out at a room temperature of 28⁰C. The coated samples were allowed the cure for about 54 hours.



Figure 3.3: Coating materials and set up



(a)



(b)



(c)

Figure 3.4: Measuring and mixing of the Base and activator for sample coating shown in (a), (b), and (c)

3.5 PREPARATION OF SOLUTIONS AND IMMERSION OF SAMPLE

i) 3.5% standard solution of $\text{NaCl}_{(\text{aq})}$ prepared at 28°C

The weighing balance was set to read at the zero mark and a graduated cylinder (previously washed with distilled water and kept clean and dry) with specification 250 ml $\pm 2\text{ml}$ was weighed at 75.422g and recorded as m_i .

Distilled water was carefully poured into the cylinder using transferring funnel to avoid the splashing of water on the walls of the cylinder and a mass of 304.90 g was obtained and recorded as m_f , at the 230 ml reading of the cylinder. The mass of water was then calculated from:

$$W_{\text{H}_2\text{O}} = m_f - m_i \text{-----}3.1$$

$$W_{\text{H}_2\text{O}} = (304.490 - 75.422)\text{g} = 229.518\text{g}$$

The mass of $\text{NaCl}_{(\text{s})}$ to be dissolved in 229.518g H_2O to obtain the desire 3.5% $\text{NaCl}_{(\text{aq})}$ was calculated from the expression:

$$\% \text{NaCl} = (W_{\text{NaCl}} \div W_{\text{soln}}) \times 100 \% \text{-----}3.2$$

Where %NaCl is the concentration, W_{NaCl} is the weight of the $\text{NaCl}_{(\text{s})}$ (the solute) and W_{soln} is the weight of the solution (the sum of $W_{\text{H}_2\text{O}}$ and W_{NaCl}).

$$3.5\% = W_{\text{NaCl}} \div (229.518 + W_{\text{NaCl}}) \times 100\%$$

Therefore, $W_{\text{NaCl}} = 8.324 \text{ g}$. This quantity of $\text{NaCl}_{(s)}$ was weighed out on the weighing balance and dissolved in 229.518 g H_2O (distilled water) to obtain a standard solution with concentration 3.5%NaCl.

ii) $\text{Na}_2\text{CO}_3(\text{aq})$ with pH of 8.20 and pH of 3.98.

Small quantity of Na_2CO_3 salt was obtained and dissolved in 250 ml beaker containing 150 ml distilled water and stirred using a glass stirring rod. The solution was thoroughly homogenized by pouring it interchangeably into another 250 ml beaker ten times. The pH meter was calibrated in a 7.05 buffer solution and then dipped into the Na_2CO_3 solution. Additional distilled water was added and stirred thoroughly to obtain a reading of 8.16 on the pH meter. Similar procedure was used to prepare the pH of 3.98 solution of Na_2CO_3 .

iii) $\text{HCl}(\text{aq})$ with pH of 2.71

Small quantity of a 1 M $\text{HCl}(\text{aq})$ was poured in 100 ml of distilled water in a 250 ml and homogenized and pH measured using similar procedures as in (ii) above, and a pH meter reading of 2.71 was obtained.



Figure 3. 5: Preparation of solution: (a) Weighing of $\text{NaCl}_{(s)}$ on Weighing Balance, (b) 250 mL Beaker Containing NaCl Solution, and (c), pH meter

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1 SURFACE MORPHOLOGY OF SAMPLE

The below images represent the surface morphology of X65 steel before, during and after 360 hours in corrosive media.

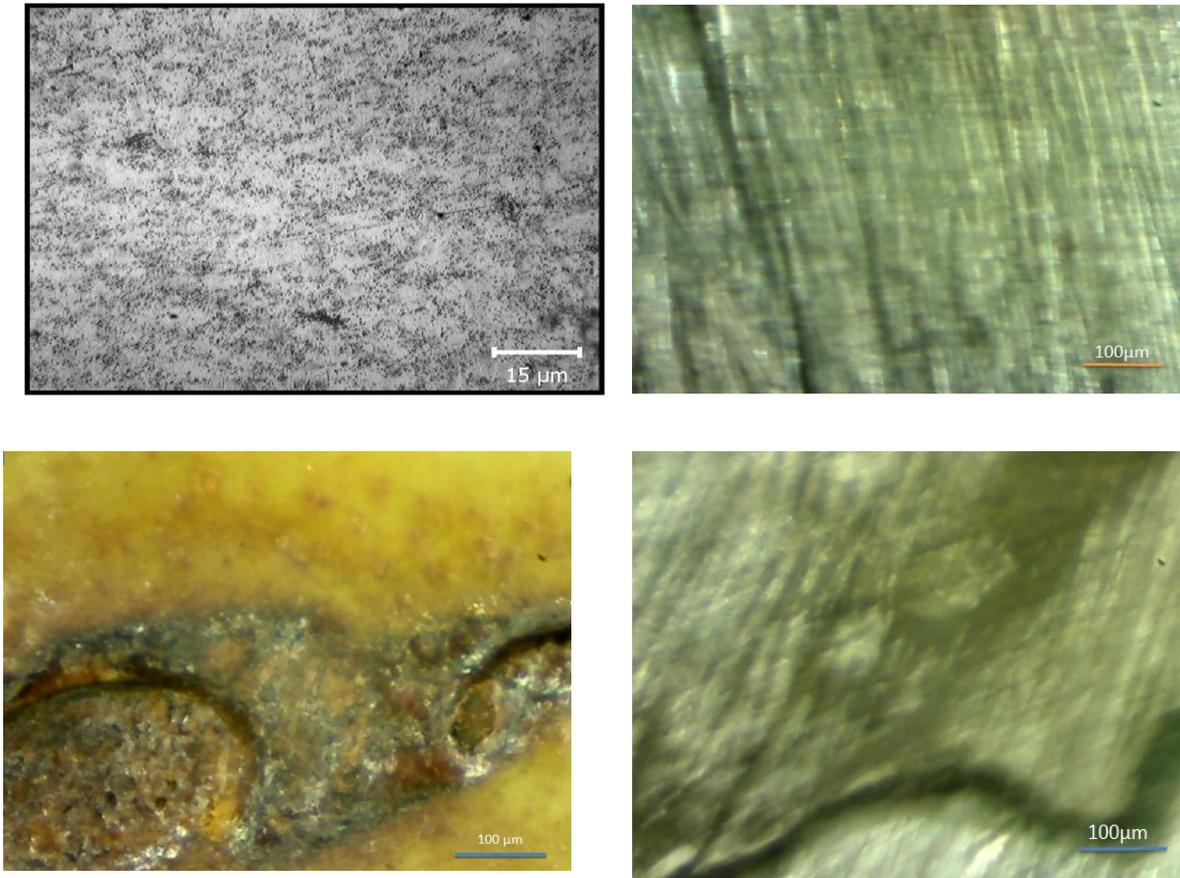


Figure 4. 1: (a) Optical microstructural Image of X65 Steel(400X); (b), (c), and (d) Surface Morphology from ProScope HR Image Analyzer for (b) Before Immersion without Coating; and After 360 Hours in HCl Solution (pH 2.71) (c) When Still Coated, (d) When Coating Removed

4.2 WEIGHT LOSS MEASUREMENT RESULTS (IN GRAMS) OF SAMPLES IN DIFFERENT CORROSIVE MEDIA AS A FUNCTION OF TIME:

4.2.1 WEIGHT LOSS VALUES MEASURED FROM WEIGHING BALANCE

The weight loss values in table 4.1 below were obtained by subtracting the weight of the samples upon immersion from their respective weights after surface preparation and curing-before immersion of samples.

Sample	Corrosive media	Number of Brush passed	Weight Loss (Grams)					
			72 hrs	144 hrs	216 hrs	288 hrs	360	
			With coating	With coating	With coating	With coating	With coating	With coating Removed
1	3.5% NaCl	1	0.000	0.000	0.000	0.001	+0.003	+0.004
2	HCl (pH 2.71)	1	0.000	0.000	0.000	0.000	+0.012	+0.014
3	Na ₂ CO ₃ (pH 3.98)	1	0.000	0.000	0.000	0.000	-0.001	0.000
4	Na ₂ CO ₃ (pH 8.16)	1	0.000	0.000	0.000	0.000	+0.003	+0.004
5	Na ₂ CO ₃ (pH 8.16)	2	0.000	0.000	0.000	0.000	+0.000	+0.002
6	3.5% NaCl	2	0.000	0.000	0.000	0.000	+0.001	+0.002
7	Na ₂ CO ₃ (pH 3.98)	2	0.000	0.000	0.000	0.000	+0.001	+0.001
8	HCl (pH 2.71)	2	0.000	0.000	0.000	0.000	+0.006	+0.008

Table 4. 1: Data Obtained from Weight Loss Measurement Using Weighing Balance

According to the data in table 4.1, higher weight loss values were observed for samples 1, 2, 4, 5, 6, and 8, upon the removal of epoxy coating from the samples compared to when the samples

were still coated. After the 360 hours of immersion in Na₂CO₃ solution (pH 3.98), the weight of sample 3 was observed to be greater than its weight before immersion thus giving a negative value. This was assumed to be due to the deposition of substances under the coating from the solution through holidays. However, there was not noticeable weight loss observed upon the removal of the coating. The weight of sample 7 was observed to be the same after 360 hours of immersion in Na₂CO₃ solution (pH 3.98), when still coated and upon the removal of the epoxy coating. There was no noticeable weight loss observed for sample 5 while the sample was still coated. Upon the removal of the coating, however, a 0.002 g difference in weight was obtained from the values displaced by the balance (weight before coating and immersion minus the weight after 360 hours of immersion when coating was removed) which implied that corrosion products and/or other substances from the solution deposited under the coating leveling out the weights.

4.3 CORROSION RATE OF SAMPLES OBTAINED FROM WEIGHT LOSS MEASUREMENT USING WEIGHING BALANCE:

The corrosion rate was calculated from the expression below:

$$mpy = k \frac{w}{DAT} \text{-----} 4.1$$

Where mpy is read as mils per year, k is a constant equivalent to 534, w is the weight loss due to metal dissolution in milligrams, D is the density of the metal in grams per cubic centimeters, A is the area of the sample in square inch, and T is the time of sample's immersion in hours.

	Number of brush passed	Corrosive medium	Corrosion (mpy) (10^{-3})		
			288 hrs	360 hrs	
			With coating	With coating	Coating removed
1	1	3.5% NaCl	10.3700	24.89184	33.18912
2	1	HCl (pH 2.71)	-	100.02509	116.69594
3	1	Na ₂ CO ₃ (pH 3.98)	-	0.000000	0.000000
4	1	Na ₂ CO ₃ (pH 8.2)	-	26.88723	35.84964
5	2	Na ₂ CO ₃ (pH 8.2)	-	0.000000	17.40721
6	2	3.5%NaCl	-	7.94434	15.88867
7	2	Na ₂ CO ₃ (pH 3.98)	-	9.23781	9.23781
8	2	HCl (pH 2.71)	-	48.33312	64.44430

Table 4.2: Corrosion Rate in meter per year (mpy) Calculated from Weight Loss Measurements using Weighing Balance

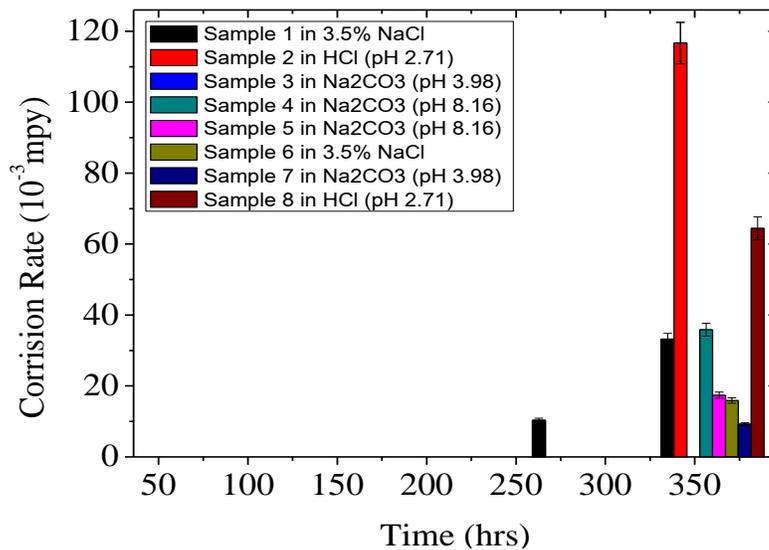


Figure 4. 2: A Bar Chart/Plot for Corrosion Rate from Table 4.2 Data (Upon Removal of Coating)

4.4 WEIGHT LOSS VALUES CALCULATED FROM CHANGE IN pH MEASUREMENTS

4.4.1 METAL DISSOLUTION IN $\text{HCl}_{(aq)}$ FROM pH MEASUREMENT

The following assumptions were made:

1. The decrease in pH of the acidic solution was a result of metal dissolution process
2. Two cathodic reactions were involved during the metal dissolution/ redox process

I. Hydrogen evolution in acidic medium



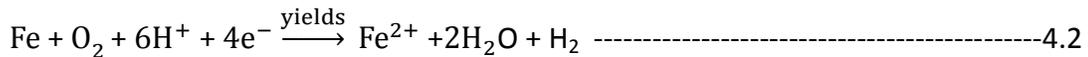
II. Oxygen reduction in acidic medium



3. *One anodic reaction*



Equations 2.8, 2.6, and 2.5 were then added to obtain 4.2



From equation 4.1, the ratio of Fe^{2+} to H^+ is 1:6

Note the followings:

$$[\text{H}^+] = 10^{-\text{pH}} \text{-----4.3}$$

so

$$[\text{Fe}^{2+}] = [\text{H}^+]/6 \text{-----}4.4$$

$$\therefore m = [\text{Fe}^{2+}](WV)\text{-----}4.5$$

where m is amount of Fe²⁺ dissolution in grams (i.e. the weight loss), [Fe²⁺] is the molar concentration (mole per liter) of iron(II) ions in the solution, W is molar weight of iron (in grams per mole), V is volume of solution in liter.

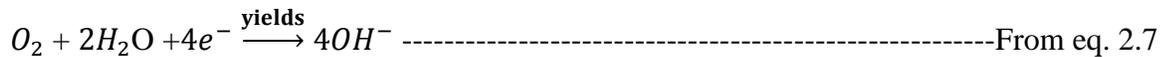
4.4.2 METAL DISSOLUTION IN 3.5% NaCl_(aq) FROM pH MEASUREMENT

NOTE: The initial pH upon preparation and prior to samples being immersed was 6.96.

Assumptions:

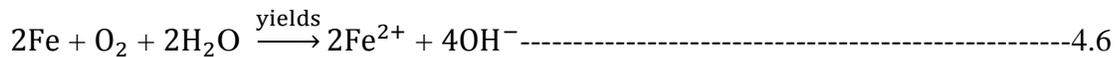
- One cathodic reaction in neutral medium

Oxygen reduction in neutral medium because NaCl_(aq) is a neutral salt.



- One anodic reaction (eq. 2.5)

Combination of equations 2.5 and 2.7 led to:



In this case the rate of Fe²⁺ dissolution was determined from the hydroxide ion concentration [OH]⁻ which is related to the hydrogen ion concentration by

$$\text{pOH} = 14 - \text{pH} \text{-----}4.7$$

but

$$[\text{OH}^-] = 10^{-\text{pOH}} \text{-----4.8}$$

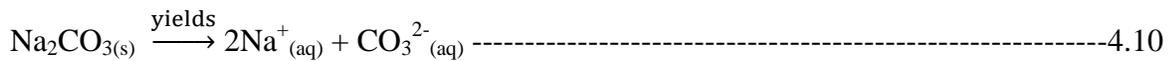
From equation 4.6, the ratio of Fe^{2+} to OH^- is 2:4 which is equivalent to 1:2

$$\therefore [\text{Fe}^{2+}] = [\text{OH}^-]/2 \text{-----4.9}$$

Equation 4.5 was used in similar manner to calculate amount of iron dissolution.

4.4.3 METAL DISSOLUTION IN Na_2CO_3 FROM pH MEASUREMENT

Sodium carbonate is a basic salt and decomposes in a single step [52]. This implies that its molar concentration is equal to its equilibrium concentration according to the stoichiometry of its dissociation of in water:



The amount of iron dissolution was calculated from hydroxide ion concentration, $[\text{OH}^-]$ of the solution with time.

Assumptions:

- One cathodic reaction in basic medium.
Oxygen reduction in basic medium; same as same as equation 2.7
- One anodic reaction same as in equation 2.5

The amount of iron dissolution was calculated in similar manner using equations 4.6, 4.7, 4.8, 4.9, and 4.5 respectively in this order.

Media	Sample	72 hrs		144 hrs		216 hrs		288 hrs		360 hrs	
		pH	W(10^{-3} g)	pH	W(10^{-3} g)	pH	W(10^{-3} g)	pH	W(10^{-3} g)	pH	W(10^{-3} g)
3.5%NaCl	1	7.57	0.010380	8.04	0.03062	8.980	0.266680	9.569	1.03513	10.336	6.05331
	6	7.38	0.006700	7.99	0.02729	8.082	0.033730	8.779	0.16788	9.904	2.23869
HCl pH 2.71	2	2.71	0.000000	2.68	19.44786	2.601	23.32770	2.53	27.4708	2.46	32.27542
	8	2.71	0.000000	2.71	0.000000	2.671	19.85509	2.613	22.6920	2.509	28.83181
Na ₂ CO ₃ pH 3.98	3	4.01	0.000003	5.04	0.000031	5.637	0.000120	6.724	0.00148	7.012	0.00287
	7	3.98	0.000000	3.98	0.000000	4.230	0.000005	6.881	0.00212	9.701	1.40279
Na ₂ CO ₃ pH 8.16	4	8.34	0.061090	8.79	0.172180	9.016	0.289730	9.397	0.69662	10.305	5.57177
	5	8.18	0.042266	8.22	0.046344	9.001	0.279890	9.026	0.29648	9.997	2.77328

Table 4. 3: Weight Loss Values Calculated from Change in pH with Time

Although there was no noticeable pH change/weight loss observed initially for samples 2 and 8, they had the highest weight loss values overall as the immersion time progressed from 72 hours to 360 hours with sample 2 having higher value than sample 8. Unlike the weight loss value obtained for sample 3, using the weighing balance as in table 4.1, the pH change/weight loss calculation gave values (as in table 4.3) with time thought infinitesimal. The pH of the solution containing sample 7 was also observed to be not changing after the first two pH measurements taken at 72 hours and 144 hours respectively. However, a change in pH was observed from the readings of the pH meter after 216 hours indicating that the solution could not easily diffuse initially across the coating layer to the metal surface. Thus, there was no metal dissolution of sample 7 until after 144 hours.

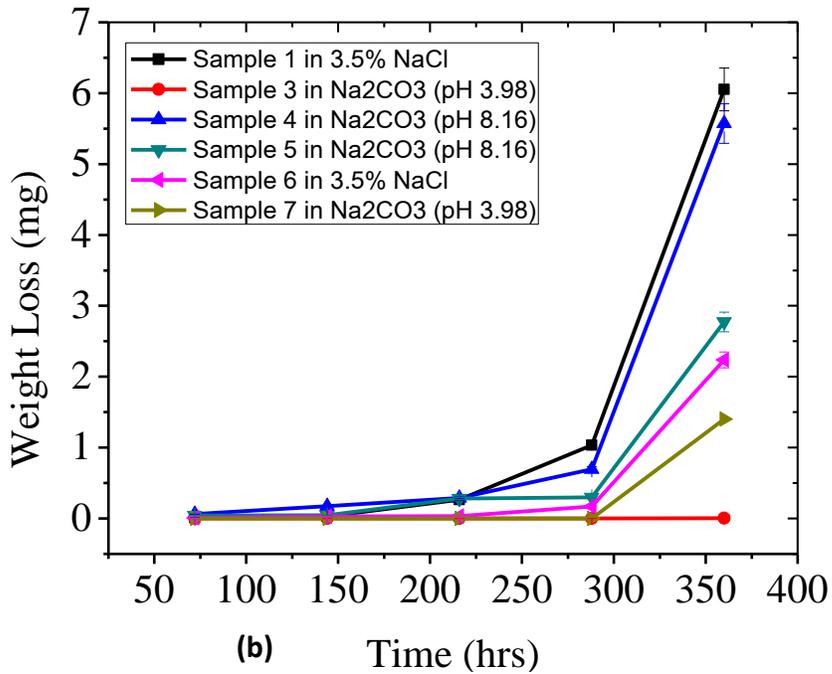
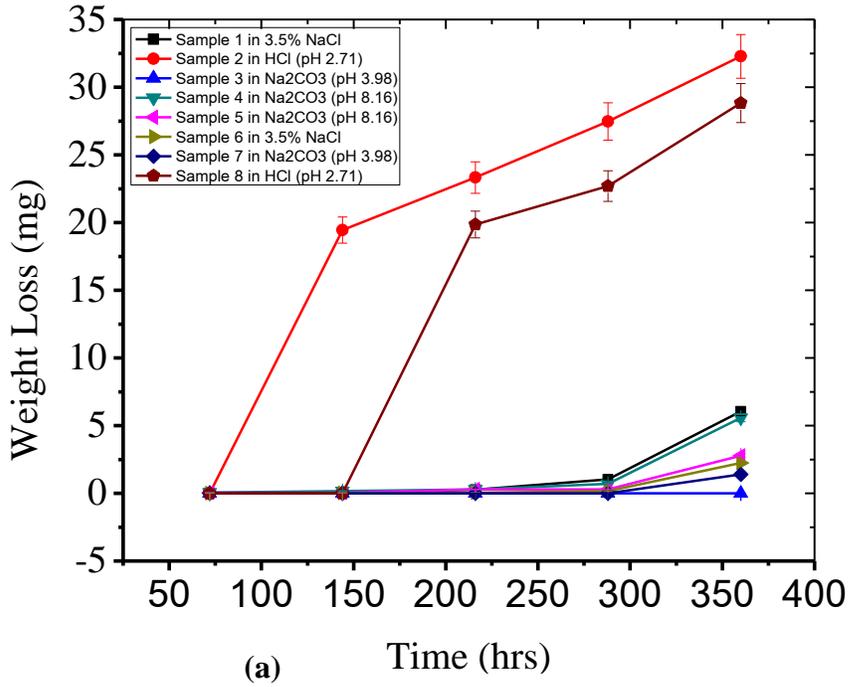


Figure 4.3: Plot of weight loss against Time (a) For all Eight Samples (b) For Sample 1,3,4,5,6, and 7

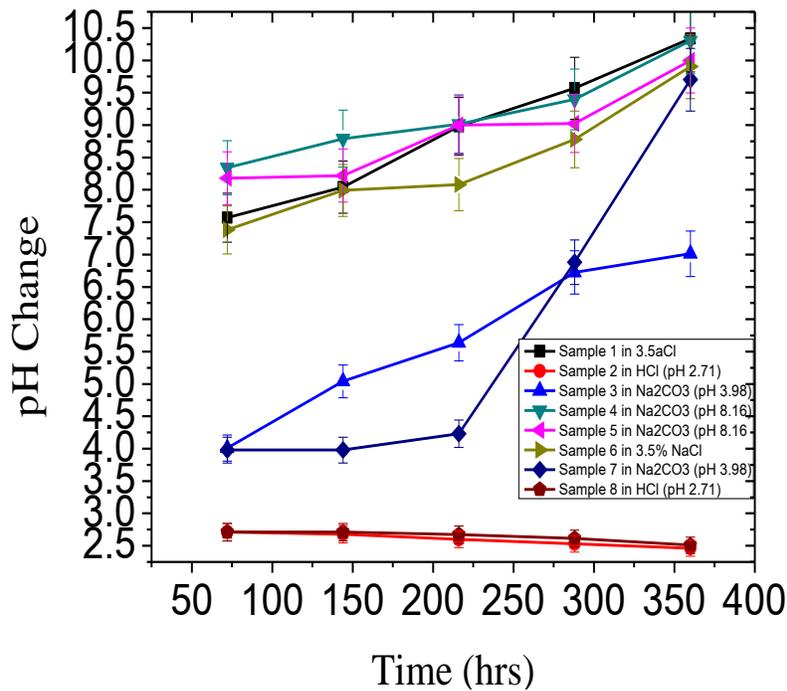


Figure 4.4: Plot of pH Change with Time

The plot in figure 4.3 indicates that the decrease in pH for the hydrochloric acid solution and the increase in pH observed from the readings of the pH meter with time in sodium chloride and sodium carbonate solutions were due to metal dissolution.

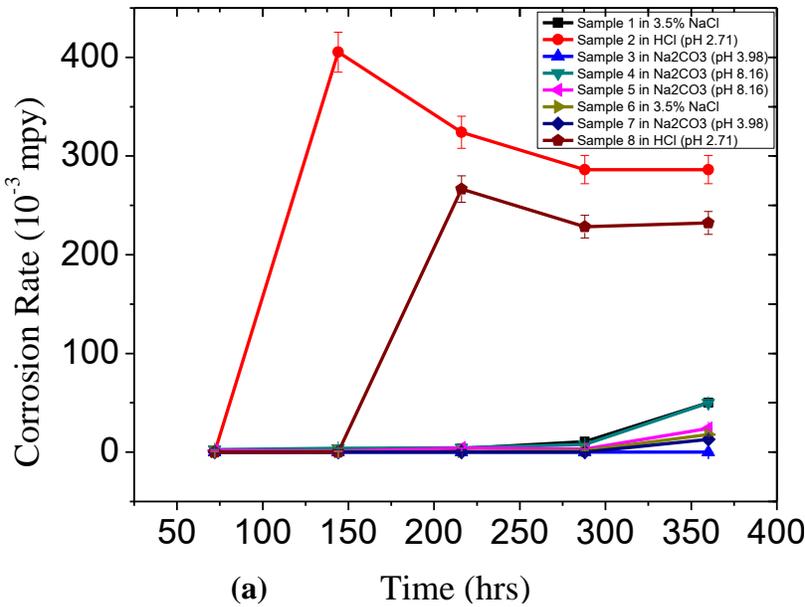
From table 4.3, it is seen that the amount weight loss by metal dissolution can be calculated as a function of pH change with time. The value of the weight loss measurements were found to increase in relation to change in pH .

From these calculated weight loss data, the corrosion rates from pH measurement with time for the different samples were obtained as in the table below:

4.5 CORROSION RATE FROM WEIGHT LOSS VALUES OBTAINED FROM pH CALCULATION

CORROSION RATE CALCULATED FROM pH CHANGE in meter per year (mpy)											
Media	Sample	72 hrs		144 hrs		216 hrs		288 hrs		360 hrs	
		pH	Rate(10^{-3})	pH	Rate(10^{-3})	pH	Rate(10^{-3})	pH	Rate(10^{-3})	pH	Rate(10^{-3})
3.5%NaCl	1	7.57	0.4306	8.04	0.6352	8.980	3.688	9.569	10.736	10.336	50.226
	6	7.38	0.2661	7.99	0.5420	8.082	0.44658	8.779	1.66710	9.904	17.78000
HCl pH 2.71	2	2.71	0.00000	2.68	405.26542	2.601	324.0771	2.53	286.22639	2.46	269.02933
	8	2.71	0.00000	2.71	0.00000	2.671	266.5718	2.613	228.49442	2.509	232.25523
Na ₂ CO ₃ pH 3.98	3	4.01	0.000120	5.04	0.0006431	5.637	0.001696	6.724	0.01554	7.012	0.02413
	7	3.98	0.00000	3.98	0.00000	4.230	0.000073	6.881	0.02448	9.701	12.96000
Na ₂ CO ₃ pH 8.16	4	8.34	2.73800	8.79	3.85800	9.016	4.32800	9.397	7.80419	10.305	49.93648
	5	8.18	1.83934	8.22	1.00884	9.001	4.06014	9.026	3.22554	9.997	24.13750

Table 4.4: Corrosion Rate in meter per year (mpy) Calculated from Weight Loss Measurements using pH change with Time



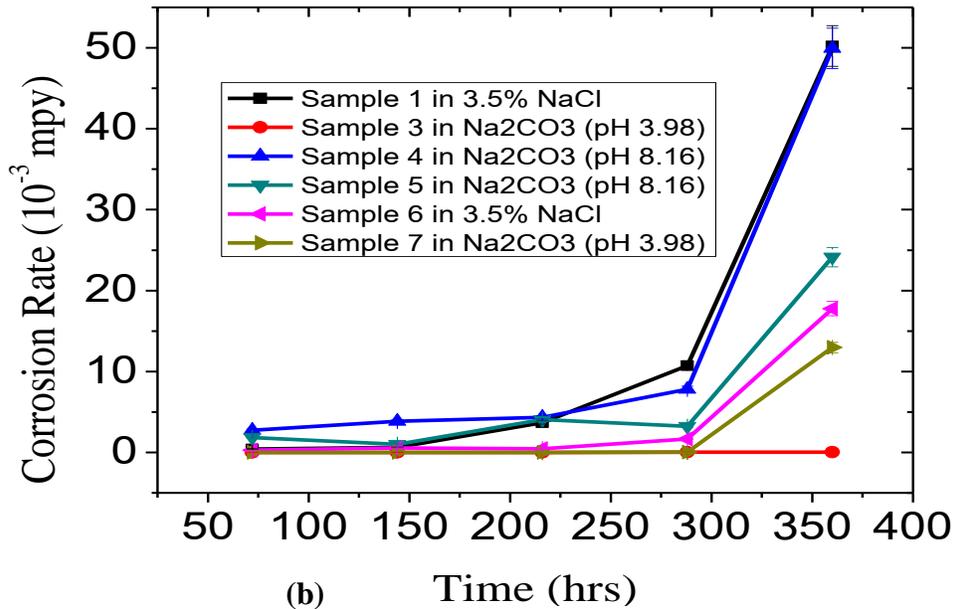


Figure 4.5: Plot weight loss from pH measurement against time (a) For all Eight Samples, (b) For Sample 1, 3, 4, 5, 6, and 7

From the plot above, the corrosion rates of samples 2 and 8 were found to increase initially to a certain peak at 144 hours and 216 hours respectively. A decreasing corrosion rates with time were observed for these samples after 144 hours and 216 hours. After 288 hours, the corrosion rate of sample 8 started to increase gradually. The rise and fall in corrosion rate for these two samples can be attributed to the formation protective film and its subsequent breaking down by the chloride ions. Corrosion rates are generally found to be retarded by the formation of protective/passive films, which have been found by many Corrosion Engineers to trigger the mechanism of pitting corrosion by chloride ions. The conformity of this explains the fluctuation in the corrosion rate of sample 2 and sample 8.

The corrosion rate for sample 1, 4, 5, 6, and 7 were found to increase gradually with time up to 288 hours and then started to increase at rate faster than the rate before 288 hours. The corrosion of sample 3 was observed to increase at an extremely infinitesimal rate.

CHAPTER FIVE

5.1 IMPLICATIONS

The results from this research have the following implications:

- a) Metal dissolution/corrosion cannot be easily prevented in corrosive environments; however, its rate can be controlled. Even though the samples were coated with epoxy which has an excellent corrosion and chemical resistant properties, the samples were still found to corrode with time.
- b) Weight loss measurement from weighing balance for a corrosion process is not a better way of determining corrosion rate. The discrepancy between the measured weight loss values obtained from the balance and the pH calculation is an evidence.

5.2 CONCLUSION

Weight loss/corrosion rate was highest in the hydrochloric acid media. The weight loss values for almost all of the samples coated using 1 brush passed were observed to be about twice the samples with 2 brush passed. However, sample 7 (with 2 brush passed) was observed to have higher weight loss and subsequently, higher corrosion rate than sample 3 (with one brush passed) in the same sodium carbonate solution of pH 3.98 though in different reaction flasks. This would have been due the a rapid formation of protective film due to ample oxygen diffused from the highly diluted basic salt solution, across the thin coating on sample 3.

Generally the solutions containing chloride ions (HCl and NaCl) were found to have high weight loss values, thus, corrosion rate than the sodium carbonate solutions. However, the sodium carbonate solution of pH 8.16, was observed to be more corrosive than one with pH 3.98.

5.3 FUTURE WORK

The results obtained from this research suggest the need for the further in-depth analysis of the following:

1. Potentiodynamic polarization measurements to measure current-potential relationship with corrosion rates
2. Nano indentation to study the adhesion of the coating layer to the sample surface
3. Atomic Force Microscope, AFM, to analyze the corrosion product and synthetic iron oxide/hydroxide film
4. Electrochemical Impedance Spectroscopy, EIS, analysis to provide reliable data for the determination of passive film structure

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