SAFETY ASSESSMENT OF A PRODUCTION PLANT IN NIGERIA: A CASE STUDY OF CORROSION DEVELOMENT MECHANISM AT KADUNA REFINERY AND PETROCHEMICAL COMPANY.

BY

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DECLARATION

I OSADARE, Elizabeth Mopelola with matriculation number M.ENG/SEET/2006/1541 hereby declares that this thesis titled: Safety Assessment of a Production Plant in Nigeria: $\overset{a}{\text{A}}$ case study of Corrosion Development Mechanism at Kaduna Refinery and Petrochemical Company, is a record of my own research finding. It has not been presented for any other qualification anywhere. Information from the works of other Scientists (Published or Unpublished) and their contributions here been duly acknowledged.

10 - 02 - 2012

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OSADARE, Elizabeth Mopelola   Date

CERTIFICATION

This thesis titled: Safety Assessment of a Production Plant in Nigeria: A case study of Corrosion Development Mechanism at Kaduna Refinery and Petrochemical Company by: OSADARE, Elizabeth Mopelola (M.ENG/SEET/2006/1541) meets the regulations governing the award of the degree of Masters of Engineering of the Federal University of Technology, Minna and it is approved for its contribution to scientific knowledge and literary presentation.

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DEDICATION

This thesis is dedicated to my late beloved brother Late Rev. Fr. (Dr.) Philip Oluwabusuyi Osadare. Some sleep early, some sleep late, but all must go to bed. God is the only interpreter of His actions.

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ABSTRACT

Corrosion in oil/water pipeline system in production plants and petroleum industry continues to be a major problem in respect of safety in oil and gas industries. Corrosion development mechanism in Kaduna Refinery and Petrochemical Company's (KRPC) cooling water return pipeline has been studied based on the available data. A comprehensive mathematical corrosion model has been developed using MathCAD for simulating the effect of temperature, corrosion scale, and pipe material elemental content on the corrosion rate in Kaduna Refinery and Petrochemical Company (KRPC). It has been found from this work that corrosion rate increases with time; it increases with increase in temperature of the fluid passing through the pipe; and also increases with increase in mineral factor (Iron II content) of the mild steel pipe. Also, Corrosion rate decreases with increase in corrosion scale. Lack of proper maintenance and inadequate monitoring of equipment as well as prolonged shut-down time has been found to be responsible for high corrosion level in Kaduna Refinery and Petrochemical Company (KRPC), which is a major threat and potential hazard to the safety of the plant; integrity of physical assets and risks to the environment.

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CHAPTER ONE

1.0 INTRODUCTION

Industrial safety assessment is a careful examination of potential hazards that may affect the operation of a business; these may be risks associated with the safety and integrity of physical assets, risks to the environment, and financial risks from various decisions and also risks from corrosion or poor corrosion mitigation procedures. At its simplest, it is a common sense approach that provides a means of checking what often good existing practice is. For example, Refinery installations that produce hydrocarbon fluids that are flammable are therefore a hazard. Some fluids contain hydrogen sulphide which are toxic gases and are hazardous with potential to cause death and injury to personnel. (Inegbenebor and Olalekan, 2002)

Corrosion in oil/water system in production plants and petroleum industry continues to be a major problem in respect of safety in oil and gas industries. It has been a source of concern to the pipeline industry for many years. This is especially true with critical service lines and systems operating at increasingly higher load level. Today's public attitude towards industrial safety and environmental protection highlight the concern over possible deterioration of production plant and pipeline systems. (Egbe, 2008)

Carbon dioxide corrosion represents the greatest risk to the integrity of carbon steel equipments in a production environment and transportation facilities of oil and gas industries. Compared with the incidences of fatigue, erosion, and stress corrosion cracking or over pressurization, the incidences of CO_2 related damage are far more common. For this reason, CO_2 corrosion of carbon steel will always be a problem that oil and gas industries have to deal with. Managing CO_2 corrosion therefore becomes a priority and it can become expensive.

Successful management of CO_2 corrosion starts off with the identification of risk and continues with the provision of suitable controls and the review of the success of the controls via monitoring. Risk based inspection is now widely adopted and as CO_2 corrosion represents one of the most important factors governing the probability of failure for much equipment, a reasoned approach should be taken. It is important that this approach is theoretically sound but also reflects past experiences.

Both corrosion models and laboratory testing are frequently used in oil and gas industry to make lifetime predictions of facilities using carbon steel and further to make decisions on material selection. Corrosion models, including empirical, semi-empirical, and mechanistic ones, have been developed over the past several decades to predict corrosion of carbon steel. These corrosion models can provide engineers with quick and economical corrosion predictions. Most of the models were validated by laboratory data and/or field data. Empirical and semi-empirical models usually provide reasonable predictions within their validation range but poor predictions outside such range. Mechanistic models generally can extrapolate to conditions outside such validation range and remain accurate to a certain degree. Consequently, one should always understand the validation range and limitations of the models to apply these correctly. Moreover, even though, part of corrosion mechanisms are well understood in laboratory investigations, due to the complexity in production operations, it is still challenging to apply laboratory short-term testing results and corrosion models to predict corrosion of facilities for twenty to thirty years of service. (Sun *et. al*, 2009). In this study, data obtained from the field has been used for the validation of the model developed. It is the purpose of this paper to develop a mathematical model that describe the effects of temperature, corrosion scale and Iron II contents on corrosion rate in cooling water unit of Kaduna Refinery and Petrochemical Company (KRPC)

1.2 Aims and Objective

The aims of this project are:

1. To develop a mathematical model for corrosion rate in cooling water return pipeline unit of Kaduna Refinery and Petrochemical Company.
2. To determine the effect of temperature, corrosion scale, and Iron II contents of the mild steel on the corrosion rate in water cooling pipeline in the KRPC using the model equation developed with the aid of MathCAD.
3. The result obtained is aimed at being a valuable tool for safety assessment of a production plant.

1.3 Scope of the Study

In order to achieve the above objectives, the following tasks were undertaken:

1. Development of mathematical model for corrosion rate in oil transportation facilities.
2. Obtaining corrosion data from KRPC
3. Simulation of the model developed in step 1
4. Comparing simulated results obtained in step 2 to that of step 3.
5. The simulated and model results obtained from the experiment carried out by Odigure, 2002 were compared with existing statistical data using statistical correlation

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Introduction

Industrial Safety is a term generally used to assess the operational efficiency of modern industry. It has been described as a discipline relating to all measures taken to ensure the general well-being of workers, prevent machine down-time and material wastage due to accidental damages in order to raise the profitability of the enterprises. (Ibhadode, 1997)

Safety practices are an essential factor for the development of the productive sector of all manufacturing industries. In any industrial set-up, the ultimate goal is to use man, machine and money effectively in order to achieve the objective of such an establishment. Seeing the importance of man in an industry, it is therefore necessary to look at safety which is one of the most prevailing factors disturbing man from achieving the organizational goal. (Esekhgbe, 1996).

Adequacy of safety equipment at working place helps to increase efficiency of labour and productivity level. However, Shaiye (1999) described health and safety in every organization as the role of the personnel department to ensure that the working environment is as conducive and safe as possible.

Industrial safety assessment is a careful examination of potential hazards that may affect the operation of a business; these may be risks associated with the safety and integrity of physical assets, risks to the environment, and financial risks from various decisions and also risks from corrosion or poor corrosion mitigation procedures. At its simplest, it is a common senses approach that provides a means of checking what often good existing practice is. For example, Refinery installations that produces hydrocarbon fluids that are flammable and are therefore a hazard. Some fluids contain hydrogen sulphide which are toxic gases and are hazardous with potential to cause death and injury to personnel. (Inegbenebor *et al,* 2002)

Corrosion in oil/water system in production plants and petroleum industry continues to be a major problem in respect of safety and has not been adequately addressed. It has been a concern of the pipeline industry for many years. This is especially true with critical service lines and systems operating at increasingly higher load level. Today's public attitude towards industrial safety and environmental protection highlight the concern over possible deterioration of production plant and pipeline systems. (Egbe, 2008)

It is the purpose of this paper to discuss and explain the occurrence of different forms of corrosion in Kaduna Refinery and Petrochemical Company (KRPC). It is also to look into the safety of production plant in KRPC with respect to corrosion development within the cooling tower water return line. It is also to check the integrity of the pipes and water drums knowing that corrosion takes place within pipes and drums. By testing and calculating the corrosion rate and by measuring of the pipe or drum thickness to check if the corrosion has eating up the line or not. If it does and has exceeded ***corrosion allowance,*** it cannot guarantee the integrity of the equipment/pipe any longer. This helps to forecast and prevent corrosion from happening.

2.2 Kaduna Refining and Petrochemical Company (KRPC) Profile

The refinery was commissioned in 1980 to supply petroleum products to Northern Nigeria with a capacity of 100,000 B/D. In 1986, the capacity of the first crude train was expanded to 60,000 B/D. The expansions have increased the current nameplate capacity of the refinery to 110,000 B/D. It comprises of the following:-

- Main plants
- Crude Distillation Unit. CDU-1 **(Fuels)**
- Crude Distillation Unit. CDU-2 **(Lubes)**
- Petrochemicals unit

2.2.1 KRPC Main Plants

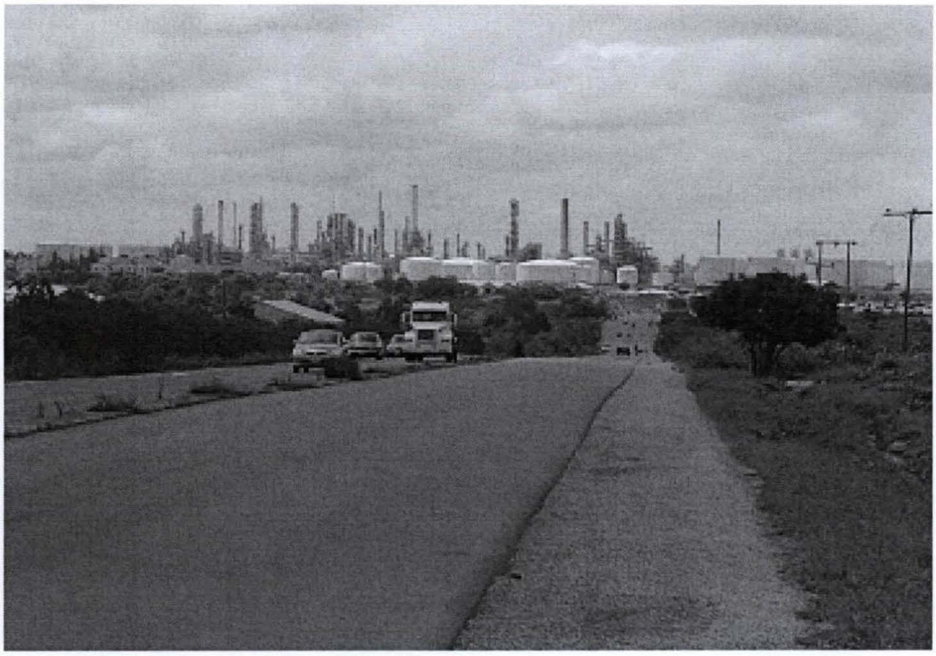


Plate i: View of entrance to KRPC Plant. (Source: KRPC catalogue)

Plate ii: View of KRPC main plant. (Source: KRPC catalogue)

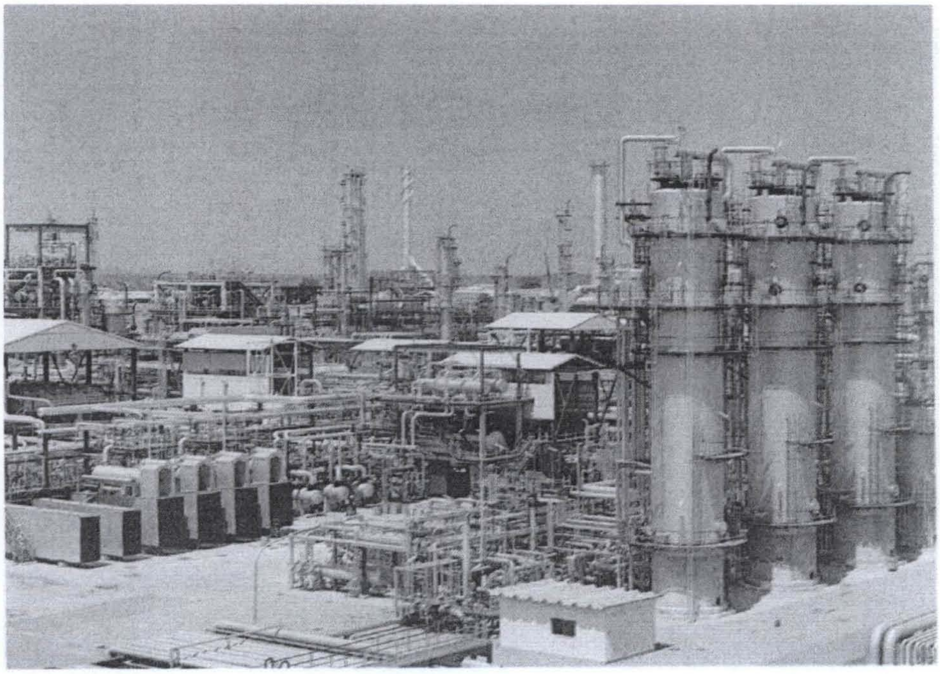


Plate iii: Lubricating oil complex. (Source: KRPC catalogue)

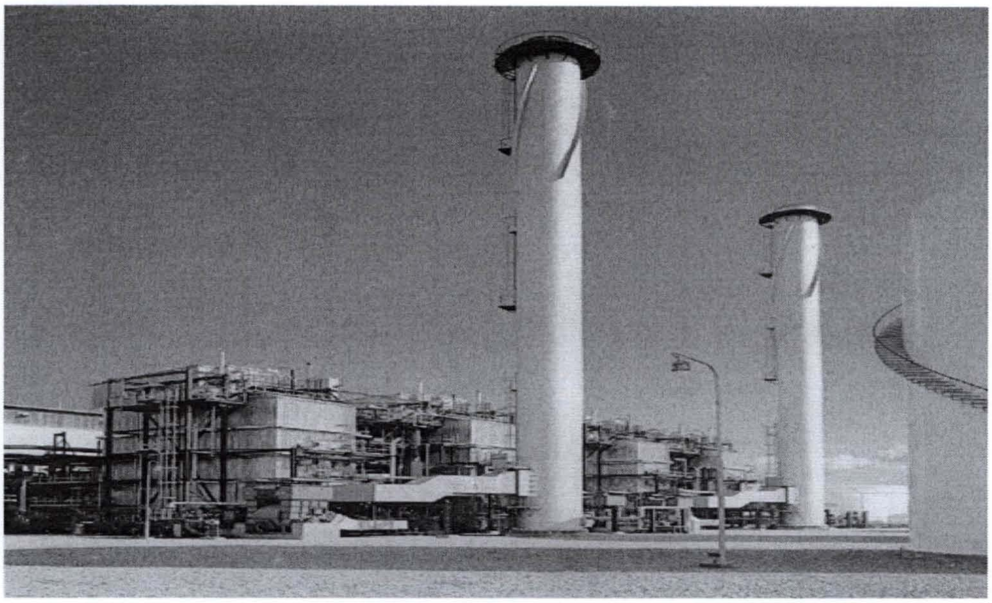


Plate iv: KRPC Power Plant. (Source: KRPC catalogue)

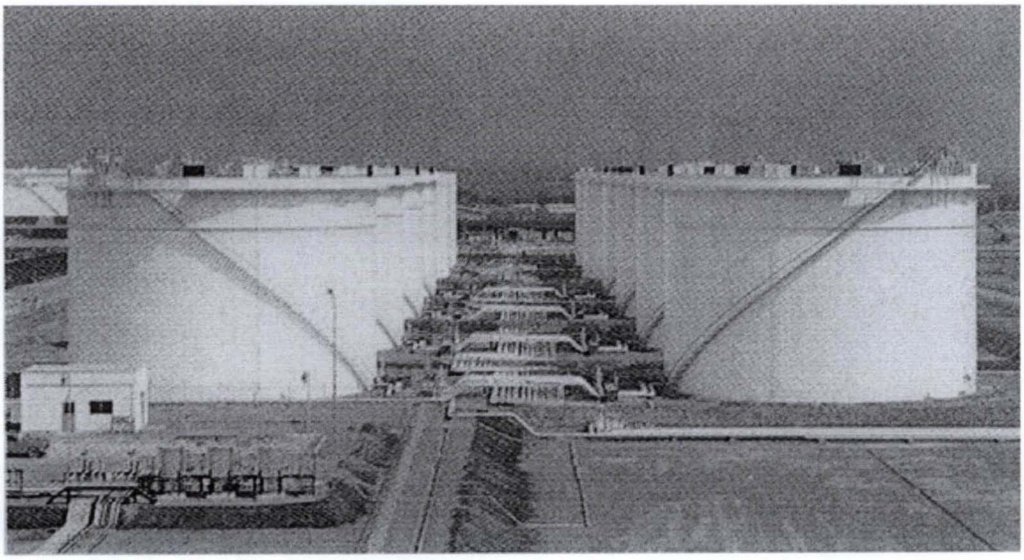


Plate v: KRPC Product Storage Tank. (Source: KRPC catalogue)

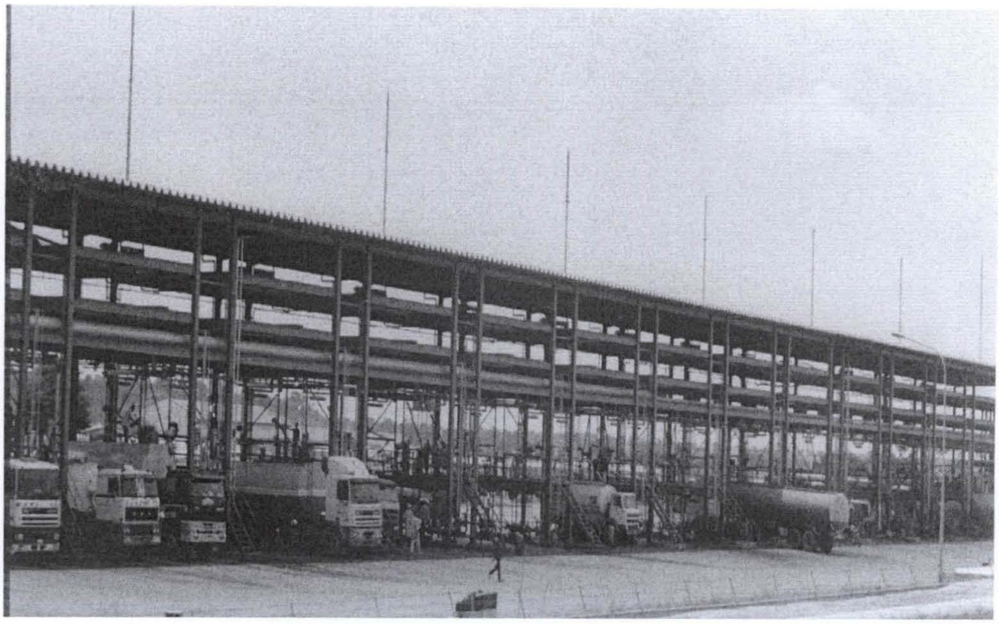


Plate vi: KRPC Truck loading station. (Source: KRPC catalogue)

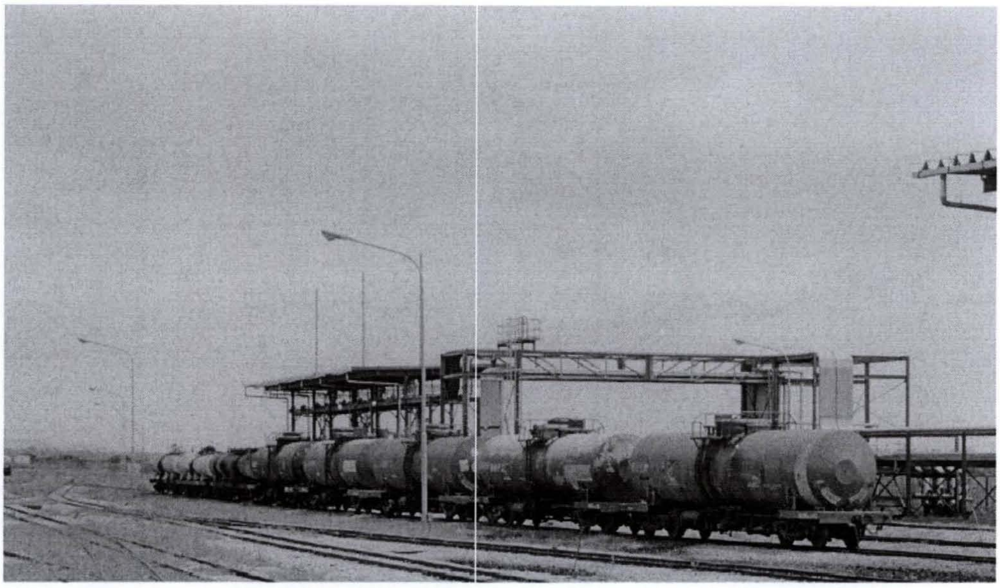


Plate vii: KRPC Rail loading station. (Source: KRPC catalogue)

2.2.2 Crude Distillation Unit. CDU-1 (Fuels)

CDU -1 feeds the fuels train of the refinery. It was designed to process 50,000 B/D of Nigerian crude (a 50/50 blend of Escravos and Forcados) and later revamped to 60,000 by adding a preflash column and a second heater. The unit is designed to late 1970s standard, which make it an energy efficient design.

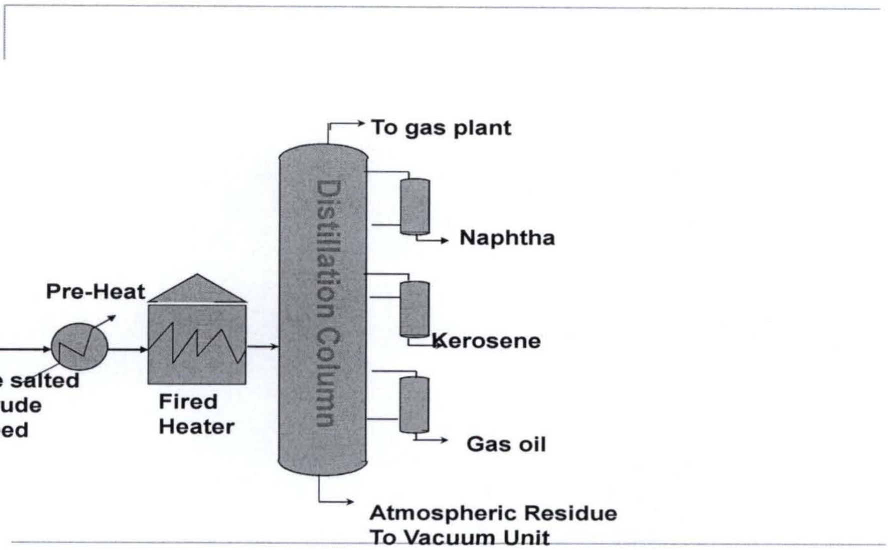


Fig.2.1 Basic Crude Distillation Unit (www.krpc.org)

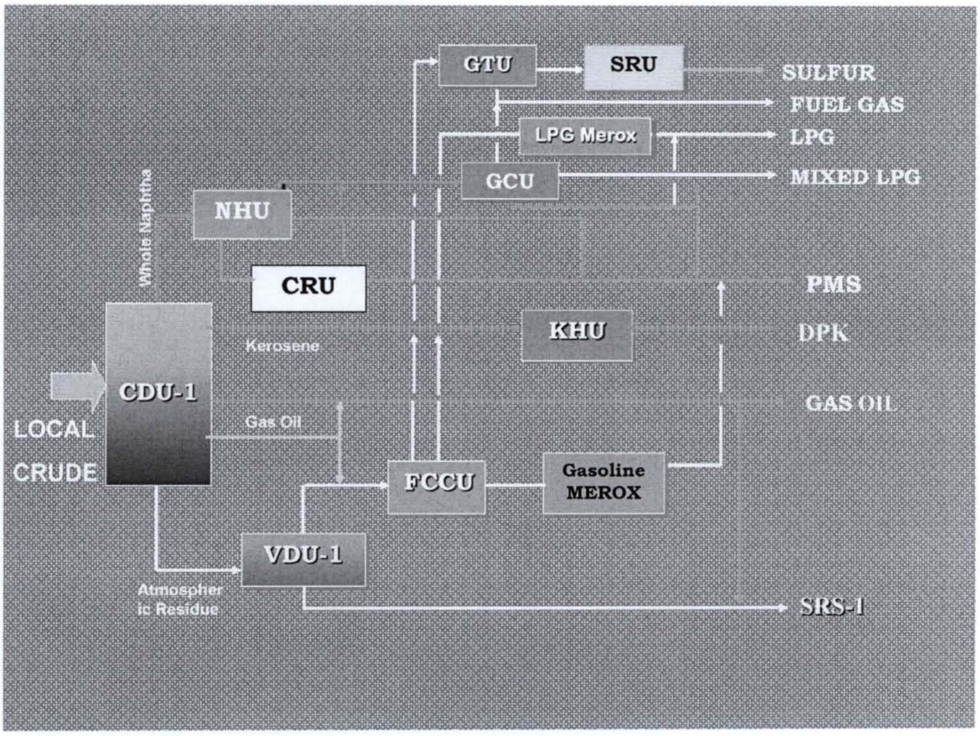


Fig. 2.2 Schematic Flow Diagram of Fuel Plant. (Egbe, 2008)

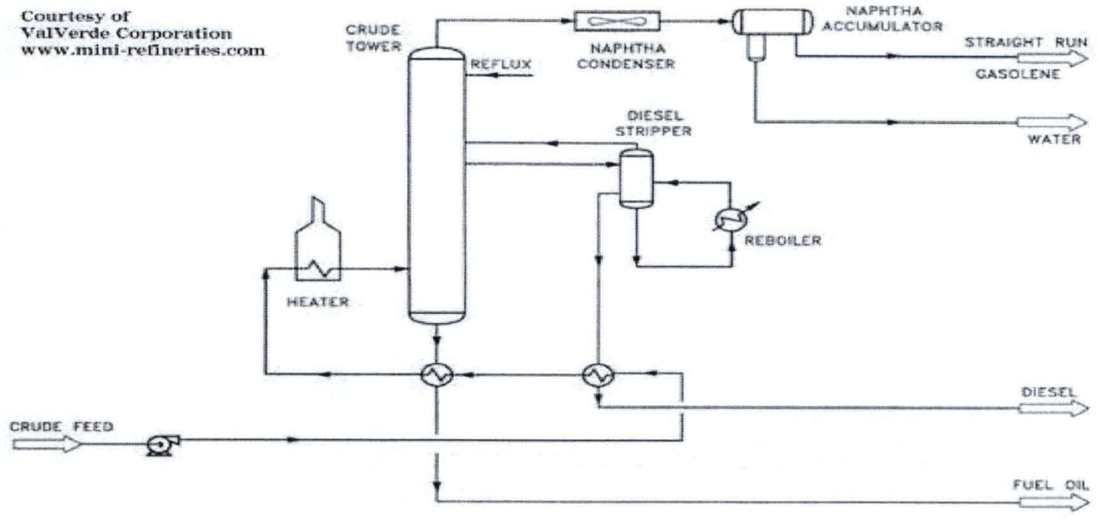


Fig.2.3 Flow Diagram of Crude Distillation Process in Refinery.

(www.mini-refineries.com)

2.2.3 Crude Distillation Unit. CDU-2 (Lubes)

CDU – 2 feeds the lube. CDU-2 is currently not functioning because the utilities performance is not up to par and cannot support the running of the unit.

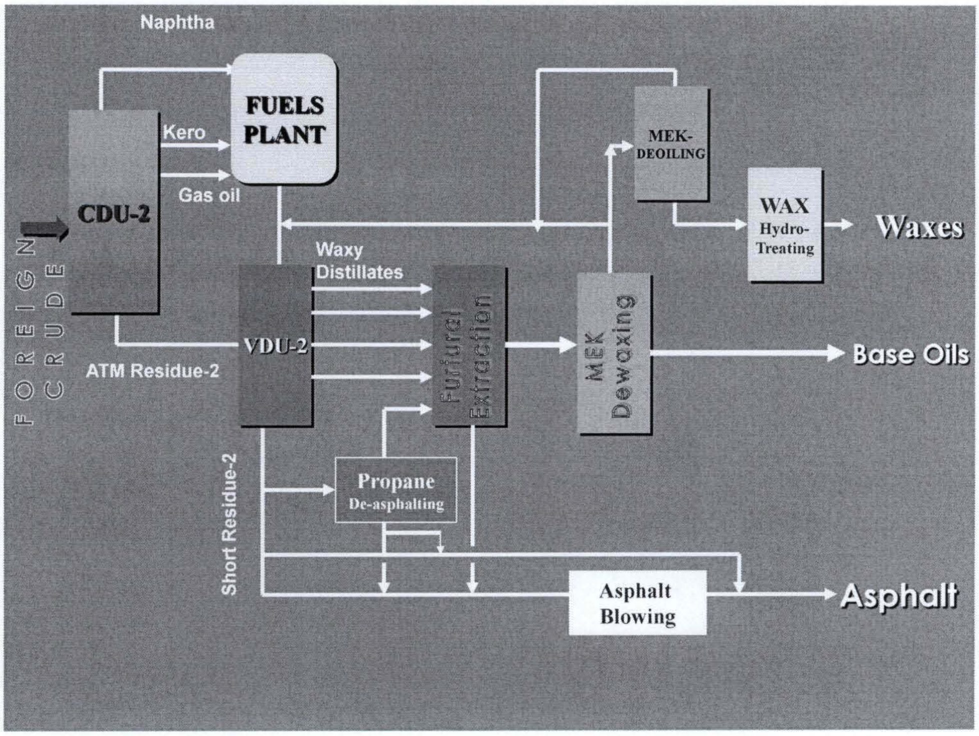


Fig.2.4 Schematic Flow Diagram of a Lube Plant. (Egbe, 2008)

2.2.4 KRPC Petrochemicals Unit

This unit consists of a production complex with a target of 91 tons per day of Linear Alkyl Benzen (LAB), which is the major feedstock for the production of detergents. It was commissioned in 1988 and uses UOP process technologies.

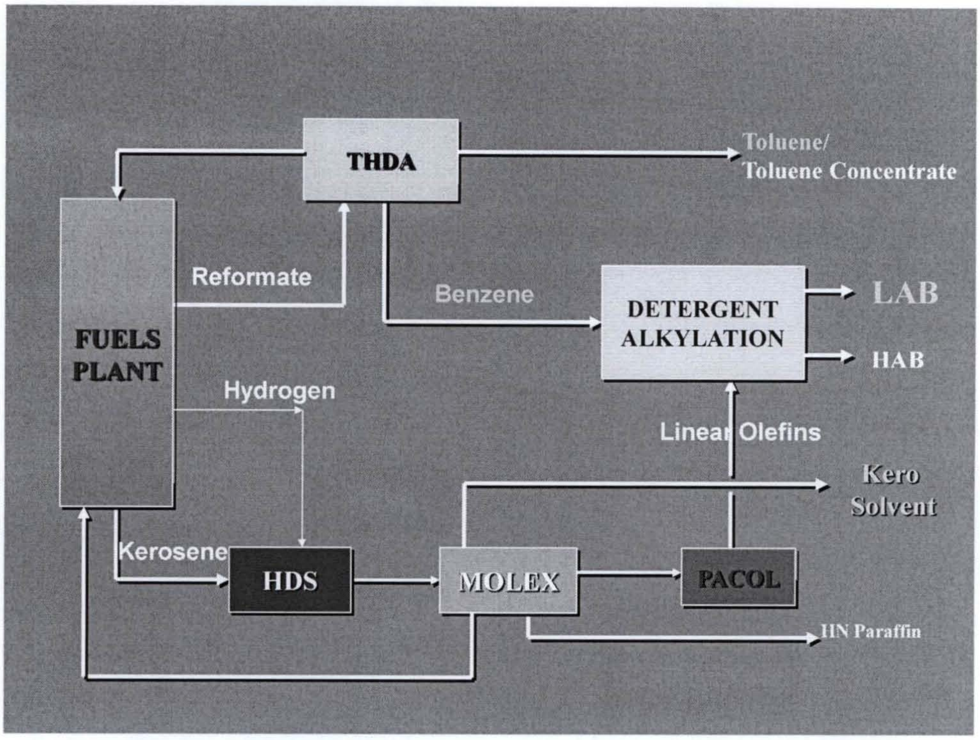


Fig. 2.5 Schematic Flow Diagram of LAB Plant. (Source: Egbe, 2008)

2.3 KRPC Operations

- KRPC receives Nigerian crude oil through pipelines, performs dewatering, takes inventory of the received crude in the storage tanks, process as the dewatered crude oil into quality petroleum products and transfers the finished products (such as PMS, AGO, KEROSENE, etc) to storage tanks.
- KRPC produces petrochemicals and Lubes products (such as LAB, kerosene solvent, wax, Bitumen, etc.) through the processing of foreign crude and stores them in tanks.

- KRPC produces utilities (such as water, steam, electricity, air) through their power plant. Water is stored in tanks.
- KRPC manufactures quality packages (such as Tins and Drums) using flat plates.

2.4 KRPC Performance

Performance refers to what is accomplished contrasted with capability. For quite some time now KRPC performance has been low due to either lack of crude supply or shut downs to enable repair/replacement works. Some of these works are as a result of damages caused by corrosion. The nitrogen plant which produces nitrogen used for corrosion prevention is shut down. Corrosion monitoring systems are absent particularly in the storage tanks.

2.5 KRPC Facilities

The facilities available in KRPC are:

- Three Process Plants
- Tin and Drum Plants
- Power Plant and Utilities
- Crude Oil and Products Handling Facilities
- Fire and Safety Management system.

The main refining units and their capacities are shown below;

PROCESS	UNIT	CAPACITY
Crude Distillation, fuel	CDU-1	60,000 B/D
Vacuum Distillation, Fuels	VDU-1	15,200 B/D
Fluid Catalytic Cracking	FCCU	21,000 B/D
Naptha Hydrotreating	NHU	24,000 B/D

Kerosene Hydrotreating	KHT	17,500 B/D
Catalytic Reforming	CRU	17,500 B/D
Sulphur Recovery	SRU	10 Tonnes/day
Crude Distillation, Lubes	CDU-2	50,000 B/D
Vacuum Distillation, Fuels	VDU-2	23,000 B/D
Propane Deasphalting	PDU	7,860 B/D
Furfural Extraction	FEU	12,450 B/D
MEK Dewaxing	MDU	5,300 – 9,400 (depending on what base oil is being produced)
WAX Deoiling	WHU	75 Tonnes/day
Asphalt Blowing	ABU	6,000 B/D
Linear Alkyl Benzene	LAB	91 Tonnes/day

2.6 KRPC Products

The refinery produces various yields of crude oil by-products as follows

LPG, Gasoline, Jet/Kerosene, Gas-oil/Diesel, Fuel oil

Asphalt Lubricants, Waxes, LAB/Petrochemicals.

The products available currently in KRPC are

PROCESS	UNIT
LPG	540,000 Liters/Day
PMS	5,075,000 Liters/Day
DPK	2,056,000 Liters/Day
AGO	3,529,000 Liters/Day
FUELOIL	2,116,000 Liters/Day
SULPHUR	10 MT/Day

(**www.krpc.org**):

2.7 Materials for Construction of Pipelines and Water Cooling System in KRPC

Pipeline composition: The components present in the pipeline of Cooling Tower Unit of KRPC are: Iron (Fe); Copper; Boron; Sulphur; Managanese; Lead. The percentage compositions of the components are not known as they are patented by the manufacturer. The coupon used for conducting the experiment is produced from mild steel by KURITA (**www.krpc.org**):

2.8 KRPC Safety Management System

- Safety Section handles the monitoring and management of work systems
- Environment Section for the control and management of effluents and emissions
- Fire Section operates installed fire fighting facilities

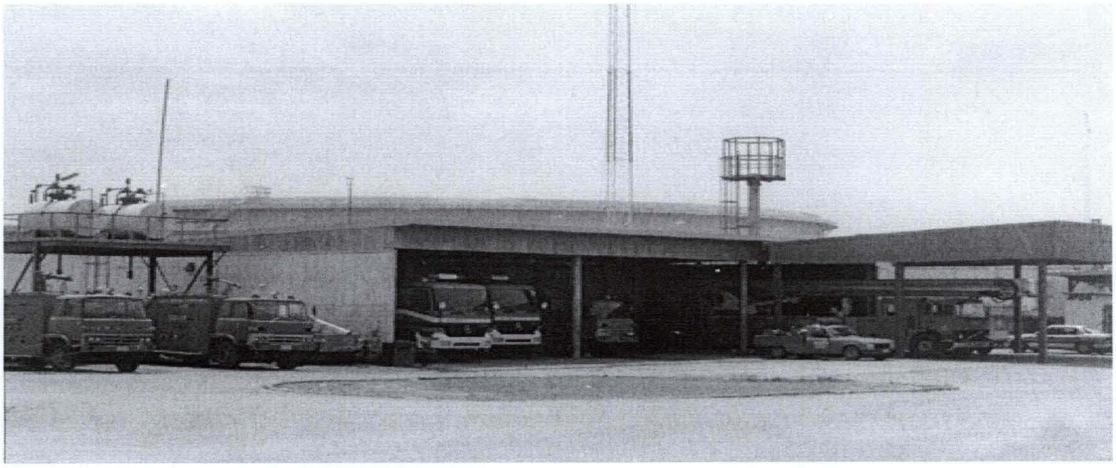


Plate viii: KRPC Fire Station No.1 (Source: KRPC catalogue)

Most offshore processing equipment (vessels and pipeworks) are fabricated from carbon-manganese steel. This is an economic choice, based on lifecycle costing at the design stage of a project. Use of carbon-manganese steels means potential hazards is present due to internal corrosion damage from aqueous produced fluids that contain acidic gasses, carbon dioxide and hydrogen sulphide. The iron corrosion product films are only partially protective and are particularly susceptible to localized erosion corrosion under highly turbulent conditions. (O.T.R, 2001; www.hsebooks.co.uk)

All offshore equipment and systems that contain sea water and injection water systems are at risk from corrosion. These include the internals of offshore firewater equipment, cooling water return pipelines and cooling water tower. The corrosive action of marine spray and the effect of wash down during periodic checks of deluge systems can result in damage to the outside of plant (under lagging / insulation corrosion). Corrosion related failures can result in hydrocarbon releases and significant loss of production, as well as increased costs for maintenance, repair or replacement. Management of corrosion is therefore a major driver for safety, environmental and economic issues within the industry. (O.T.R, 2001; www.hsebooks.co.uk)

In the refinery, unscheduled shutdowns can result in loss of production time that can never be made up. In today's complete market, avoiding unscheduled shutdowns and protecting workers from serious injuries or loss of life as a result of catastrophic equipment failure or fire explosions are always critical. Also the metal loss from the inside of vessels usually contaminates the product thereby rendering them non-saleable (Egbe, 2008)

Corrosion of production plant systems cannot be avoided but the rate could be lowered. Its concentration at a point could be reduced as well. Most of the corrosion problems in production plant systems are associated with the presence of liquid water. However, the corrosiveness of water is dictated by what is dissolved in it. The "wet" corrosion of equipment can occur due to exposure to produced fluids. It can also occur due to external factors such as exposure to atmosphere, the sea and /or soil. The main corrosion agents in pipelines are Carbon dioxide (CO_2), Hydrogen sulphide (H_2S) and Oxygen (O_2). To begin the discussion of corrosion development mechanism, it must first be recognized that corrosion begins the moment an ingot of a metal is made from an ore. It continues until the metals rust/decompose into the oxide or salt that nature intended it to be. (Egbe, 2008)

The most common material for construction of equipment used in pipeline production is carbon steel. Steel is relatively cheap and often suitable in terms of strength, ductility, and weld-ability. However, it can corrode quite easily. In many cases, the speed with which corrosion occurs can be expressed as a corrosion rate. The corrosion rate of any construction material may be dependent on the design life foreseen in relation to the corrosion allowance applied. Internal corrosion and the integrity of installation is typically monitored by recognized inspection procedures (for example, ultrasonic testing, coupon testing etc). In many pipelines and processing systems the rate of corrosion is controlled by injection of inhibitor chemicals. External surfaces and the internals of vessels are usually protected by corrosion control coatings whilst the water wet internals of some vessels will also have cathodic protection systems installed. (www.krpc.org)

Monitoring of corrosion refers to the observation and checking of equipment for corrosive spots with the aim of early detection of possible hazards, and protection against loss of life, injury, production and property. It also assesses the effectiveness of corrosion control measures via accurate judgments of corrosion rates. (Abdullahi, 2001)

Corrosion monitoring is an essential part of a well-planned corrosion control program in the refinery. A high corrosion rate over a period of time can give useful information about the technical condition of the plant and consequently instigates possible corrosion control measures to be adopted. (Odigure, 2002)

The presence of carbon dioxide (CO_2), hydrogen sulphide (H_2S) and free water can cause severe corrosion problems in oil and gas pipelines. Internal corrosion in wells and pipelines is influenced by temperature, CO_2, and H_2S contents, water chemistry, and flow velocity, oil or water wetting and composition and surface condition of the steel. A small change in one of these parameters can change the corrosion rate drastically due to changes in the properties of the thin layer of corrosion products that accumulates on `the steel surface. (Nyborg, 2003).

One significant factor in the degradation of pipelines used for oil and gas production is internal pitting corrosion. The penetration of the pipe wall by pits is a process that consists of three stages: (i) formation of a passive layer of the steel; (ii) initiation of pits at localized regions on the steel surface where film breakdown occurs; and (iii) pit propagation and eventual penetration of the pipe wall. Pipelines carrying oil and gas may suffer from internal corrosion if there is water present. The corrosivity will vary depending on many factors such as the temperature, total pressure, carbon-dioxide (CO_2), and hydrogen sulphide (H_2S) content in the gas, pH of the water, flow conditions, use of inhibiting chemicals etc. The wall thickness of the pipe is normally selected from design considerations, in which one assumes a certain design pressure and corrosion allowance. The corrosion allowance is based on assumptions of the corrosivity during the production period, in order to maintain integrity; many pipelines are subject to intelligent pig inspection at certain time intervals. Corrosion monitoring at fixed locations is sometimes used to verify the inhibiting chemicals. (Garland and Johnsen, 2003)

For many pipelines, considerable cost savings can be obtained if the intelligent pig inspection planning is based on Risk Based Inspection (RBI) principle. This implies that a risk assessment is carried out for the actual pipeline, and that the time to next pig inspection is determined from the risk assessment. A RBI procedure for pipelines requires a means to assess the corrosivity and the corresponding risk of corrosion related failures. The corrosivity can be accessed from previous inspections from monitoring or from corrosion models based on the process data. (Gartland, 2003)

This paper considers application of mathematical modeling to corrosion problems to assess the safety of KRPC plant in general. It uses the mathematical modeling techniques to forecast the life expectancy of industrial equipment in the refinery, petroleum reservoirs and gas pipelines distribution.

Mathematical modeling is richly endowed with many analytic computational techniques for analyzing real life situations. Recent reports have confirmed that several billion dollars were lost to corrosion, in addition to environmental pollution and economic wastage in cleaning up the environmental mess caused by corrosion. Mathematical modeling is as old as mathematics and has extended its tentacles to unforeseeable directions. Mathematical modeling can best be described as a sandwich between mathematical theory and applied mathematics. It is an encyclopedia of theories and techniques as applicable to real life situations. (Oyelami and Asere, 2008)

Corrosion in the modern society is one of the outstanding challenging problems in the industry. Most industrial design can never be made without taking into consideration the effect of corrosion on the life span of the equipment. Recent industrial catastrophes have it that many industries have lost several billion of dollars as a result of corrosion. Reports around the world have confirmed that some oil companies had their pipeline ruptured due to corrosion, oil spillages are experienced which no doubt created environmental pollution, in addition, resources are lost in cleaning up this environmental mess and finally large scale ecological damage resulted from corrosion effects. (Oyelami and Asere, 1994)

The possibility of occurrence of corrosion in an industrial plant has been posing a lot of concern to Petroleum, Chemical, Mechanical Engineers and Chemists. It is now known that corrosion can have some effects on the chemistry of a chosen process, and product of corrosion can affect reaction and purity of the reaction products. Furthermore, it is also true that a lot of profit can run out of a hole in any industrial plant if care is not taken, but early advice from corrosion experts can prevent that from happening. The study of corrosion is multi-disciplinary in nature. Its calculation involves knowledge of viscosity, specific heat capacity, thermal conductivity and density of the fluid concerned, in some cases; a thorough study of the property of the material from which the plant is fabricated is highly required. (Oyelami and Asere, 1994)

Before we embark on the formulation of mathematical models, it is pertinent to make a detailed exposition of mathematical modeling and corrosion itself.

2.9 Mathematical Modeling and its Usefulness

Mathematical modeling is the act of relating abstract ideas of mathematics to real life problems. The process involves expressing a real life situation in mathematical terms, manipulating the mathematics and translating the mathematical results back into the real life. It is an undisputable fact that every human activity involves one mathematical problem or the other; the need to use mathematical modeling is increasingly realised in modern times. It gives us insight into many real life processes and the interplay between or among variable(s) quantifying such models. This process saves cost and labour that would unnecessarily have been expended. (Oyelami and Asere, 2008)

Mathematical modeling offers several powerful intuition appealing tools for studying and analyzing the chemical kinetics and the thermo chemistry of compounds (e.g. in petroleum crude and products). Mathematical modeling also offers quantitative and qualitative techniques for investigating the material science of the industrial plant for producing, storing and transporting the petroleum products. Different researchers have expressed various steps taken to model a problem. The most outstanding one is summarized by Ale, 1981; 1986, described the process involved in a modeling a process as follows:

"The identification of the real life problem, which involves modifying and simplifying the original problem into a reasonable precise and succinct manner".

To have a full grasp of the idea of modeling, the following flow chart, states the steps to be taken when modeling a problem.

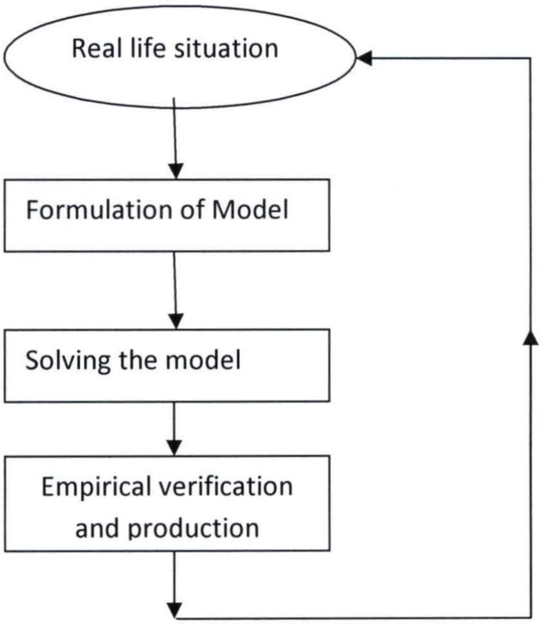


Fig.2.6 Idealization of real life problem into a model

In real life, there is the problem whose solution is sought. This problem need to be identified, in which case, the significant features are identified and translated into mathematical entities, leading to the mathematical model. Once a model is constructed, it needs validation, that is:

- The mathematical structure it represents is self- consistent (i.e., it contains no contradictory statements) and obeys all usual mathematical laws underlying it;
- It represents the situation it is actually designed for. Various branches of mathematics have been created in an attempt to solve some problems or the other. One may want to predict the weather, estimate the loss caused by corrosion and so on. If one needs to analyze a problem, it is often a good idea to start by building up a model. (Oyelami and Asere, 2008)

2.9.1 Process Modeling and Simulation

A model is a simplified representation of a system intended to enhance our ability to understand, explain change, preserve, predict and possibly control the behavior of a system. Modeling is thus the process of establishing inter-relationship between important entities of a system (Abdulkareem, 2000).

Process modeling has proven to be an extremely successful engineering tool for the design and optimization of physical, chemical and biological processes. It provides an avenue of understanding qualitative and quantitative aspects of the phenomenon of interest. Mathematical modeling is versatile and is widely used in practice, and is a recognized and valuable adjunct, and usually a precursor of computer simulation.

2.9.2 Importance of Mathematical Modeling

- To improve the understanding of the process: Process model can be analyzed or used in a computer simulation of the process to investigate process behavior without the expense and perhaps, without the unexpected hazard of operating the real process. This approach is necessary when it is not feasible to perform dynamic experiment in the plant or before the plant is actually constructed.

- To train plant-operating personnel: Plant operator can be trained to operate a complex process and to deal with emergency situation by use of a process simulator. With the help of a model, a realistic environment can be created for operator training without the cost or exposure to dangerous conditions that might exist in a real plant situation.
- To design the control strategy for a new process: A process model allow alternative control strategies to be evaluated such as the selection of the variables that are to be measured, controlled and those that are to be manipulated.
- To optimize process operating conditions: In most processing plants, there is an incentive to adjust operating conditions periodically so that the plant maximizes profits and minimizes costs. A steady state model of the process and appropriate economic information can be used to determine the most profitable process conditions as in supervising control. (Abdulkareem, 2000).

2.9.3 Types of model

Models can be classified depending on how they are derived

- Critical models: These are developed using the principle of chemistry and physics.
- Empirical models: The output is related mathematically to the input and a mathematical relationship is established between the two.
- Semi-empirical models: These are developed from a compromise between (i) and (ii) with one or more parameters to be evaluated from plant data.

The processes involved in the working of the model are mathematically expressed and these expressions are linked together to form the complete model. This is also called working model. (www.wikipedia.org).

Model can also be classified as follows (www.wikipedia.org).

- Linear model and non-linear model: In linear Model, the objective function and constraints are in linear form while in a non-linear model, part or all of the constraints and/or the objective function are non-linear.
- Deterministic model: In this type, each variable and parameter is assigned a definite fixed number or a series of fixed numbers for any set of conditions.
- Probabilistic (stochastic) model: The variables and parameters and the structure of the model may be more difficult to define.
- Static model and dynamic model: Static Model do not explicitly take the variable time into account while dynamic models do.
- Lumped parameter and distributed parameter model: In lumped parameter model, the various parameters and dependent variables are homogeneous throughout the system. A distributed parameter model takes account of variations in behavior from point to point throughout the system.

Mathematical models can be very complex or very simple. The simple, short model gives only elementary answers and of limited value. It can usually be written and made to work in a short period of time. Complex model includes many variables, but as the degree of complexity increases, so does the amount of information which has to be available in order to get the model to give appropriate answers. A balance must be found between the time and the complexity of the answer desired. In the process of model building, system analysis must initially be undertaken. A lot of decisions must be made which are crucial for further development. These include finding solution to the followings: (Abdulkareem, 2000)

- Model aims must be stated clearly and unambiguously as possible.
- Various kinds of constraints and omissions must be taken into account.
- General assumptions and omission must be carefully argued.
- The possibilities of measurement and experimentation on the system being studied must be investigated.
- A solution strategy must be chosen. This may include methods of collection and analysis of data, estimation of parameter, type of model, available computational facilities and flexibility of simulation tools, generality of solution, possibilities of model extension etc.

The purpose of studying systems through the modeling and simulation approach is to achieve different goals without actually constructing or operating real processes. These goals include the followings:

- To improve understanding of some mechanisms in the studied process
- To predict system behaviors in different situation where any level of predictive ability represents a benefit.
- To enable the design and evaluation of synthesized control system.
- To estimate the process variables which are not directly measurable
- To test the sensitivity of system parameters.
- To optimize system behavior and efficient fault diagnosis
- To verify models obtained in some other ways.

(Abdulkareem, 2000).

2.9.4 Modeling techniques

The principal Modeling techniques have been classified by Meta system as follows:

- Analytical optimization techniques: These include the methods that use the classical calculus and LaGrange multiplier as well as the mathematical programming techniques; linear, non-linear, and dynamic.
- Probabilistic techniques: These are used to describe stochastic system elements by means of appropriate statistical parameters. Techniques of queuing and inventory theory are examples of this type.
- Statistical technique: This technique includes such methods as multi-variable analysis, statistical inference and decision theory.
- Simulation and search or sampling techniques: These are widely used in water resources planning. Simulation is a descriptive technique that incorporates the quantifiable relationships among variables and describes the outcome of operating a system under a given set of input and operating conditions. If an objective function is defined, the values of the objective for several runs generate a "response surface". The model then becomes prescriptive by combining it with sampling or search techniques that explore the response surface and seek near-optimal or optimal solutions. (www.wikipedia.org).

2.9.5 Simulation

This is a means of gaining relevant information on the characteristics of full-size prototypes without incurring the expense of building a full-size prototype to test. (www.wikipedia.org).

Occasionally, plants are built which fail to produce the required product or fail to produce sufficient quality or quantity. Simulation is used to avoid such costly mistakes. In simulation, many alterations and changes in processes can be made and the output of the plant checked, all before the design is finalized.

In mathematical modeling, simulation consists of a series of sub-programming modules, each of which attempts to recreate a segment of the prototype. In considering any simulation, it is necessary to know what is required. The problem must be defined in order that an acceptable solution may be found. Part of that definition must be the extent of the problem, and this usually defines a system or collection of subunits. One unit such as an activated sludge tank can be simulated, but one of the purposes of simulation is to optimize and ultimately control the process. It is possible to take an isolated unit such as an activated sludge and optimize its design to the exclusion of all other units.

Process simulation is now an accepted tool for understanding chemical processes and in addition, some of the simulation programs are useful tools in design and process synthesis. A computer simulation can be used to predict the effect of changing conditions and capacity in mass and energy balance and to optimize operation easily and quickly. It can be used to provide in-depth knowledge about complete system behavior, improve and facilitate cost calculation and planning of operations.

2.10 Corrosion.

Corrosion is defined as: A destructive attack (Chemical Breakdown) on a material by its environment. This definition includes the partial or complete wearing away, dissolving, or softening of any substance by chemical or electrochemical reaction with its environment. (Odigure, 2002). We normally think of metals when we think of corrosion, but a good definition is one which deals more broadly with materials in general to include any material such as metal, wood, plastics, etc. Admittedly, the most familiar example of corrosion occurs with rusting of iron. It is a complex chemical reaction in which the iron combines with both oxygen and water to form an oxide. As a matter of practical concern, the corrosion of metals is more problematic than that of other materials.

2.10.1 Reason for Study Corrosion

Many petrochemical plants are large-scale equipments and could be corroded after some time. Mathematical models to determine the amount of contamination arising from corrosion will have to investigate the deleterious effect of corrosion on the process and on the product quality.

The classic example of intergranular corrosion in chemical plant is the weld delay of unstabilized stainless steel. This is caused by the precipitation of chromium carbides at the grain boundaries in a zone adjacent to the weld, where the temperature has been between 500^0C - 800^0C during welding. Corrosion rate and the form of attack can change if the material is under stress. For some combination of metal, corrosive media and temperature, the phenomenon called stress cracking can occur. This leads to premature brittle failure of the metal that constitutes the petrol chemical plant. The conditions that cause corrosion can arise in a variety of ways. For the brief discussion on the selection of material, it is convenient to classify corrosion into different categories. (Oyelami and Asere, 2008)

2.10.2 Common Forms of Corrosion

The general types of Corrosion include uniform, electrochemical, galvanic, concentration cell, erosion, embrittlement, stress corrosion, filaform, corrosion fatigue, intergranular, fretting, impingement, dezincification, and chemical reaction. For convenience we will categorize the various kinds of corrosions into eight different forms. In any event we could have some subcategories if needed. (www.corrosionsource.com).

Those eight forms are:

i. Galvanic corrosion - dissimilar metals in contact;
ii. Pitting - localized attack;
iii. Crevice corrosion
iv. Stress corrosion Cracking / Leasing
v. Intergranular corrosion;
vi. Uniform corrosion- General wastage of material;
vii. Corrosion fatigue;
viii. Erosion corrosion;

Metallic corrosion is essentially an electrochemical process. Fair components are necessary to set - up an electrochemical cell:

- Anode - the corroding electrode;
- A cathode - the positive, non - corroding electrode;
- The conducting medium - the electrolyte - the corroding fluid;
- Completion of the electrical circuit - through the material.

Cathode areas can arise in many ways: (Oyelami and Asere, 1994)

- Dissimilar metals;
- Corrosion products;
- Inclusions in the metal, such as slag;

- Less aerated areas;
- Areas of differential concentration;
- Differential strained areas.

2.10.2.1 Galvanic corrosion

Galvanic corrosion can result when a metal is in contact with another *dissimilar* metal. Galvanic corrosion is an electrochemical process in which one metal corrodes preferentially when in electrical contact with a different type of metal and both metals are immersed in an electrolyte. A common example of galvanic corrosion is the rusting of corrugated iron sheet, which becomes widespread when the protective zinc coating is broken and the underlying steel is attacked. The zinc is attacked preferentially because it is less noble, but when consumed, rusting will occur in earnest. With a tin can, the opposite is true because the tin is more noble than the underlying steel, so when the coating is broken, the steel is attacked preferentially. Another common example is the carbon-zinc cell where the zinc corrodes preferentially to produce a current. When two or more different sorts of metals come into contact in the presence of an electrolyte a galvanic couple is set up as different metals have different electrode potentials. In order for galvanic attack to take place, there must be four things present. (a) *Anode*, this is the material which corrodes (e.g., the formation of rust takes place if the metal is iron). (b) *Cathode*. (c) An *electrical connection* must exist between the *anode* and *cathode* through which electrons can flow. (d) An *electrolyte* through which chemical ions can flow. This is generally an aqueous (water) solution yet even damp soil can make an excellent electrical conductor. The arrangement of these four specific components is always necessary for an electrochemical chemical cell to function. However in the case of galvanic corrosion, the anode and cathode are clearly dissimilar metals, copper and zinc, iron and brass, or mild steel and cast iron. (www.nowccs.com).

The electrolyte provides a means for ion migration whereby metallic ions can move from the anode to the cathode. This leads to the anodic metal corroding more quickly than it otherwise would; the corrosion of the cathodic metal is retarded even to the point of stopping. A typical illustration of galvanic corrosion is shown below.

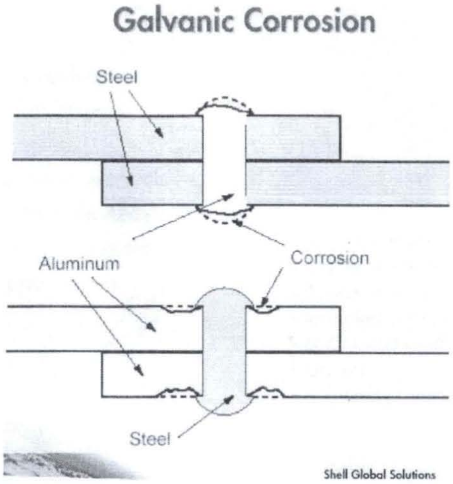


Fig. 2.7 Galvanic corrosion. (source: Shell Global solution, 2000)

2.10.2.2 Pitting Corrosion

Some materials are more subject to *pitting* than others. Imagine that we find a stainless steel spoon lying on the beach near the ocean where it has been for several days. It has corroded. Little pits have formed. *Pitting corrosion* is a form of corrosion that most of us see on almost a daily basis. This corrosion cell, i.e., the electrochemical mechanism of the corrosion, is very similar to that of crevice corrosion. There is a stagnant solution at the bottom of the pit, i.e., a lower oxygen concentration is outside of the pit than inside, resulting in another *oxygen concentration* cell. Corrosion takes place at the bottom of the pit as the pit gets deeper; the solution at the bottom of the pit becomes more stagnant creating more driving force to promote corrosion. A pit is said to be *self-catalyzing*. (www.nowccs.com). A typical pitting corrosion is illustrated in the figure below.

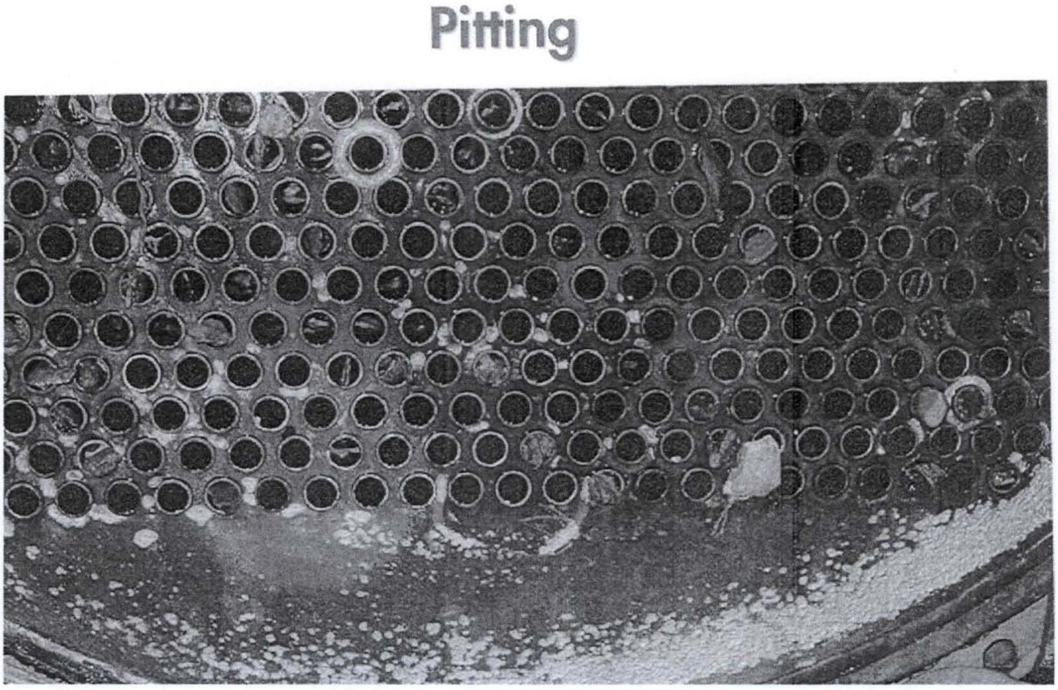


Plate ix: Heat exchanger showing pitting corrosion. (Source: Shell Global Solutions, SGS. The Hague, Netherlands).

Basically, three processes are involved in pitting corrosion. These are:-

- Pitting initiation
- Pitting propagation
- Pitting termination

Pitting Initiation involves formation of anodic sites by distortion of protective passive film and metal surface. The dissolution takes place at the anode and pitting is initiated.

Pitting propagation involves accumulation of passives metal ions due to continuous metal dissolution at the anodic area. This process is self stimulating and self propagating. Conditions are produced within a pit which is necessary for continuing the activity of the pit to maintain charge neutrality; -ve ions (anions) like chloride, migrate from the electrolyte. The increase in the rate of dissolution at the anode increases the rate of migration of the chloride ions and the reaction being time dependent continues, resulting in the formation of more and more M^+Cl^- by hydrolysis. The process continues until the metal is perforated. This process is autocatalytic and it increases with time resulting in more and more metal dissolution. Finally, the metal is perforated and the reaction is terminated. (www.wikipedia.org)

2.10.2.3 Crevice corrosion

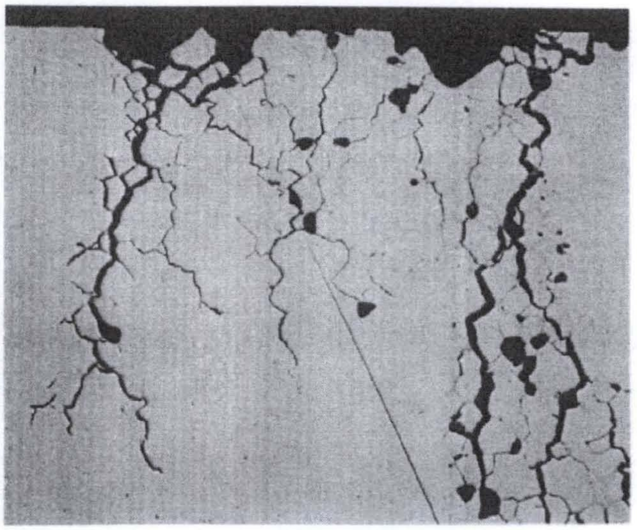
Crevice corrosion is a corrosion occurring in spaces to which the access of the working fluid from the environment is limited. These spaces are generally called crevices. Examples of crevices are gaps and contact areas between parts, under gaskets or seals, inside cracks and seams, spaces filled with deposits and under sludge piles (www.wikipedia.org). Consider a sheet of stainless steel that has been immersed in the ocean for some time, years perhaps. It has had a bolt with a washer on it to hold it in place. We notice that corrosion has taken place underneath the washer. The reason for the corrosion is that a crevice had been created under the washer. Stagnant water, an electrolyte, accumulated in the crevice. An electrochemical, corrosion cell had been produced and corrosion resulted. This cell is called a differential aeration, or oxygen concentration cell. It results because there is a difference in the composition of the electrolyte under the washer and that outside of the washer. One may have associated corrosion with a higher oxygen concentration which is a true general statement. But, remember, in the case of a crevice, or a pit, there are two oxygen concentrations in the electrochemical cell such that corrosion takes place at the lower oxygen concentration. (www.nowccs.com).The photo below is showing an example of crevice corrosion.

Plate x. Crevice Corrosion. (www.corrosion-club.com)

2.10.2.4 Stress corrosion cracking (SCC)

A common form of crevice failure occurs due to stress corrosion cracking, where a crack or cracks develop from the base of the crevice where the stress concentration is greatest. Selective leaching corrosion is corrosion accelerated by the selective leaching of an alloying element out of the alloy matrix. The most common form of this type of corrosion is Dezincification, the selective leaching of zinc out of the brass matrix. Brass is made of zinc and copper. Zinc is more corrosive than is copper. In certain cases, e.g., when brass is exposed to an aggressive environment, the zinc will corrode preferentially and *leaching* zinc from the brass alloy leaving behind a weak network of copper. It may look strong but it has been severely weakened. Example of stress corrosion cracking is illustrated below. (www.nowccs.com)

Stress Corrosion Cracking



Polythionic stress corrosion cracking in
Sensitised Austenitic Stainless Steel

Fig. 2.8 Stress Corrosion Cracking (SCC) (www.wikipedia.org).

2.10.2.5 Intergranular corrosion.

Intergranular corrosion (IGC), also termed intergranular attack (IGA), is a form of corrosion where the boundaries of crystallites of the material are more susceptible to corrosion than their insides. This situation can happen in otherwise corrosion-resistant alloys, when the grain boundaries are depleted of the corrosion-inhibiting compound by some mechanism. Consider a stainless sheet that has been welded to another. Along each side of the weld you see a corrosion attack called *weld decay*. This attack takes place by *intergranular corrosion*. That is, the attack is into the boundaries of the metallic grains that make up the metal. As the metal is heated during the weld, chromium is precipitated out of the heated grains and deposits in the grain boundary, an area that separates the grains and is burdened with impurities. Again, the components of a chemical corrosion cell are the result.

In nickel alloys and austenitic stainless steels, where chromium is added for corrosion resistance, the mechanism involved is formation of chromium carbide at the grain boundaries, forming chromium-depleted zones (this process is called sensitization). Around 12% chromium is minimally required to ensure passivation, mechanism by which a thin invisible layer forms at the surface of stainless steels. (www.wikipedia.org).

Stainless steels can be stabilized against this behavior by addition of titanium, niobium, or tantalum, which form titanium carbide, niobium carbide and tantalum carbide preferentially to chromium carbide, by lowering the content of carbon in the steel and in case of welding also in the filler metal under 0.02%, or by heating the entire part above 1000 °C and quenching it in water, leading to dissolution of the chromium carbide in the grains and then preventing its precipitation. Another possibility is to keep the welded parts thin enough to not hold elevated temperature for time sufficiently long to cause chromium carbide precipitation. Aluminium based alloys may be sensitive to intergranular corrosion if there are layers of materials acting as anodes between the aluminium-rich crystals. Intergranular corrosion is a concern especially for alloys with high content of copper (www.wikipedia.org).

An example of intergranular corrosion is illustrated below.

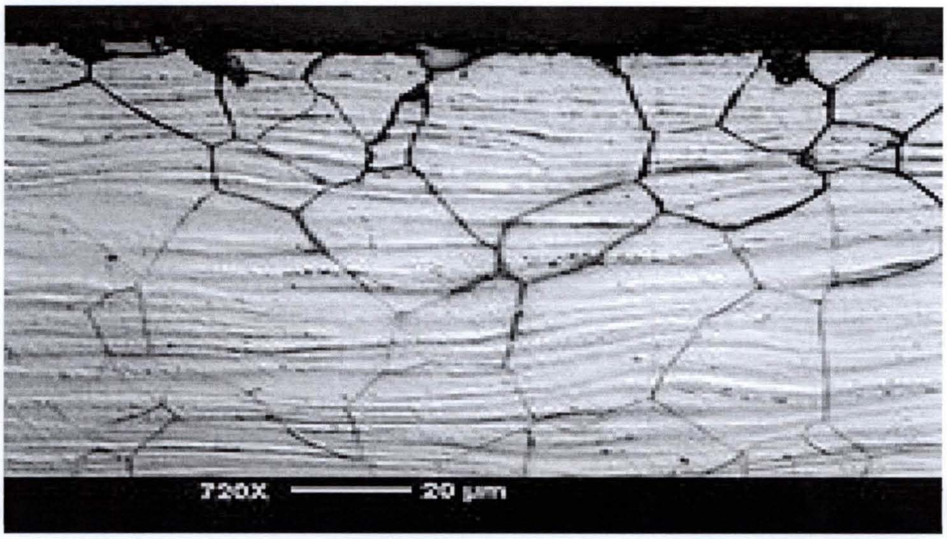


Figure 2.9: Microscope view of a polished cross section of a material attacked by intergranular corrosion (www.wikipedia.org).

2.10.2.6 Uniform Corrosion

Uniform (or general) corrosion refers to the relatively uniform reduction of thickness over the surface of a corroding material. It is relatively easy to measure, predict and design against this type of corrosion damage. While uniform corrosion may represent only a small fraction of industrial corrosion failures, the total tonnage wasted is generally regarded as the highest of all forms. Uniform corrosion is usually controlled by selecting suitable materials, protective coatings, cathodic protection and corrosion inhibitors. It is relatively easy to monitor uniform corrosion; generally the simplest methods suffice (coupons, ER, NDT techniques for thickness measurements). Much data on uniform corrosion has been published that can be used for design purposes and estimating a "corrosion allowance". Corrosion monitoring is therefore advisable. Caution: Unexpected rapid uniform corrosion failures can occur if the material's surface changes from the passive (low corrosion rate) to the active (high corrosion rate) state. The resultant increase in uniform corrosion rate is typically several orders of magnitude. This undesirable transition can occur if the passive surface film is disrupted by mechanical effects, flow rate changes, a chemical change in the environment etc. Real-time corrosion monitoring systems can detect such transitions. (Graver, 1995). A typical example of uniform corrosion is as shown below:

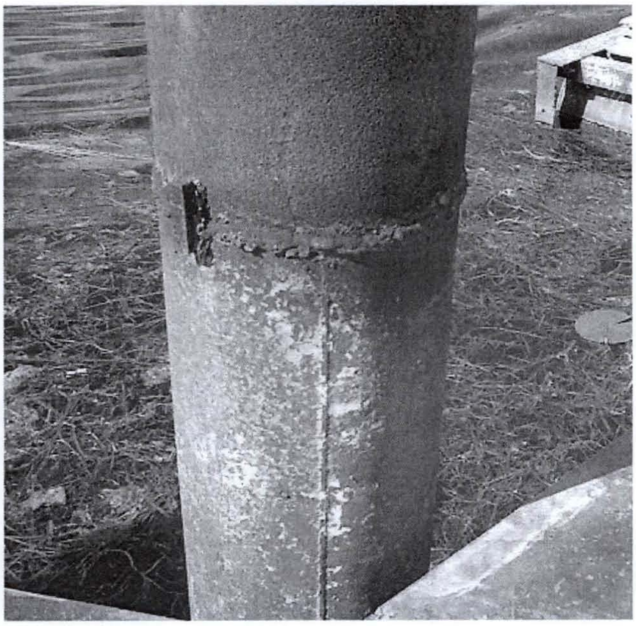
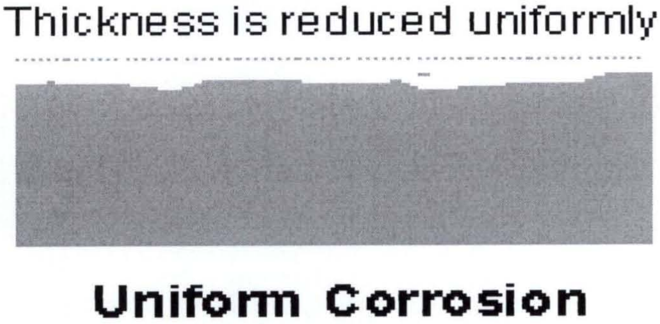


Plate xi. Uniform Corrosion on oil well pipe. (www.corrosion-club.com)



www.corrosion-club.com

Fig. 2.10 Uniform Corrosion

2.10.2.7 Corrosion Fatigue

Corrosion-fatigue is the result of the combined action of an alternating or cycling stresses and a corrosive environment. The fatigue process is thought to cause rupture of the protective passive film, upon which corrosion is accelerated. If the metal is simultaneously exposed to a corrosive environment, the failure can take place at even lower loads and after shorter time. The fatigue fracture is brittle and the cracks are most often transgranular, as in stress-corrosion cracking, but not branched. The picture shown here reveals a primary corrosion-fatigue crack that in part has been widened by a secondary corrosion reaction. The corrosive environment can cause a faster crack growth and/or crack growth at a lower tension level than in dry air. Even relatively mild corrosive atmospheres can reduce the fatigue strength of aluminum structures considerably, down to 75 to 25% of the fatigue strength in dry air. No metal is immune from some reduction of its resistance to cyclic stressing if the metal is in a corrosive environment. webmaster@nace.org

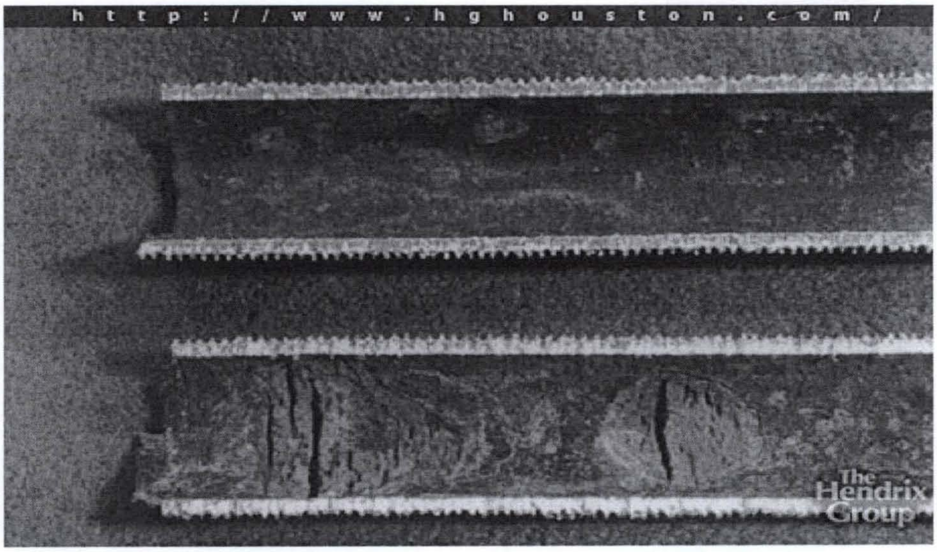


Plate xii. Picture showing corrosion fatigue of oil pipe. (www.corrosionlab.com)

2.10.2.8 Erosion Corrosion

Thinning or removal of surface films by erosion from the flowing stream results in accelerated corrosion, called erosion-corrosion. The attack is accelerated at elbows, tube constrictions, burrs, and other structural features that alter flow direction or velocity, and increase turbulence. Erosion-corrosion takes the form of grooves, waves, gullies, teardrop-shaped pits, and horseshoe-shaped undercutting in the surface. The effects of the hydrodynamic are not well understood. Undercutting may occur in either upstream or the downstream direction. As described in the schematic below, turbulent eddies thin the protective film locally to produce undercutting, which is seen in the accompanying photograph. (web@corrosionlab.com)

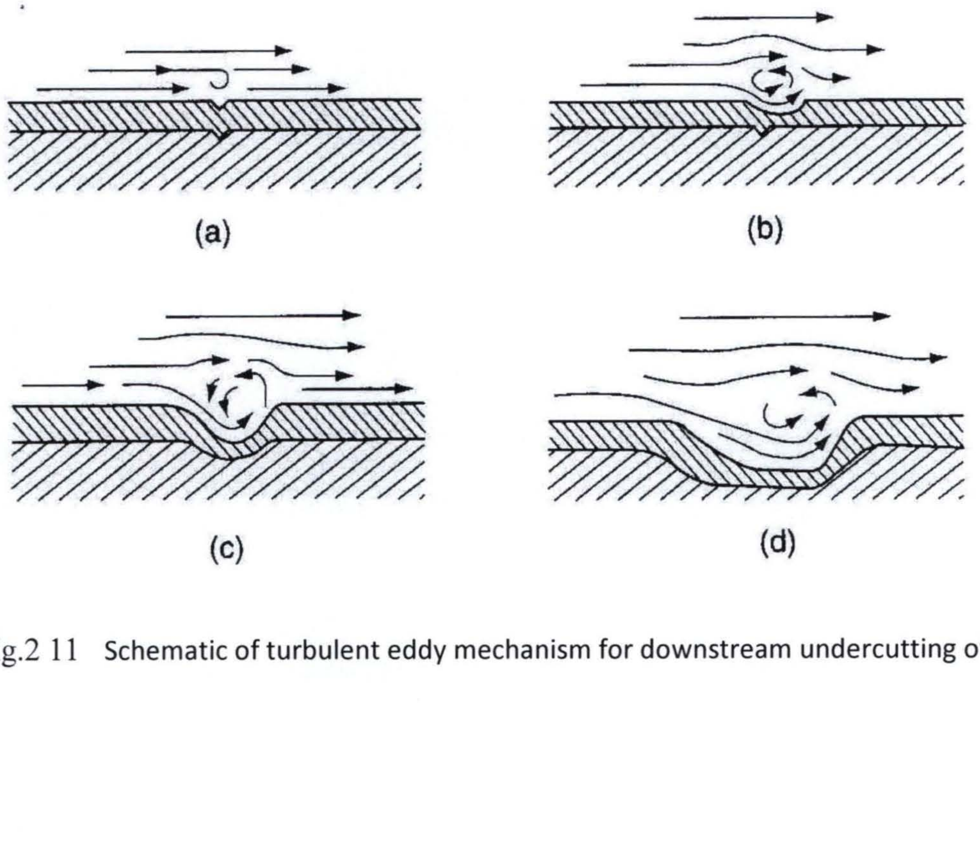


Fig.2 11 Schematic of turbulent eddy mechanism for downstream undercutting of erosion-corrosion pits

2.10.3 Method of Controlling Corrosion

Corrosion control is primarily an economic problem. Whether or not to apply a control method is usually determined by the cost savings involved. The method or methods utilized must be the optimum economic choice. For example, reduction of plant investment means less money must be earned, and lower maintenance or operating costs increases the profit. Hence, proper selection of materials and good design reduces cost of corrosion.(Osadare , 1999)

There are five methods of corrosion prevention or control that are generally used. They are:

- Material Selection,
- Environmental Change,
- Cathodic and Anodic Protection,
- Coatings, and
- Design.

Material Selection: Material selection consists of obtaining a material which will do the job that we want done. But corrosion control is almost always an economic situation. Assume that you have some steel that is corroding. Perhaps you could stop the corrosion if only you were to use some noble metal such as platinum. But platinum is too expensive. It is this type of economic consideration that we have to take into account. We select the material which is best for the job. This includes cost and strength as well as corrosion resistance considerations.

Environmental Change: Sometimes we can change the environment in which the corroding material is enclosed. When we think of environment, we might think of temperature and the possibility that we can control it. We might consider the concentration of solutions and the ions in the solution. Or we might think of our ability to add inhibitors to provide some control over the corrosion. An everyday example of a corrosion inhibitor of which almost everyone is aware is the inhibitor put into automobile-engine cooling radiator.

Cathodic and Anodic Control: Cathodic protection is used extensively worldwide as a corrosion control method. Anodic protection is used to a lesser extent, but nevertheless has some very interesting possibilities with respect to providing corrosion protection. Cathodic protection results when we impress a negative potential onto the material we want to protect. Anodic protection is possible in very specific cases when we impress a positive potential. However this must be done with quite stringent controls.

Coatings: When we think of coatings, many of us think of paints. But in addition to paints there are other types of coating such as metallic coatings, electro-plating, galvanizing, etc. coatings generally have two purposes, one is cosmetic; the other purpose is corrosion protection. The latter purpose is of particular interest to engineers. The corrosion engineer has a wide range of coatings from which to select.

Design: Normally, design is simply a common sense approach such: how to drain tanks, where to locate a plant, and how to install various parts of a plant, etc. Most offshore processing equipment (vessels and pipework) are fabricated from carbon-manganese steel. This is an economic choice, based on lifecycle costing at the design stage of a project. Use of C-Mn steels means potential hazards are present due to internal corrosion damage from aqueous produced fluids that contain acidic gasses, carbon dioxide and hydrogen sulphide. For this reason, Design and construction Regulations (DCR) require an installation to possess high integrity as is reasonably practiceable. (O.T.R., 1999)

2.10.4 Electrochemical Phenomenon of Corrosion

Most of the corrosion processes occur by electrochemical mechanism involving the reaction of a metal with electrically conductive solution (electrolytes). They involve two essentially dependent processes namely anodic process and cathodic process. The anodic process involves the transfer of metal into the solution as ions with an equivalent number of electrons left on the metal while the cathodic process is the assimilation of the electrons in the metals by the atoms, molecules or ions in solution that can be reduced on the cathode. For corrosion to progress both the anodic and cathodic reactions must occur simultaneously and at the same rate, otherwise a charge builds-up, stopping corrosion. Thus, the important and basic principle of corrosion is that during matellic corrosion, the rate of oxidation is equal to the rate of reduction in terms of electron production and consumption. (Odigure *et al*, 2002).

2.10.5 The Corrosion Mechanism and Reactions

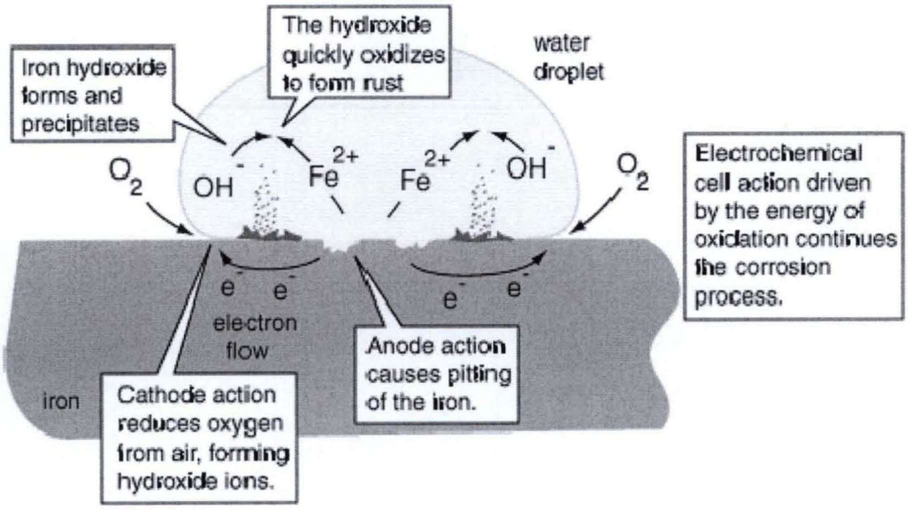


Fig. 2.12 corrosion reaction (source: www.corrosionsource.com)

Consider a piece of iron rod exposed to water droplets over a period of time as sketched above, the oxidizing iron supplies electrons at the edge of the droplet to reduce oxygen from the air (***reduction process***). The iron surface inside the droplet acts as the ***anode*** for the process.

The equations of reaction at Anode and Cathode are given below:

At **Anode**: (Oxidation reaction)

$$Fe - 2e^- \rightarrow Fe^{2+} \tag{2.1}$$

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^- \tag{2.2}$$

At **Cathode**: (reduction reaction)

$$2H + 2e^- \rightarrow H - H \rightarrow H^+ : H^- \tag{2.3}$$

The electrons can move through the metallic iron to the outside of the droplet where

$$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)} \tag{2.4}$$

Within the droplet, the hydroxide ions can move inward to react with the Iron (II) ions moving from the oxidation region. Iron (II) hydroxide is precipitated.

$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_{2(s)} \tag{2.5}$$

Rust is then quickly produced by the oxidation of the precipitate.

$$4Fe(OH)_{2(s)} + O_{2(g)} \rightarrow 2Fe_2O_3.H_2O_{(s)} + 2H_2O_{(l)} \tag{2.6}$$

The rusting of unprotected iron in the presence of air and water is then inevitable because it is driven by an electrochemical process. However, other electrochemical processes can offer protection against corrosion. For magnesium rods can be used to protect underground steel pipes by a process called ***cathodic protection.*** (Odigure, et al, 2002)

2.10.6 Types of Corrosion Reactions;

- Chemical Reaction
- Electrochemical Reaction

2.10.6.1. Chemical Corrosion Reaction

Consider the simplest corrosion problem in nature where iron is exposed to the atmospheric oxygen in the presence of moisture leading to formation of rust, iron (III) oxide as well as iron (III) chloride respectively.

The chemical reaction can be summarized as follows:

a. $4Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)}$ (2.7)
[Oxidation State of Fe is 0-, +3]

b. $2Fe^{0}_{(s)} + 3Cl^{0}_{2(g)} \rightarrow 2Fe^{3}Cl^{-1}_{3(s)}$ (2.8)
Reducing Oxidizing

The processes A and B illustrates the importance of redox reaction, i.e. oxidation and reduction processes. In these processes, iron is an oxidizing agent since it gains 3 electrons and chlorine is a reducing agent since it loses 1 election. (Oyelami and Asere, 2008)

2.10.6.2 Electrochemical Corrosion Reaction

The anode reaction, which results in the corrosion of iron immersed in water or seawater and exposed to the atmosphere, is:

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{2.9}$$

The ferrous hydroxide precipitates from solution and being unstable in oxygenated solutions, it undergoes further oxidation to produce hydrated iron or rust

$$2Fe(OH)_2 + H_2O + \tfrac{1}{2}O_2 \rightarrow 2Fe(OH)_3 \tag{2.10}$$

During corrosion more than one oxidation and one reduction reaction may occur. When an alloy is corroded, its component metal goes into solution as their respective ions depending on their relative electrode potentials with more than one oxidation reaction. (Abdullahi, 2001; Kammar, 2000)

2.10.7 Corrosion Monitoring

Monitoring of corrosion refers to the observation and checking of equipment for corrosive spots with the aim of early detection of possible hazards and protection against loss of life, injury, production and property. (Odigure, et al, 2002). Corrosion monitoring is an essential part of a well-planned corrosion control program in the refinery. A high corrosion rate over a period of time can give useful information about the technical condition of the plant and consequently instigates possible corrosion control measures to be adopted. (Fontana, 1978; Uhlig and Revive, 1985)

Corrosion monitoring, inspection and equipment surveillance play a crucial role in industrial corrosion control program. Monitoring is used to assess plant integrity and fitness for purposes and also to achieve process control. Corrosion costs the oil field millions of dollars annually. Therefore, considerable financial benefits can accrue from the application of appropriate corrosion monitoring technology. (Odigure et al, 2002).

Current corrosion monitoring system in Kaduna Refinery Petrochemical Company:

Existing practices of corrosion monitoring in the plants include: Visual Inspection, Corrater Probes, Ultrasonic Thickness Measurements (UTM), Cathodic Protection and Coupon Tests. There are various methods that can be employed in the monitoring of corrosion in the petroleum industries; this project focuses on the coupon test method.

2.10.7.1 Ultrasonic Thickness Measurement (UTM)

Refinery applications of ultrasonic thickness measurements are normally confined to the use of portable thickness and weld flaw detectors. The metal thickness measurement by ultrasonic used sound travelling at a known velocity (different for each metal type) via a transducer, travels through a couplant into the steel and reflects at a metal to air, liquid etc.., interface, then reflects back to the transducer. The time it takes for a sound wave to travel through the steel and back is measured by the ultrasonic instrument where it is converted in the instrument. The thickness is read out on a digital display. The thickness measurement can also be obtained using an instrument equipped with a Cathodic Ray Tube (CRT). When searching for lamination or the discontinuities oriented parallel to the test surface, an instrument equipped with CRT is better suited for evaluation than a digital readout instrument. (Egbe, 2008)

Transducer commonly used for longitudinal wave (straight beam) testing in refineries ranges from 3/8" - 5/8" diameter, dual 5.0MHZ for digital readout instrument to 1/2" - 1" diameter, single 1-

5MHZ for instrument with a CRT screen. Sound is transmitted at a 45°, 60°, 70° angle from a normal perpendicular to the test piece surface. When a discontinuity struck by a sound wave, the sound is reflected back to the transducer where the mechanical energy of sound is turned to electrical energy that gives a signal back reflection of certain amplitude on the CRT screen. The location of the back reflection on the calibrated screen gives the length of sound travel. (KRPC Inspection Report, 2008)

2.10.7.2 Coupon Test Method

Coupons are pieces of materials placed in the environment to corrode and later analyzed to determine the rate of corrosion. They are useful in monitoring corrosion in pipelines and process vessels. The coupon is generally of the same metallurgical composition as the material whose corrosion is being studied. (Odigure et al, 2002)

The process of using the coupons involves careful cleaning, weighing before and after they have been exposed into the corroding environment for sometimes. The coupons are electrically isolated from other metals. Coupons are installed with spool, which are just short pipe section flanged for easy removal. With this spool bigger sample of the system is studied and another advantage is that it has the same shape location. Spool reflects more accurately the build-up of protective film deposits of corrosion products. The corrosion results from coupons test are affected by their location, handling on installation and removal. It is important that the coupons are protected from corrosion before installation and on retrieval before they are analyzed. The spool is usually removed periodically cleaned and weighed to determine the loss within the period, pit depth and the nature of localized corrosion can be measured directly. (Roley, 1986).

The exposure time of the coupon can affect the result, short exposure time can be misleading as pits (tiny corrosive holes) may not have developed which means the exposure time of the coupon may have to be increased for some more time to ascertain the presence of pits. (Abdullahi, 2001)

Coupons are relatively cheap, readily available and offer a permanent record of the corrosion suffered. The weakness of the method is the assumption that there is a uniform corrosion all through the material. (Odigure et al, 2002). The diagram showing the points of coupon installation along the cooling water pipeline in KRPC is sketched below.

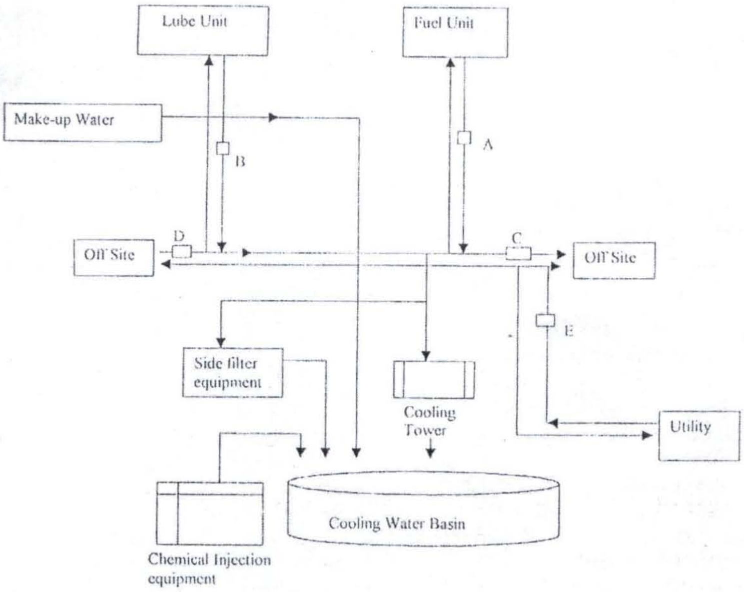


Fig.2.13 Schematic diagram showing the points of coupon installation along the cooling water pipeline. *(Odigure et al, 2002)*

2.10.7.2.1 Benefits of Corrosion Coupon Testing

- Simple and straightforward principle
- Provides specimens for post-test examinations

- Allows comparison between different alloys and inhibitors
- Assesses all forms of corrosion Low cost

2.10.7.2.2 Limitations of Corrosion Coupon Testing

- Measures only the average corrosion rate during the time of exposure.
- Corrosion rates can only be calculated after coupon removal.
- Short exposure periods can yield unrepresentative corrosion rates, especially for alloys that form passive films, such as stainless steels. Normal exposure periods frequently approach 90 days. For example, ASTM G311 recommends minimum exposure time, in hours, as

Exposure with hours = 2000 / Expected corrosion rate in mpy

Therefore, if a corrosion rate of one mil per year (0.001 inches) is expected, the minimum recommended exposure time would be 2000 hours or 83 1/3 days.

2.10.7.2.3 Calculations of Corrosion Rate

The corrosion rate is calculated for each coupon using the initial and final weights, control weight loss, coupon surface area, and density of the alloy and exposure time in the formula. The rate of corrosion is expressed in several different forms. The simplest in dimensionless units is the percentage change in weight of a coupon in an exposed time interval. This figure is usually extrapolated to give the percentage change per annum. The corrosion rate calculated using corrosion coupons assumes uniform corrosion across the coupon (e.g. uniform corrosion of the pipe wall at the monitoring point). This approximation is acceptable for most circumstances to determine the average rate of corrosion. www.caproco.com

The corrosion rate depends on Faraday's Law:

$$Corrosion\ Rate = \ weight\ of\ metal\ dissolving(g)\ - \left\{\frac{atomic\ weight\ of\ metal\ \left(\frac{g}{mol}\right)}{No.of\ electrons\ transferred\ x\ 96{,}500\frac{Amp}{Sec}}\right\}\ x\ \ Current\ (amps) x\ time\ (sec) \tag{2.11}$$

By dividing both sides of the equation by the coupon surface area, this gives the corrosion rate as equal to a constant multiplied by the current density (amp)/area (cm^2). In other words, the rate of weight loss from a given area is proportional to the current density. www.caproco.com

Corrosion Rate Calculation in Metric Units:

$$\boldsymbol{umpa}\ (micrometers\ per\ annum)\ =$$

$$\left\{\frac{weight\ loss\ of\ coupon\ (g)}{total\ exposed\ area\ of\ coupon\ (cm^2)}\right\}\ X\ \left\{\frac{3.65\ x\ 10^6}{[exposed\ time\ (days)]\ x\ \left[density\ of\ metal\ (\frac{g}{cm^3})\right]}\right\} \tag{2.12}$$

Corrosion Rate Calculation in U.S Customary Units: (most commonly used)

$$\boldsymbol{mpy}\ (mils\ \ per\ year) =$$

$$\left\{\frac{weight\ loss\ of\ coupon\ (g)}{total\ exposed\ area\ of\ coupon\ (in^2)}\right\}\ X\ \left\{\frac{2.23\ x\ 10^4}{[exposed\ time\ (days)]\ x\ \left[density\ of\ metal\ (\frac{g}{cm^3})\right]}\right\} \tag{2.13}$$

Corrosion Rate Calculation from the coupon test from KRPC Inspection Report is:

$$\text{Corrosion Rate,} \qquad \text{MDD} \ = \frac{(Wt_1 - Wt_2) * 10^3}{A * D} \tag{2.14}$$

where,

MDD = mg. dm^{-2} .day^{-1}

Wt_1 = Initial Coupon Weight, (gm)

Wt_2 = Final Coupon Weight, (gm)

A = Exposed Surface Area, (dm^2)

D = Days of Exposure, (days). i.e. resident time

Acceptable Kurita Standard (see appendix ‘E’)

$0 - 10MMD, \ \ Very\ Good$

$10 - 20MDD, \ Good$

$21 - Above, \ Not\ Satisfactory$

Pitting Rate Calculation

$$Pit_{umpa} = \frac{pit\ depth\ (Um)\ X\ 365}{expossure\ time\ in\ days} \tag{2.15}$$

$$Pit_{mpy} = \frac{pit\ depth\ (mils)\ X\ 365}{expossure\ time\ in\ days} \tag{2.16}$$

2.10.7.2.4 Constraints to corrosion monitoring in KRPC

Following are the constraints to corrosion monitoring in KRPC: [Sources: staff response to questionnaire shared in 2009]

- Coupon tests have been limited due to lack of apparatus such as: coupons/coupon columns, hot air dryer, weighing balance, pH meter, agitating machine and reagents such as: corrosion inhibitors, Toluene, KURIZET S-204 and KURIZET T-225, etc.
- Corrater probes have not been used because at the time they were

handed over at completion of plant construction project, there was no formal training of any inspector on how to use them. Lately, the measuring devices got burnt during the fire incident of ETSD caravan in 1993.

- Corrosion monitoring by thickness survey is hindered in some cases due largely to inadequate Ultrasonic Thickness Meters (UTM). Currently only two meters are functional. These meters use only cold probes. Hot probes are not available.
- Lack of training for plant inspectors to cope with modern methods of on-line corrosion monitoring.
- Non-release of vessels at the scheduled time for corrosion monitoring.
- Inaccessibility to current technical journals, codes, specifications and standards for updating knowledge and ease of references.
- Inadequate operational vehicles to cover entire plant equipment.
- Corrosion monitoring systems were completely absent for storage tanks.

2.10.8 Corrosion Agents

The known corrosive agents are:

- Carbon dioxide (CO_2)
- Oxygen (O_2)
- Hydrogen Sulphide (H_2S)
- Bacterial

Carbon dioxide (CO_2)

Dissolved carbon dioxide causes gas condensate corrosion. CO_2 dissolved in water corrodes steel. This corrosion is found most frequently in gas wells where CO_2 is present. If water vapor condenses in tubing or pipelines (flow lines), the carbonic acid formed produces corrosion pits in the exposed metal. The top portion of pipelines is most susceptible to this type of corrosion. Corrosion rates are usually higher with high well head pressures, because more CO_2 will dissolve in the water vapor at higher pressures creating a stronger acid. The corrosiveness of a gas well is based on partial pressure of carbon dioxide thus (REF)

$$Partial\,pressure\ = Total\,well\,head\,pressure\ X\ CO_2 \tag{2.17}$$

Note: $partial\,pressure\ >\ 30,\ corrosive\,well$

$partial\,pressure\,from\ 7\ -\ 30,\ possible\ corrosive$

$partial\,pressure\,form\ 0\ -\ 7,\ non-corrosive$

Co-corrosion equation:

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (carbonic\ acid) \tag{2.18}$$

$$FeO + H_2CO_3 \rightarrow FeCO_3 + H_2O \tag{2.19}$$

$$(Iron\ Carbonate)$$

Oxygen (O_2)

Oxygen dissolved in water causes very rapid corrosion. This corrosion forms a scale which may vary from dense and adherent to loose, porous and thick. Down-hole oxygen corrosion in production wells is usually caused when air enters the casing-tubing annulus. Serious corrosion has been indicated in Hydrogen Sulphide bearing water containing as little as 0.9ppm oxygen with corrosion problems eliminated after oxygen is removed.

For good corrosion control, the oxygen contents should be below 50 ppb or thrice the amount of O_2 that get in through faulty flanges. Also, leaky control valves can cause a special type of corrosion known as cell corrosion. This can destroy pipelines and equipment in a very short time.

Hydrogen sulphide (H_2S)

Hydrogen sulphide gas causes sour corrosion when it dissolves in water, even in small amounts, can create a very corrosive environment. Black scale (Iron Sulphide) on a steel surface is indicative of a Hydrogen sulphide attack.

The equation of action of H_2S on steel or iron is shown below:

$$\underset{\text{(Iron oxide)}}{FeO} + H_2S + H_2O \rightarrow \underset{\text{(Iron sulphide)}}{FeS} + H_2O \tag{2.20}$$

Steel is anodic to the Iron Sulphide, so corrosion continues beneath sulphide scales, forming numerous deep pits with underlying deep cracks. Cracking is usually due to embrittlement and stress concentration at root of pits. Atomic hydrogen diffuses into the grain boundaries of the metal and reacts with itself to form the larger size molecules of hydrogen. These larger molecules of hydrogen are tapped and cause excessive pressure within the steel, resulting in splitting, blistering or cracking, and loss of ductility and yield strength.

Bacteria as a Corrosive Agent

Many different kinds of bacteria are contained in oil field brine. Aerobic bacteria exist where oxygen is present. The major bacteria problem with water containing oxygen is molds, algae, funguses, and other slimy growths which tend to plug and foul equipment. Chlorine treatments will kill any organism living in air. Oxygen is usually excluded or removed from water to be injected down hole to reduce corrosion. This prevents the growth of the green molds, funguses and algae. The most satisfactory approach is to slug-treat the sulphate-reducing bacteria with 100ppm bactericide once every two weeks.

2.11 Effects of Corrosion on Production Plants

Some of the deleterious effects of corrosion on production pipelines are:-

- Contamination of products
- Loss of valuable products
- Hazard, no safety and reliability
- Maintenance and operating cost
- Plant shut-down
- Appearance

Contamination of products: In many cases, the market value of the product is directly related to its purity and quality. Hence, the presence of rust in production plants is undesirable for the product standpoint.

Loss of Valuable Products: Physical damage appears in the form of pots, holes, cracks, general metal loss and loss of strength or ductility. In a severe case, a catastrophic failure may occur (e.g. explosion), which also leads to loss of valuable product.

Hazard effect on safety and reliability: Corroding drums and pipes can cause oil or gas explosion. Economizing on materials of corrosion is not desirable if safety is risked. Other health considerations are also important such as; contamination of portable water, corrosion products could make sanitizing of equipment more difficult.

Maintenance and Operating Costs: Corrosion controls costs oil field millions of dollars annually. Therefore, considerable financial benefits can accrue from the application of appropriate corrosion monitoring technology.

Plant Shut-Down: Frequently, plants are shut down, or portions of a process stopped because of unexpected corrosion failure. Corrosion monitoring is helpful in preventing unexpected corrosion failure and plant shut down.

Appearance: Automobiles are painted because rusted surfaces are not pleasing to the eye. So also, badly corroded and rusted plants would leave a poor impression on the observer. Products transported with corroded pipes to the storage tank and to the sales end tend to change the original color of the products. (Osadare, 1999)

2.12 Electrochemical Corrosion Models

2.12.1 Basic Mathematical Model:

In corrosion testing, the basic corrosion rate is measured by the reduction in weight of a specimen of known area over a fixed period of time. This is expressed by the formula: (Oyelami and Asere, 1994)

$$Ipy = \frac{12w}{tAP} \tag{2.21}$$

where

w = mass loss in time 't',(kg)

t = time, (yr)

p = density of material, (kg/m^3)

A = surface area,(m^2)

In SI units, ipy = 25mm per year.

2.12.2. Zhimz - Hoffman (ZH) Model:

Zhimz - Hoffman's model takes care of phase transition that arises as a result of corrosive fluid on the solid surface of the plant. This model is particularly useful in cracking process in the refinery; it is worthy of note to mention that corrosion of the surfaces into globules of impurities may cause catalytic poisoning of a petrol chemical plant. The Zhimz - Hoffman's process is a typical non-linear parabolic partial differential equation whose solution exists in $\Omega X\ (0, T)$. One striking thing about the ZH model is that it relates the relevant constants such as K, T, and L that are in fact the properties of the surface of the material from which the plant is fabricated. (Zhimz and Hoffman, 1994).

Zhimz-Hoffman's equation is stated as;

$$\frac{\partial u}{\partial t} + \frac{1}{2}\frac{\partial \emptyset}{\partial t} - K\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right) = f \tag{2.22}$$

$$\tau\frac{\partial \emptyset}{\partial t} + \varepsilon^2\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right) = g(u) + 2u \tag{2.23}$$

where

$$U(x,0) = u_0(x), \varphi(x,0) = \varphi_0(x)\ as\ \Omega x\ \{0\} \tag{2.24}$$

$$g(\varphi) = a(x)\varphi + b(x)\varphi^2 - c(x)\varphi^3\ ;\ c^0, k, l, \tau, \varepsilon^2 \tag{2.25}$$

u = the temperature of the phase transition.

k = the conductivity,

l = the latent heat released or absorbed during phase transition

ε = measures sharpness of the free boundary

τ = the surface tension.

The Advantage of the ZH method being its accuracy is highly guaranteed to some degree of freedom. The usefulness of ZH model can be buttressed by the fact that, most heat generation problem in a corrosive media is often accompanied by phase changes. The problem can thus be modeled by well-known phase field model, which describes the phase transition between two different phases, e.g. solid and liquid. The Zhimz and Hoffman's model adequately take care of this.

2.12.3. Oyelami and Asere Model:

This model combined the idea of perturbation theory with the heat-mass transfer equation, Zhim-Hoffman's equation and equation arising from electrolysis and gas pipeline distribution.

$$Corrosion\ A = \frac{12w}{tnp} \tag{2.26}$$

where,

w = mass loss in time't',(kg)

t = time, (yr)

p = density of material, (kg/m^3)

A = corrosion rate in SI units, = 25mm per year.

Using the idea of perturbation theory to calculate the life expectancy of the plant as a result of corrosion;

$$a = a^1 + h \tag{2.27}$$

where

a^1 = thickness of the surface after corrosion, (m)

h = the part lost into the chemical reaction as a result of the corrosion and may be in form of impurities, (m)

Assuming, a = Q

$$h = \frac{\alpha}{\beta Q + \gamma} \tag{2.28}$$

where

Q = thickness of the surface before corrosion takes place, (m)

By dimensional analysis, the life expectancy of the plant is related to *h* and *A*

$$T \ \frac{C}{hA} \tag{2.29}$$

where

C = constant, is a dimensionless constant that can be determined experimentally,

Hence, the life expectancy *T is*

$$T = \frac{tAPC}{12 \propto w} \ (\beta\alpha + \gamma) \tag{2.30}$$

Early Life Failure [ELF] due to Corrosion

The early-life failure (ELF) of the equipment caused by other forms of corrosion according to Oyelami, 1994, can be empirically derived from the Weibull distribution function given by:

$$f(t) = \frac{\beta}{\lambda} (\frac{t}{\lambda})^{\beta-1} \exp\, (\frac{t}{\lambda}) \beta \tag{2.31}$$

where,

β = shape parameter

λ = characteristics life –time of the equipment

t = time, (year)

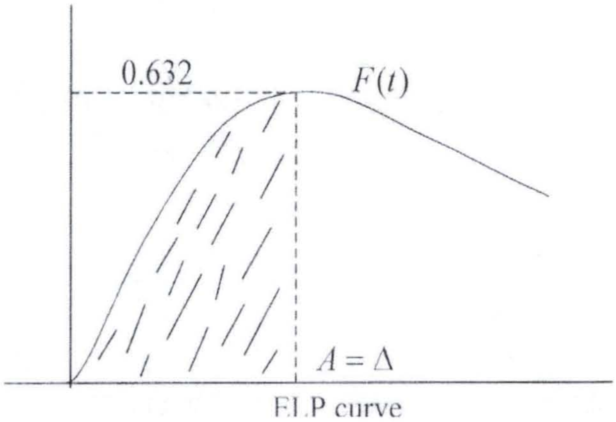


Fig.2. 14 Early Life Failure (ELF) due to Corrosion Curve (Oyelami and Asere, 2008)

2.12.4. ExxonMobil's Corrosion Prediction Model:

ExxonMobil's corrosion prediction model is one of the key components of ExxonMobil's integrated approach for corrosion prediction. This integrated approach enables the optimal use of carbon steel in corrosive service for down hole, pipeline, and facilities applications. The software, **CorrCast,** provides a window based, user-friendly tool for performing corrosion rate predictions in sweet (CO_2) and sour (H_2S) services. CorrCast is based on a mechanistic corrosion model that accounts for the relevant chemistry and physics of the corrosion process in a mixed aqueous-liquid hydrocarbon environment. CorrCast predicts corrosion rates by modeling the chemistry and physics of the corrosion process, including CO_2 and H_2S solubility in the aqueous phase, solution equilibrium reactions, electrochemical reactions, mass transfer to and from the steel surface, scale formation, and inhibition. The model requires users to input test/field conditions, gas composition, water analysis, flow parameters, and hydrocarbon properties. Corrosion rates can be predicted in CorrCast at selected points in pipes for field application or for a metal coupon in a test condition-controlled vessel for laboratory application. Rate can also be predicted as a function of length along a pipeline for field application, and as a function of time for a metal coupon in an autoclave for laboratory application. Sun et al, (2009).

Detailed description of the model and calculation methodology of CorrCast is described below:

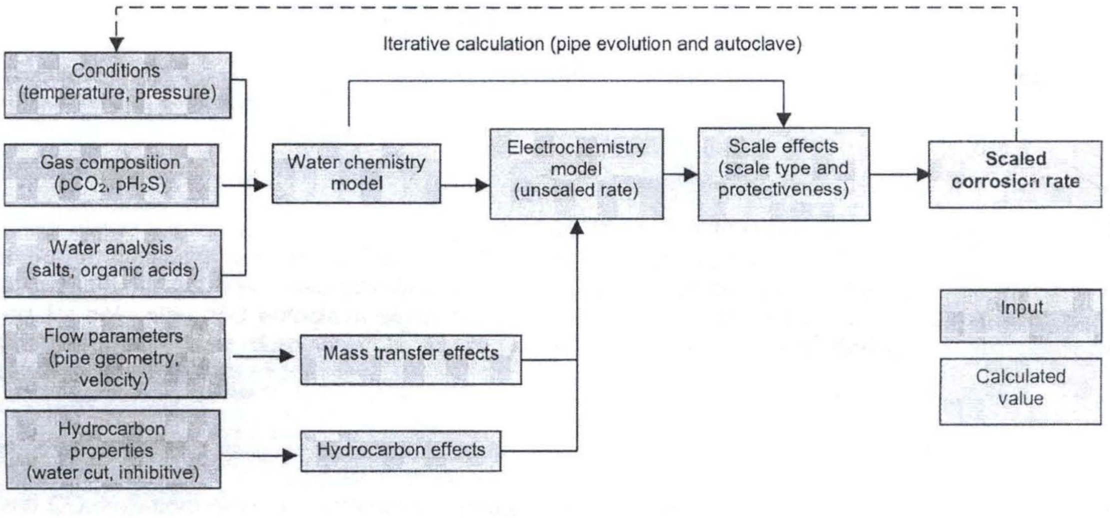


Fig: 2.15 Schematic depicting the calculation methodology of CorrCast. (Wei et al, 2009).

Water chemistry and electrochemistry models are then applied to calculate an unscaled corrosion rate. The effects of iron carbonate and iron sulfide scales are modeled by first calculating scale protectiveness factors, which are then applied to the unscaled corrosion rate. CorrCast models the corrosion current by assuming direct attack by H^+, $H_2CO_3HCO_3^-$, and HA at the surface of the metal. The electrochemical reactions include the cathodic and anodic reactions listed below:

$$2H_2CO_3^0 + 2e^- = + 2HCO_3^- \quad (2.32)$$

$$2HCO_3^- + 2e^- = H_2 + 2CO_3^{2-} \quad (2.33)$$

$$2H^+ + 2e^- = H_2 \quad (2.34)$$

$$2HA^+ + 2e^- = H_2 + 2A \quad (2.35)$$

$$Fe = Fe^{2+} + 2e^{-} \tag{2.36}$$

The Corrosion current is equal to the anodic current which is equal to the sum of the cathodic currents.

$$i_{corr} = i_{Fe^{2+}} = i_{H^+} + i_{H_2CO_3} + i_{HCO_3^-} + i_{HA} \tag{2.37}$$

The unscaled corrosion rate according to Sun et al (2009), is calculated using the following equation.

$$CR = \frac{i_{corr} M_{Fe}}{\rho_{Fe} n F} = 1.155\, i_{corr} \tag{2.38}$$

where i_{corr} is in A/m^2

M_{Fe} is the Molecular weight of iron in g/mol

ρ_{Fe} is the density of iron in kg/m^3

N is the number of moles of electrons used in reducing or oxidizing a given species

F is the Faraday's constant

CR is in mm/s which can be conveniently converted to mm/y.

When H_2S is present in the water solution, it is assumed that the adsorption of sulphur on iron affects the potential. This effect varies with coverage and is fit by a Langmuir isotherm. [Sun et al, 2009]

2.12.5. Sankara's Review of Electrochemical Models:

Merits and demerits of seven passivity models, sixteen nucleation models and twelve propagation models were reviewed. Based on these findings by Sankara et al (2005), the following conclusions can be made:

1. The models are complicated, based on solid scientific principles and carefully carried out laboratory experiments. They should be made more user-friendly
2. Because the laboratory experiments carried out to develop the models are relevant to oil and gas pipeline-operating conditions, they could not be readily used.
3. These models accurately describe localized pitting corrosion, which is the main cause of failure in the field. Several significant electrochemical parameters have been identified that could be used to determine pitting corrosion susceptibility
4. The accuracy of the models is not validated even in laboratory experiments under oil and gas conditions
5. Within the scientific limitation of the models, can predict the main mechanism of pitting corrosion and hence when the first failure might occur

The pitting corrosion is one of the most destructive and insidious form of corrosion and it is particularly destructive in that it causes leakage of pipelines and failure of equipment in a short time because of peforation with negligible overall weight-loss of the entire structure. The penetration of the pipe wall and equipment by pits is a process that consists of three stages. Electrochemical reactions are involved in all the three stages; as a result, each stage of pitting corrosion can be modeled based on electrochemical principles.

The three stages involved in the pitting corrosion are:

- Formation of a passive layer on the steel surface
- Initiation of pits at localized regions on the steel surface where film breakdown occurs
- Pit propagation and eventual penetration of the pipe wall

(Sankara et. al, 2005)

2.12.6. Internal Corrosion Modeling In the Risk Assessment of Pipeline:

Gartland and Johnsen, created a model in 2003 for prediction of corrosion profiles in oil and gas pipelines. The model is based on multiphase flow modeling, water wetting predictions, pH calculations and models of CO_2 and H_2S corrosion. The input data were typically the pipeline profile, fluid composition data, production rates and data on injected chemicals. The pipeline corrosion model was developed at CorrOcean (Smart, 1993) under the name CorPos (McMahon and Paisley, 2007, 2010). The model composed of several modules as shown in the fig 2.16 below.

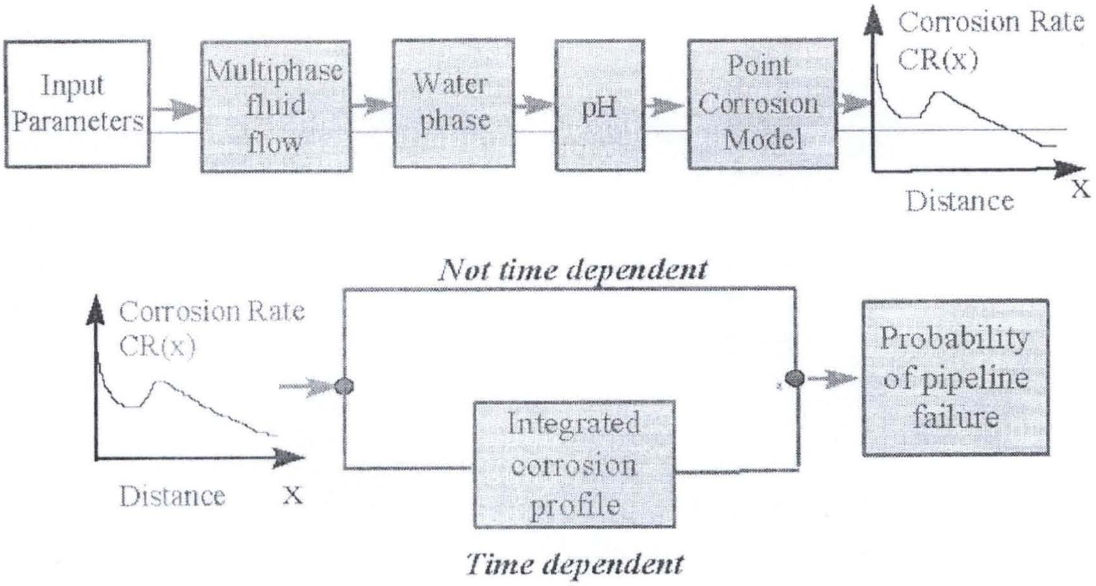


Fig: 2.16 Flow chart of the pipeline corrosion model

The multiphase flow module was based on the OLGAS 2000 (Smart, 93) and PVTSim (McMahon, 1997) simulators. It provides information on the temperature profile, the velocity profiles of each phase, phase hold-ups, shear stresses and flow regimes. The purpose of water phase module is to come up with values for the water wetting factor F_w.

$$\text{CR (actual water wetting)} = \text{CR (100\% water)} * F_w \tag{2.39}$$

pH and water chemistry is calculated by the XLpH-module, which has been developed for BP's CASSANDRA CO_2 corrosion prediction program (McMahon, 1997). XLpH is applicable to pure water as well as brines with a wide variety of ion concentrations. The point corrosion model for pure CO_2 corrosion applies the point corrosion module known as the NORSOK-model (N.T.I.S).

The corrosion rates are calculated from a general formula given by Gartland, 2003 is

$$CR_t = K_t\,(fCO_2)^{0.62}\left(\frac{S}{19}\right)^{0.146+0.0324\log(fCO_2)} f(pH)_t \tag{2.40}$$

Where;

CR_t = *corrosion* rate at temperature't' [mm/y]

t = temperatures 20, 40, 60, 80, 90, 120 or 150°C

K_t = constant for a given temperature't'

f_{CO2} = fugacity of CO_2 [bar]

$f_{(pH)t}$ = the pH factor at temperature 't'

Values of 'Kt' and formula for f(pH0t were obtained from the NORSOK M506 document.

The Model Verification:

In the period 1999-2001 a Joint Industry Project (JIP) was run by Institute of Energy Technology (IET) in Norway. The goal was to compare different calculation tools for CO_2 corrosion with field data. A total of 12 different models were included in the project. The results from the project showed that this prediction (Per Gartland and Roy Johnsen) model was one of the models that correlated best with the field data. When inspection data (ip) and monitoring data (mon) were combined with measurements and model predictions (mod), it gives;

$$CR_{ave} = w_{mod}CR_{mod} + w_{ip}CR_{ip} + w_{mon}CR_{mon} \tag{2.41}$$

Where

w_{mod} , w_{ip} , and w_{mon} are the weight factors that can take the values between 0 and 1 depending on an evaluation of the data available but such that

$$w_{mod} + w_{ip} + w_{mon} = 1 \tag{2.42}$$

The main problem with this procedure is that corrosion rates are not always available from inspection data and that monitoring data are limited to one or few locations. (Gartland and Johnsen, 2003)

2.12.7 Corrosion Prediction through an integrated approach

Rendy, Nelson and Pacheco worked on corrosion prediction through an integrated approach. The model focuses on an evaluation of pitting because of the relatively high levels of H_2S. Autoclave corrosion tests designed to simulate the actual mass transfer for the anticipated stratified pipe flow were conducted at the materials and corrosion laboratory under the simulated field conditions, using synthetic brines designed on the basis of the field water analysis. Acid-gas charging pressure were designed such that the dissolved H_2S and CO_2 in the autoclaves would be equivalent to that found in the field, and the coupons were made of pipeline steel. Test durations varied from 5 to 42 days to characterize the pitting corrosion rates fully, including a pitting incubation time prior to introduction of the inhibitor. General corrosion rates were calculated based on weight loss, and the maximum expected pit depths as a function of time were calculated using JGEV procedure. (Bondos et. al, 2007).

Pitting prediction is more complicated since the rate of pit growth changes with time. The advantage of using JGEVs is that they provide high –precision results using a limited number of samples and do not require knowledge of the actual pit size distribution. According to the method of Scarf et al, (1992), the mean maximum pit depth, μ_{max} is defined by:

$$\mu_{max} = \left\{\mu + \frac{\alpha}{k} \cdot \left(1 - \frac{\Gamma(1+k)}{M^k}\right)\right\} \cdot t^{\beta} \qquad (2.43)$$

where,

$\boldsymbol{\alpha}$ = is a scaling parameter,

$\boldsymbol{M}$ = is the ratio of the actual (in service) to test coupon surface areas

$\boldsymbol{\Gamma}$ = is the gamma function

$\boldsymbol{k}$ = is the shape parameter, and

$\boldsymbol{\beta}$ = is the pitting factor.

μ_{max} = mean maximum pit depth, L, mm [mil]

The experimental pit depth data from a number of samples of actual area are input to the JGEV equation using a Monte Carlo search routine, and the optimum values for the shape parameter and pitting factor are found by calculating the value of a maximum likelihood function. Overall, this approach provides a mathematically-based method for extrapolating over time (weeks to years) and area (a few cm^2 to thousands of m^2) to connect laboratory data to conditions in the field.

2.12.8 Computer simulation of the corrosion pit growth

Maliki and Baroux, 2004 carried out Computer simulation of the corrosion pit growth. In their work, numerical simulations of the corrosion pit growth were performed using both Monte Carlo (MC) and Cellular Automata (CA) techniques. In the MC technique, a dissolution algorithm is proposed for elementary dissolution events. Varying the re-passivation probability at the atomic scale on the pit walls is shown to control the pit growth kinetics (t_n law, with n varying from ½ to 2). In the CA technique, the Metal/Film/Electrolyte system is considered as an automaton with some specific transition rules. The dissolution probability is shown to strongly influence both pit morphologies and the t_n law. Last, predominant effect of the IR drop inside the pit is evidenced. These preliminary investigations motivate future works to simulate in more details the pit growth process and the repassivation of metastable pits. (Reigada et-al, 1994).

2.12.9 Atmospheric corrosivity modeling

Roberge, (2001), carried out Atmospheric corrosivity modeling. In that work it was revealed that corrosion of metals exposed to the atmosphere is expensive to our societies in terms of aesthetics, safety and functionality. The factors that influence atmospheric corrosivity were reviewed as well as classification schemes, statistical and mechanistic models. The mechanistic models and have shown that corrosion rates can vary dramatically between locations that are only meters apart. Another implication is that the most influential step in the corrosion process was the deposition rate of corrodent, i.e. aerosols or gaseous pollutants. Thus the principles of mass transfer and deposition of pollutants and aerosols, namely convection and turbulent diffusion, can form a theoretical framework for interpreting and predicting atmospheric corrosivity. The implications for the design of structures is that local corrosivity rates can be predicted based on simulated airflow patterns. Analysis to date has also revealed that:

- Smaller objects can be expected to corrode faster because of a greater efficiency of salt aerosols;
- Objects exposed to faster wind speeds and aerosols will corrode faster;
- Objects in the lee of prevailing winds from an aerosol source will corrode faster than objects on the windward side of an aerosol source

  Roberge, (2001).

2.12.10 Computational modeling of cathodic limitations on localized corrosion of wetted SS 316l at room temperature. (Fushuang et al, 2005)

(Fushuang, (2005) observed that the ability of a SS 316L surface wetted with a thin electrolyte layer to serve as an effective cathode for an active localized corrosion site was studied computationally.

The dependence of the total net cathodic current, Inet, supplied at the repassivation potential Erp (of the anodic crevice) on relevant physical parameters including water layer thickness (WL), chloride concentration ([Cl^-]) and length of cathode (Lc) were investigated using a three-level, full factorial design. The effects of kinetic parameters including the exchange current density ($i_{o,c}$) and Tafel slope (β_c) of oxygen reduction, the anodic passive current density (i_p) (on the cathodic surface), and Erp were studied as well using three-level full factorial designs of [Cl^-] and Lc with a fixed WL of 25 lm. The study found that all the three parameters WL, [Cl^-] and L_c as well as the interactions of Lc · WL and Lc · [Cl^-] had significant impact on I_{net}. A five-factor regression equation was obtained which fits the computation results reasonably well, but demonstrated that interactions are more complicated than can be explained with a simple linear model. Significant effects on I_{net} were found upon varying either $i_{o,c}$, β_c, or E_{rp}, whereas i_p in the studied range was found to have little impact. I_t was observed that Inet asymptotically approached maximum values (I_{max}) when Lc increased to critical minimum values. I_{max} can be used to determine the stability of coupled localized corrosion and the critical Lc provides important information for experimental design and corrosion protection.

2.13.11 A simplified method for estimating corrosion cavity growth rates (Engelhardt et-al, 1997)

This simplified method is proposed for calculating corrosion cavity propagation rates. This method is based on an assumption that if the rate of an electrode reaction depends (in an explicit form) only on the potential, the pit growth rate depends only on the concentration of those species that determine the potential distribution near the metal within the cavity. The advantage of this method is that it permits one to predict the rates of cavity propagation without knowing various parameters, such as the equilibrium constants of some chemical reactions and diffusion coefficients of species that are present at relatively low concentrations near the electrode surface. The analytical expressions for calculating propagation rates of cylindrical and hemispherical pits are compared with available experimental data. The influence of aggressive anions on the pit propagation rate has been investigated. It is shown that transport processes in the internal environment do, in the general case, influence the kinetics of metal corrosion. (Engelhardt et-al, 1997)

2.12.12 Corrosion of Mild Steel

As the oil and gas emerge from the geological formation they are always accompanied by some water and varying amounts of "acid gases": carbon dioxide, CO_2 and hydrogen sulfide, H_2S . This is a corrosive combination which affects the integrity of mild steel. Even if this has been known for over 100 years, yet aqueous CO_2 and H_2S corrosion of mild steel still represents a significant problem for the oil and gas industry. (Bonis & Crolet, 1989). Although corrosion resistance alloys exist that are able to withstand this type of corrosion, mild steel is still the most cost effective construction material used in this industry for these applications. All of the pipelines, many wells and much of the processing equipment in the oil and gas industry are built out of mild steel. The cost of equipment failure due to internal CO_2 / H_2S corrosion is enormous, both in terms of direct costs such as: repair costs and lost production, as well as in indirect costs such as: environmental cost, impact on the downstream industries, etc.(Faruk, 2007)

2.12.12.1 Aqueous CO_2 Corrosion Of Mild Steel

Aqueous CO_2 corrosion of carbon steel is an electrochemical process involving the anodic dissolution of iron and the cathodic evolution of hydrogen. The overall reaction is:

$$Fe + CO_2 + H_2O \rightarrow FeCO_3 + H_2 \qquad (2.44)$$

CO_2 corrosion of mild steel is reasonably well understood. A number of chemical, electrochemical and transport process occur simultaneously.

2.12.12.2 Chemistry of CO2 Saturated Aqueous Solutions – Equilibrium considerations;

The CO_2 gas is soluble in water:

$$CO_{2(g)} \overset{K_{hyd}}{\Longleftrightarrow} CO_2 \tag{2.45}$$

For ideal gases and ideal solutions in equilibrium, Henry's law can be used to calculate the aqueous concentration of dissolved CO_2, C_{CO2}, given that the respective concentration in the gas phase (often expressed in terms of partial pressure, P_{CO2}) and given as:

$$H_{sol(CO_2)} = \frac{1}{K_{sol(CO_2)}} = \frac{P_{CO_2}}{C_{CO_2}} \tag{2.46}$$

The CO_2 solubility constant, $K_{sol(CO_2)}$, is a function of temperature, T_f, and ionic strength, I according to Oddo and Tomson, (1982)

$$K_{sol(CO_2)} = \frac{14.5}{1.00258} 10^{-(2.27+5.65 \text{ x } 10^{-3} T_{f-8.06x10^{-6}} T_f^2 + 0.075I)} \tag{2.47}$$

Since the solubility of CO_2 decreases with temperature, at 100oC the respective concentration are 3.3 mol/l in the gas and 1.1 mol/l in the water. A rather small fraction (about 1/500) of the dissolved CO_2 molecules hydrate to make a "weak" carbonic acid, H_2CO_3 due to a relatively slow forward (hydration) rate.

$$CO_2 + H_2O \overset{K_{hyd}}{\Longleftrightarrow} H_2CO_3 \tag{2.48}$$

Assuming that the concentration of water remains unchanged, the equilibrium concentration $c_{H_2CO_3}$ is determined by:

$$H_{hyd} = \frac{C_{H_2CO_3}}{C_{CO_2}} \tag{2.49}$$

where

H_{hyd} = equilibrium hydration/hydrated constant is $2.58\text{x}10^{-3}$.

Carbonic acid is considered to be "weak" because it only partially dissociates to produce hydronium, H^+ ions and bicarbonate ion, HCO_3^-

$$H_2CO_3 \overset{K_{ca}}{\Leftrightarrow} H^+ + HCO_3^- \tag{2.50}$$

HCO_3^- dissociates further to give some more H^+ and carbonate ion, CO_3^{2-};

$$HCO_3^- \overset{K_{bi}}{\Leftrightarrow} H^+ + HCO_3^{2-} \tag{2.51}$$

The respective equilibrium relations can be written as:

$$K_{ca} = \frac{C_{H^+} C_{HCO_3^-}}{C_{H_2CO_3}} \tag{2.52}$$

$$K_{bi} = \frac{C_{H^+} C_{CO_3^{2-}}}{C_{HCO_3^-}} \tag{2.53}$$

The low molecular weight organic acids are primarily soluble in water and can lead to corrosion of mild steel. Higher molecular weight organic acids are not water soluble but are typically soluble in the oil phase and pose a corrosion threat at higher temperatures in the refineries.

The occurrence of chemical reactions can significantly alter the rate of electrochemical processes at the surface and the rate of corrosion. This is particularly true when, due to high local concentrations of species, the solubility limit of salts is exceeded and precipitation of a surface layer occurs.

In a precipitation process, *heterogeneous nucleation* occurs first on the surface of the metal or within the pores of an existing layer since *homogenous nucleation* in the bulk requires a much higher concentration of species. Nucleation is followed by *crystalline layer growth.* Under certain conditions surface layers can become very protective and reduce the rate of corrosion.

In CO_2, corrosion when the concentrations of Fe_2^+ and CO_3^{2-} ions exceed the solubility limit, they form solid ferrous carbonate as shown below

$$Fe^{2+}\ CO_3^{2-} \overset{K_{sp(FeCO3)}}{\Longleftrightarrow} +\ FeCO_{3(s)} \tag{2.54}$$

where, the solubility product constant for ferrous carbonate $K_{sp(FeCO3)}$ is given according to (Sun et, al, 2009.)

$$K_{sp(Fe\ CO_3)} = 10^{-59.3498\ -\ 0.041377.T_k - \frac{2.1963}{T_k} + 24.5724\ .\ logT_k + 2.518\ .\ I^{0.5} - 0.657\ .\ I} \tag{2.55}$$

Actual ferrous carbonate is frequently found in the aqueous solution at concentrations much higher than predicted by the equilibrium $K_{sp(Fe\ CO_3)}$. This is termed *supersaturation* and is a necessary condition before any substantial precipitation can occur. The ferrous carbonate supersaturation, $ss_{(FeCO_3)}$ is defined as:

$$SS_{(FeCO_3)} = \frac{C_{Fe^{2+}} C_{CO_3^{2-}}}{K_{sp(feCO_3)}} \tag{2.56}$$

And the rate of precipitation R_{FeCO_3} is therefore often expressed as:

$$R_{FeCO_3} = K_{r(FeCO_3)} \frac{A}{V} K_{sp(FeCO_3)} (ss_{(FeCO_3)} - 1) \tag{2.57}$$

Where,

$K_{r(FeCO_3)}$ is the kinetics constant, which can be derived from the experimental results as a function of temperature, using Arrhenius type equation. (Sun and Nesic, 2008).

$$K_{r(FeCO_3)} = e^{A_{(FeCO_3)} - \frac{B_{(FeCO_3)}}{RT_k}} \quad (2.58)$$

where,

$A_{(FeCO_3)}$ = 21.3J/mol and

$B_{(FeCO_3)}$ = 64,851.4 J/mol

The ferrous carbonate layer can slow down the corrosion process by presenting a diffusion barrier for the species involved in the corrosion process and thereby changing the conditions at the steel surface. For high precipitation rates, and low corrosion rates, a dense and protective ferrous carbonate layer is obtained and vice versa, low precipitation rates and high corrosion rates lead to formation of porous unprotective ferrous carbonate layers. (Sun et, al, 2009.)

Standard Tendency (ST):

This is a non-dimensional parameter which can be used to quantify the relative rates of precipitation ($R_{(FeCO_3)}$ and corrosion rate (***CR)*** expressed in the same volumetric units:

$$ST = \frac{R_{(FeCO_3)}}{CR} \quad (2.59)$$

For ST << 1, porous and unprotective films are likely to form.

For ST >> 1, conditions become favorable for formation of dense, protective ferrous carbonate films.

2.12.12.3 Electrochemistry of Mild Steel Corrosion in CO_2 Saturated Aqueous Solutions

The electrochemical dissolution of iron in a water solution is the dominant anodic reaction in CO^2 corrosion. The reaction is pH dependent in acidic solutions with a reaction order with respect to OH^- between 1 and 2, decreasing towards 1 and 0 at $pH > 4$, which is the typical range for CO_2 corrosion.

$$Fe \rightarrow Fe^{2+} 2e^- \qquad (2.60)$$

The presence of CO2 increases the rate of corrosion of mild steel in aqueous solutions primarily by increasing the rate of the hydrogen evolution reaction.

$$2H^+ + 2e^- \rightarrow H_2 \qquad (2.61)$$

In CO_2 solutions where typical $pH > 4$, this limiting flux would be small and therefore it is the presence of H_2CO_3 which enables hydrogen evolution at a much higher rate. Thus, for $pH > 4$, the presence of CO_2 leads to a much higher corrosion rate than would be found in a solution of a strong acid at the same pH. This can be readily explained by considering that the homogenous dissociation of H_2CO_3, as given in equation (2.50) serves as an additional source of H^+ ions, which are subsequently absorbed at the steel surface and reduced according to reaction (2.61). (Bonis and Crolet, 1989).

A different pathway is also possible, where the H_2CO_3 first adsorbs at the steel surface followed by heterogeneous dissociation and reduction of H+ ion. This is often referred to as "direct" reduction of carbonic acid shown below. (Waard et. al, 1995).

$$2H_2CO_3 + 2e^- \rightarrow H_2 + 2HCO_3^- \qquad (2.62)$$

Clearly the addition of reactions (2.50) and (2.61) gives (2.62) proving that the overall reaction is the same and the distinction is only in the pathway, i.e in the sequence of reactions. The rate of reaction (2.62) is limited primarily by the slow hydration step (2.48) and in some cases by the slow CO2 dissolution reaction (2.45). It can be conceived that in CO2 solutions at pH > 5 the direct reduction of the bicarbonate ion becomes important. (Waard et. al, 1995).

$$2HCO_3^- \quad + 2e^- \rightarrow H_2 + 2CO_3^{2-} \tag{2.63}$$

CHAPTER THREE

3.0 MATERIALS AND METHOD

3.1 Mathematical Modeling of Corrosion Rate. Development and Computer Model Simulation

3.1.1 Assumptions

1. The effect of additives are tolerated and regarded to be of negligible risk for corrosion under these circumstances
2. The temperature of the line does not drop below the water dew point.
3. The effect of pH on corrosion is negligible.
4. The effect of corrosion under condensing condition is very small.
5. Corrosion inhibitors are not injected into the system.

3.1.2 Rust Model Development

The rust is assumed to occur at a rate proportional to the surface Area, Ac, available for growth and the deviation of the saturation ratio from unity (Faruk, 2007).

$$PGR = f[Ac(Fs - 1)] \tag{3.1}$$

where

$(Fs - 1) =$ Deviation of the saturation ratio from unity

$PGR = Particle\ Growth\ Rate$

PGR = Rust growth rate

$Fs =$ Saturation ratio

$Ac =$ Growth surface area

Particle rate can be expressed as:

$$PGR\ \alpha\ A_c \tag{3.2}$$

Also

$$PGR\ \alpha\ (F_s - 1) \tag{3.3}$$

Combining equations 3.2 and 3.3 we have:

$$PGR = k_c A_c (F_s - 1) \tag{3.4}$$

where k_c is the rate constant

Also rust rate is defined as change in crystal mass per time.

$$PGR = \frac{dm_c}{dt} \tag{3.5}$$

Combining equations 3.4 and 3.5 we have,

$$\frac{dm_c}{dt} = k_c A_c (F_s - 1) \tag{3.6}$$

where,

dm_c/dt = change in crystal mass per time.

The initial amount of rust crystals present per unit bulk medium is given by

$$m_c = m_c^o,\ t = 0 \tag{3.7}$$

Relating the crystal shape to spherical shape, the mass and surface area of the crystalline particle according to Faruk, 2007 is given as

$$m_c = \rho_c \frac{\pi D_c^3}{6} C_1 \tag{3.8}$$

And

$$A_c = \pi D_c^2 C_2 \tag{3.9}$$

in which C_1 and C_2 are the shape factors, ρ_c is the density, and D_c is the diameter and k_c is a crystallization rate constant.

Substituting for (3.8) and (3.9) in (3.6) to give:

$$\frac{d}{dt}\left(\rho_C \frac{\pi D_c^3}{6} C_1\right) = k_c \pi D_c^2 C_2 (F_s - 1) \tag{3.10}$$

$$\rho_C \frac{d}{dt} D_C \frac{C_1}{6} = k_c C_2 (F_s - 1) \tag{3.11}$$

$$\rho_C \frac{dD_C}{dt} = \frac{6 k_c C_2}{C_1} (F_s - 1) \tag{3.12}$$

Therefore,

$$\rho_C \frac{dD_C}{dt} = k\grave{}_c (F_s - 1) \tag{3.13}$$

where, $$k_c' = \frac{6 k_c C_2}{C_1} \tag{3.14}$$

$$\frac{dD_c}{dt} = \frac{k`_c(F_S - 1)}{\rho_c} \qquad (3.15)$$

$$D_c = D_{c_o},\ t = 0 \qquad (3.16)$$

if $F_S > 1$, *Crystal growth*

$F_S = 1$, *Equilibrium*

$F_S < 1$, Crystal dissolution

3.1.3 Scale dissolution Model Development

The rate of rust dissolution at the surface can be expressed similarly to crystal growth. According to Faruk, (2007), the pore volume is related to the diameter of an equivalent spherical shape pore space as;

$$\phi = C_3 D^3 \qquad (3.17)$$

indicating that

$$D = (\phi/C_3)^{1/3} \qquad (3.18)$$

Thus, the pore surface relates to the porosity according to Faruk (2007) thus

$$A = C_4 D^2 \qquad (3.19)$$

$$= C_4(\phi/C_3)^{2/3} \qquad (3.20)$$

$$= C_5 \phi^{2/3} \qquad (3.21)$$

where, C_3 and C_4 are some shape factors and $C_5 = \frac{C_4}{{C_3}^{2/3}}$.

It is assumed in this model that the porosity of the solid porous matrix can be expressed as a sum of the instantaneous porosity, Φ, and the pore space occupied by the rust, Φ_S, thus;

$$\phi_r = \phi + \phi_s \tag{3.22}$$

Therefore, the mass of the scale formed over the pore surface is given by

$$m_c = \rho_s \phi_s = \rho_s(\phi_r - \phi) \tag{3.23}$$

Therefore, substituting equation 3.19 and 3.22 into equation 3.6

$$-\rho_s \frac{d\phi}{dt} = k_c' \phi^{2/3}(F_s - 1) \tag{3.24}$$

$$\phi = 0, \;\; \phi_S = \phi \tag{3.25}$$

If, $F_S > 1$, Crystal *growth*

$F_S = 1$, Equilibrium

$F_S < 1$, Crystal dissolution

where **k'$_c$** is a scale dissolution rate constant incorporating the above mentioned shape factors and some constants. The minus sign in equation 3.24 is for the reduction of porosity by scale dissolution at the pore surface. Thus, assuming the rust porosity,Φ_S, remains constant and substituting eq.3.22 into 3.24 leads to an equation eq. 3.26 below;

$$-\rho_s \frac{d\phi_s}{dt} = k_c'(\phi_r - \phi_s)^{2/3}(F_s - 1) \tag{3.26}$$

$$\phi_s = \phi_r - \phi_o, \; t = 0 \tag{3.27}$$

Assuming that the surface area of rust crystal available for growth can be expressed empirically by:

$$A_c = f(\phi) m_c \tag{3.28}$$

in which $f(\Phi)$ is the specific surface of the mineral-fluid contact area (surface area per unit mineral mass) expressed as a function of porosity. This function can be approximated according to eq. 3.19. Thus, substituting eq. 3.28 into eq. 3.6 leads to equation:

$$-\frac{dm_c}{dt} = k_c m_c f(\phi)(1 - F_s) \tag{3.29}$$

This function $\left(f(\varphi) = \left(\frac{1}{F_0}\right)\right.$ is inversely proportional to corrosion scale

$$\frac{-dm_c}{dt} = k_c m_c \frac{1}{F_0}(1 - F_s) \tag{3.30}$$

where k_c is the kinetic constant for formation of $FeCO_3$ given by Sun and Nesic, (2003);

$$k_c = e^{A_{(FeCO3)} - \frac{B_{(FeCO3)}}{RT}} \tag{3.31}$$

where

$$A_{(FeCO3)} = 21.3 J/mol$$

and $$B_{(FeCO3)} = 64{,}851.4 J/mol$$

Therefore,

$$-\frac{dm_c}{dt} = e^{A_{(FeCO3)} - \frac{B_{(FeCO3)}}{RT}} m_c \frac{1}{F_0}(1 - F_s) \tag{3.32}$$

Hence the final corrosion rate model equation is:

$$\frac{dm_c}{dt} = \exp\left(A - \frac{B}{R \cdot T}\right) \cdot \left[m_c \cdot \frac{1}{F_o} \cdot \left(1 - F_s\right)\right] \tag{3.33}$$

where:

F_s = Mineral Factor (Fe II content of the metal)

A_{FeCO3} = Constants in the Arrhenius-type equation for $K_{r(FeCO_3)}$

B_{FeCO3} = Constants in the Arrhenius-type equation for $K_{r(FeCO_3)}$

$K_{r(FeCO_3)}$ = Kinetic constants in the ferrous carbonate precipitation rate equation in 1/(mol s) for formation of Fe_2CO_3

F_0 = Corrosion scale

dm_c/dt = change in crystal mass per time

3.2 Simulation of the Mathematical Model

The model equation 3.33 is simulated using MathCAD as presented below:

CORROSION RATE MODEL SIMULATION USING MATHCAD

d(mc)/d(t) = kc*mc*(1/fo)*(1-Fs) # Scale Growth Dynamic Model

d(mc)/d(t) =exp(A-B/(R*T)*(mc*(1/Fo)*(1-Fs) # The Explicit Equations

g=mc_0-mc_i # Metal Weight Loss Dynamic Model

mc_0 = 0.001# Initial Mass of metal

kc = (A-(B/R*T))# Rate Constant by Arrhenius Equation

Fs = 0.88 # Mineral Factor (Iron II content of the pipe)

A = 21.3 # Kinetic Model Constant

B = 64851.8 # Kinetic Model Constant

Fo = 1.5 # Corrosion scale

T= 313 # Temperature of the Fluid

Initial values of the differential variables

mc(0) = 0.001# Initial Mass of metal

Initial/final values of the independent differentiation variable

t(0) = 0 # day

t(f) = 2500 # days

3.3 Data Gathering:

Data for this study were generated through the primary and secondary sources as follows:

- Primary data are the coupon test data collected from records. (see Appendix 'E')
- Secondary data are the data gathered with respect to the research questions through one-on-one interview with the selected staff of KRPC.

➢ Primary data:

Two sets of Coupon Test Data were obtained as primary data for this project.

(A) Group 'A' Coupon Test Data were obtained from KRPC inspection reports of 2007, 2008 and 2010. The plant was short down for Turn-Around Maintenance in 2009, so there was no data available for 2009. The data obtained in this group were limited to the Cooling Tower cooling water Return Line of KRPC. For continuity reason, Data obtained for 2010 may not be used in the validation of the model.

(B) Group 'B' Coupon Test results for points A to E of KRPC Cooling Water Pipeline were obtained from Odigure et al, (2002)

- Secondary Data.

Data under this group were obtained through interview of key personnel in the relevant department. A population of 50 staff was randomly considered from five key departments in KRPC; Production, Maintenance, Material Management [MMD], Engineering & Technical Services Department [ETDS], and Safety Unit. 80% of the staff that received the questionnaires responded and the whole 80% were used as the sample for this study.

Data Group 'A'. Corrosion Test Coupon Weight-Loss Evaluation of KRPC Cooling Tower Cooling Water Return Line.

Table 3.1 KRPC Corrosion test Coupons Weight –Loss Evaluation for September 2007

S/N	COUPON NO	INITIAL WEIGHT (gm) Wt1	FINAL WEIGHT (gm) Wt2	SURFACE AREA, A (dm^2)	LOSS IN WEIGHT (gm)	RESIDENT TIME, D (days)	CORROSION RATE (MDD)
1	008	11.3698	11.3394	0.31	0.0004	60	0.0215
2	041	11.4102	11.3874	0.31	0.0228	60	1.2258
3	068	11.5108	11.4764	0.31	0.0344	60	1.8495

where $MDD = \{(Wt_1 - Wt_2) \times 10^3\}/(A * D)$

Table 3.2 KRPC Corrosion test Coupons Weight –Loss Evaluation for November 2007

S/N	COUPON NO	INITIAL WEIGHT (gm) Wt1	FINAL WEIGHT (gm) Wt2	SURFACE AREA, A (dm^2)	LOSS IN WEIGHT (gm)	RESIDENT TIME, D (days)	CORROSION RATE (MDD)
1	019	11.3585	11.2997	0.31	0.0588	60	3.1613
2	057	11.5171	11.4592	0.31	0.0579	60	3.1129
3	070	11.5789	11.1919	0.31	0.0187	60	10.0538

where $MDD = \{(Wt_1 - Wt_2) \times 10^3\}/(A * D)$

Table 3.3 KRPC Corrosion test Coupons Weight –Loss Evaluation for January 2008

S/N	COUPON NO	INITIAL WEIGHT (gm) Wt1	FINAL WEIGHT (gm) Wt2	SURFACE AREA, A (dm^2)	LOSS IN WEIGHT (gm)	RESIDENT TIME, D (days)	CORROSION RATE (MDD)
1	001	11.5148	11.5122	0.31	0.0026	64	0.1310
2	027	11.5182	11.5147	0.31	0.0035	64	0.1764
3	060	11.4175	11.4147	0.31	0.0028	64	01411

where MDD = $\{(Wt_1 - Wt_2) \times 10^3\}/(A * D)$

Table 3.4 KRPC Corrosion test Coupons Weight –Loss Evaluation for March, 2008

S/N	COUPON NO	INITIAL WEIGHT (gm) Wt1	FINAL WEIGHT (gm) Wt2	SURFACE AREA, A (dm^2)	LOSS IN WEIGHT (gm)	RESIDENT TIME, D (days)	CORROSION RATE (MDD)
1	001	11.3927	11.1742	0.31	0.2185	60	11.7473
2	027	11.4827	11.2686	0.31	0.2141	60	11.5107
3	060	11.4987	11.2721	0.31	0.2266	60	12.1827

where MDD = $\{(Wt_1 - Wt_2) \times 10^3\}/(A * D)$

Table 3.5 KRPC Corrosion test Coupons Weight –Loss Evaluation for July, 2008

S/N	COUPON NO	INITIAL WEIGHT (gm) Wt1	FINAL WEIGHT (gm) Wt2	SURFACE AREA, A (dm^2)	LOSS IN WEIGHT (gm)	RESIDENT TIME, D (days)	CORROSION RATE (MDD)
1	008	11.3411	10.9345	0.31	0.4066	68	19.2884
2	041	11.3877	11.0019	0.31	0.3858	68	18.3017
3	068	11.4769	11.0717	0.31	0.4052	68	19.9373

where MDD = $\{(Wt_1 - Wt_2) \times 10^3\}/(A * D)$

Table 3.6 KRPC Corrosion test Coupons Weight –Loss Evaluation for March, 2010

S/N	COUPON NO	INITIAL WEIGHT (gm) Wt1	FINAL WEIGHT (gm) Wt2	SURFACE AREA, A (dm^2)	LOSS IN WEIGHT (gm)	RESIDENT TIME, D (days)	CORROSION RATE (MDD)
1	2731	8.7202	8.5561	0.174	0.1641	90	10.4789
2	2732	8.6999	8.5510	0.174	0.1489	90	9.5083
3	2733	8.7090	8.5489	0.174	0.1601	90	10.2234

where MDD = $\{(Wt_1 - Wt_2) \times 10^3\}/(A * D)$

Table 3.7. KRPC Corrosion test Coupons Weight –Loss Evaluation for May, 2010

S/N	COUPON NO	INITIAL WEIGHT (gm) Wt1	FINAL WEIGHT (gm) Wt2	SURFACE AREA, A (dm^2)	LOSS IN WEIGHT (gm)	RESIDENT TIME, D (days)	CORROSION RATE (MDD)
1	2586	8.6581	8.3480	0.174	0.3101	62	28.7449
2	2587	8.6544	8.3662	0.174	0.2882	62	26.7148
3	2588	8.6665	8.4439	0.174	0.2226	62	20.6348

where MDD = $\{(Wt_1 - Wt_2) \times 10^3\}/(A * D)$

Note that since there was no test result for the period of 2009 due to overall Turn Around Maintenance been carried out in KRPC. Hence, the data for 2010 were ignored for continuity reason.

Data Group 'B': Corrosion Coupon Test Results for points A to E of KRPC Cooling Water Pipeline. [Extract from *Odigure et al, 2002*]

Table 3.8 Corrosion test Coupons Weight –Loss Evaluation for point A [*see fig.2.7*]

COUPON LOCATION	INITIAL WEIGHT (gm) Wt_1	FINAL WEIGHT (gm) Wt_2	LOSS IN WEIGHT W_1-W_2 *(g)*	MDD (mg dm^{-2} day^{-1})
Top	11.1420	10.6999	0.4423	38
Middle	11.3683	11.0061	0.3622	31
Bottom	11.3758	10.9764	0.3994	34

Table 3.9 Corrosion test Coupons Weight –Loss Evaluation for point B [*see fig.2.7*]

COUPON LOCATION	INITIAL WEIGHT (gm) Wt_1	FINAL WEIGHT (gm) Wt_2	LOSS IN WEIGHT W_1-W_2 *(g)*	MDD (mg dm^{-2} day^{-1})
Top	10.5105	10.24498	0.2656	25
Middle	11.3436	11.1485	0.1951	18
Bottom	10.7109	10.2806	0.4303	40

Table 3.10 Corrosion test Coupons Weight –Loss Evaluation for point C [*see fig.2.7*]

COUPON LOCATION	INITIAL WEIGHT (gm) Wt_1	FINAL WEIGHT (gm) Wt_2	LOSS IN WEIGHT W_1-W_2 *(g)*	MDD (mg dm^{-2} day^{-1})
Top	11.4549	10.9209	0.5340	27
Middle	11.3630	10.6809	0.6821	34
Bottom	11.3397	10.4960	0.8437	42

Table 3.11 Corrosion test Coupons Weight –Loss Evaluation for point D [*see fig.2.7*]

COUPON LOCATION	INITIAL WEIGHT (gm) Wt_1	FINAL WEIGHT (gm) Wt_2	LOSS IN WEIGHT W_1-W_2 *(g)*	MDD (mg dm^{-2} day^{-1})
Top	11.1917	10.8860	0.3057	17
Middle	10.9742	10.6710	0.3032	17
Bottom	10.9262	10.6716	0.2546	14

Table 3.12 Corrosion test Coupons Weight –Loss Evaluation for point E [*see fig.2.7*]

COUPON LOCATION	INITIAL WEIGHT (gm) Wt_1	FINAL WEIGHT (gm) Wt_2	LOSS IN WEIGHT W_1-W_2 *(g)*	MDD (mg dm^{-2} day^{-1})
Top	11.5788	11.1636	0.4152	26
Middle	11.5119	11.2324	0.2795	18
Bottom	11.5893	11.3273	0.2620	16

Note that figures A, B, C, D and E are the points of coupon installation along the cooling water pipeline

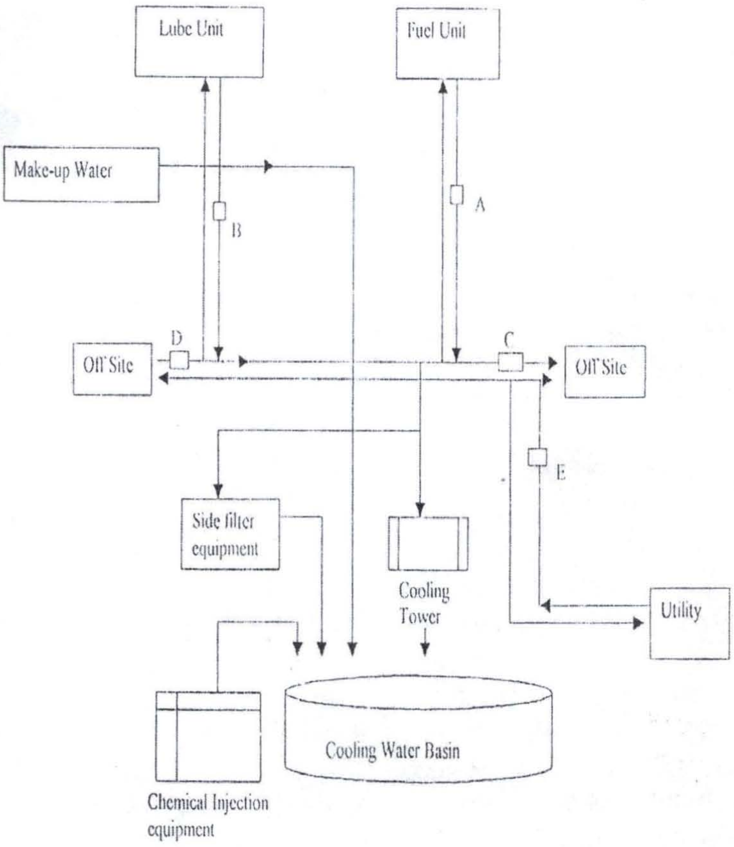


Fig.2.17 Schematic diagram showing pipeline as shown below: the points of coupon installation along the cooling water pipeline. *(Odigure et al, 2002)*

3.4 Calculations of Corrosion Rate

The corrosion rate is calculated for each coupon using the initial and final weights, control weight loss, coupon surface area, and density of the alloy and exposure time in the formula. The rate of corrosion is expressed in several different forms. The simplest in dimensionless units is the percentage change in weight of a coupon in an exposed time interval. This figure is usually extrapolated to give the percentage change per annum. The corrosion rate calculated using corrosion coupons assumes uniform corrosion across the coupon (e.g. uniform corrosion of the pipe wall at the monitoring point). This approximation is acceptable for most circumstances to determine the average rate of corrosion. www.caproco.com. Corrosion Rate calculation from the coupon test by KURITA is given as:-

Corrosion Rate, $$\text{MDD} = \frac{(Wt_1 - Wt_2) * 10^3}{A * D} \tag{2.13}$$

where,

MDD = mg dm^{-2} day^{-1}

Wt_1 = Initial Coupon Weight, (gm)

Wt_2 = Final Coupon Weight, (gm)

A = Exposed Surface Area, (dm^2)

D = Days of Exposure, (days). i.e. resident time

Acceptable Kurita Standard: - $0 - 10MMD,\ (Very\ Good),\ \ 10 - 20MDD, (Good),$

$21 - Above,\ Not\ Satisfactory$

CHAPTER FOUR

4.0 RESULTS

The primary data used in this project work were collected from the existing inspection records in KRPC and that according to Odigure, (2002). These primary data were basically the data used in the simulation of the corrosion rate model equation developed in chapter three.

The experimental and simulated results as well as the results of statistical analyses are presented as Tables 4.1, 4.2, 4.3 and 4.4 respectively. Figure 4.1 shows the graph of weight loss versus time for both experimental and simulated samples for corrosion in KRPC Cooling Water Pipeline while figure 4.2 shows the graph of weight loss versus time for both experimental and simulated samples for corrosion in KRPC Cooling Tower Water Return Line.

The secondary data are the statistical data obtained from interview of some key personnel in KRPC. These data are presented in Tables, 5.1, 5.2, 5.3 and 5.4 respectively and has been used to generate the pie charts in figures 5.1, 5.2, 5.3 and 5.4 respectively. These are discussed under brainstorming findings and discussions in this chapter.

Table 4.1: Weight Loss of Metal and Time for Corrosion in KRPC Cooling Water Pipeline for both Laboratory samples and simulated values.

Time (days)	Experimental Mass of Crystal Dissolved (gm)	Simulated Mass of Crystal Dissolved (gm)
0	0	0
35	0.2656	0.302
73	0.4423	0.387
123	0.4152	0.322
180	0.3057	0.357
245	0.5346	0.392

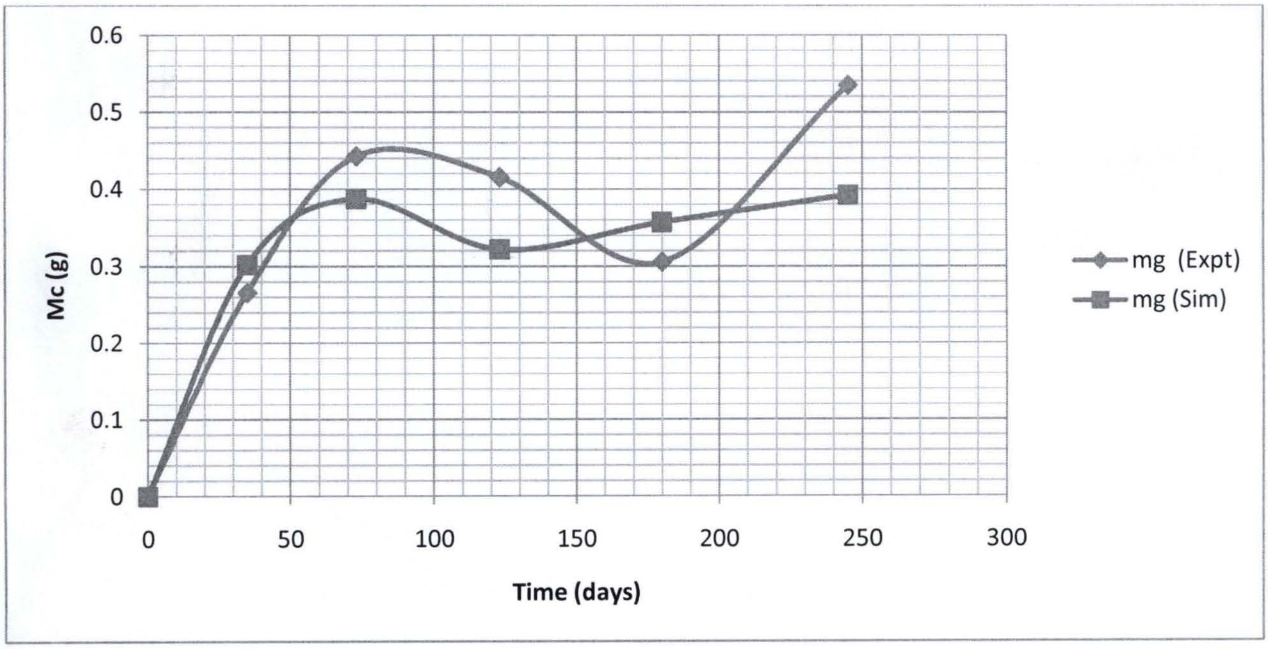


Figure 4.1: A graph of Weight Loss of Metal versus Time for Corrosion in KRPC Cooling Water Pipeline at Temperature of 333K.

Table 4.2: Statistical Analysis for Comparing the Experimental to the Simulated Results for Corrosion in Cooling Water Pipeline

Statistical Parameters	**Value (Cooling Water Pipeline)**
Correlation Coefficient	0.9227
Adjusted Correlation Coefficient	0.8513
Covariance	0.0213
Standard Error	0.0638
Standard Deviation	0.1550
Variance	0.0240

Table 4.3: Weight Loss of Metal and Time for corrosion in KRPC Cooling Tower Water Return Line for both Laboratory Sample and Simulated value.

Time (days)	Experimental Mass of Crystal Dissolved (gm)	Simulation Mass of Crystal Dissolved (gm)
0	0	0
35	0.0453	0.2656
73	0.2423	0.4423
123	0.2240	0.4152
180	0.1106	0.3057
245	0.2734	0.5346

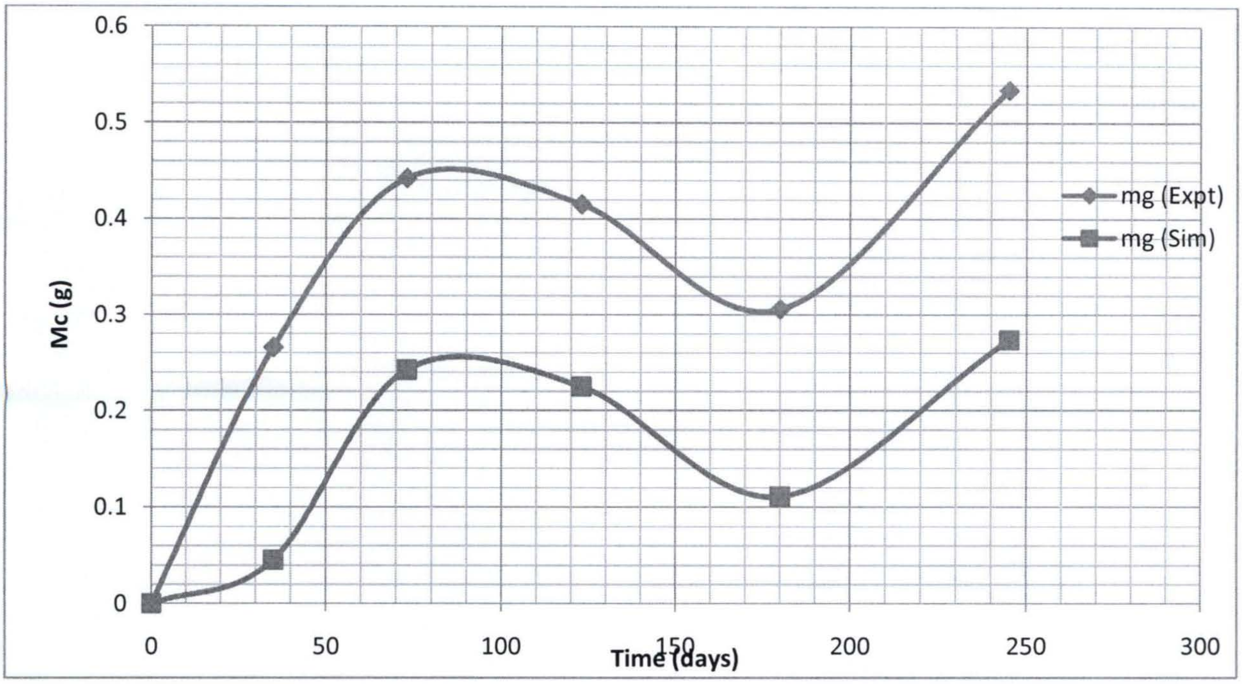


Figure 4.2: A graph of Weight Loss of Metal versus Time for Corrosion in KRPC Cooling Tower Water Return Line at Temperature of 333K.

Table 4.4: Statistical Analysis for Comparing the Experimental to the Simulated Results for Corrosion in Cooling Water Return Line respectively

Statistical Parameters	Value Cooling Water Return
Correlation Coefficient	0.9339
Adjusted Correlation Coefficient	0.8722
Covariance	0.0165
Standard Error	0.0749
Standard Deviation	0.1670
Variance	0.0279

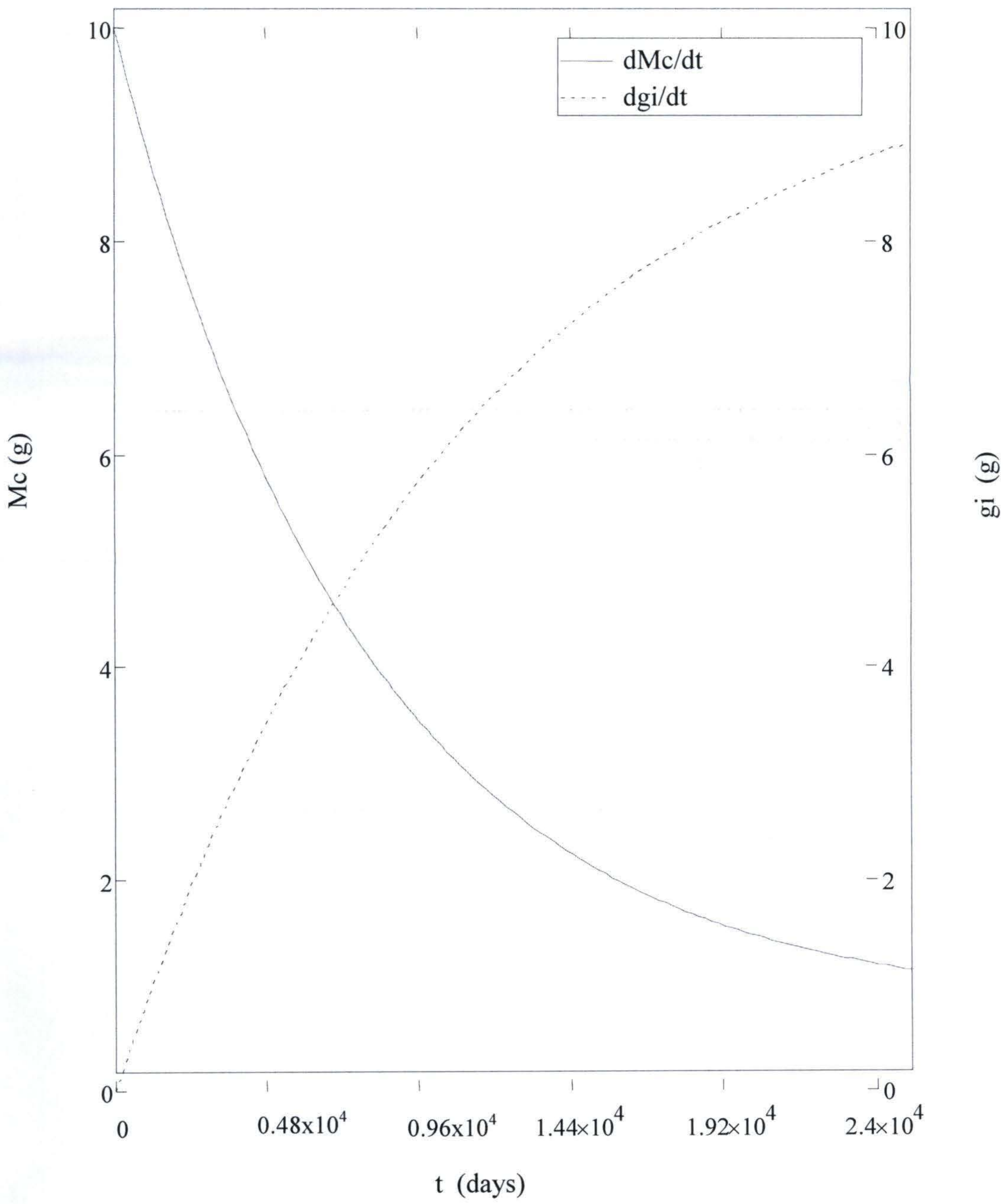


Figure 4.3: Mass of Metal and Weight Loss of Metal and Time for Corrosion in KRPC Cooling Water Pipeline at constant T = 333K; $F_o = 1.9462$; $F_s = 1.5$; and $P_{CO2} = 0.5$ respectively.

4.1 Effects of Temperature on Corrosion Rate:

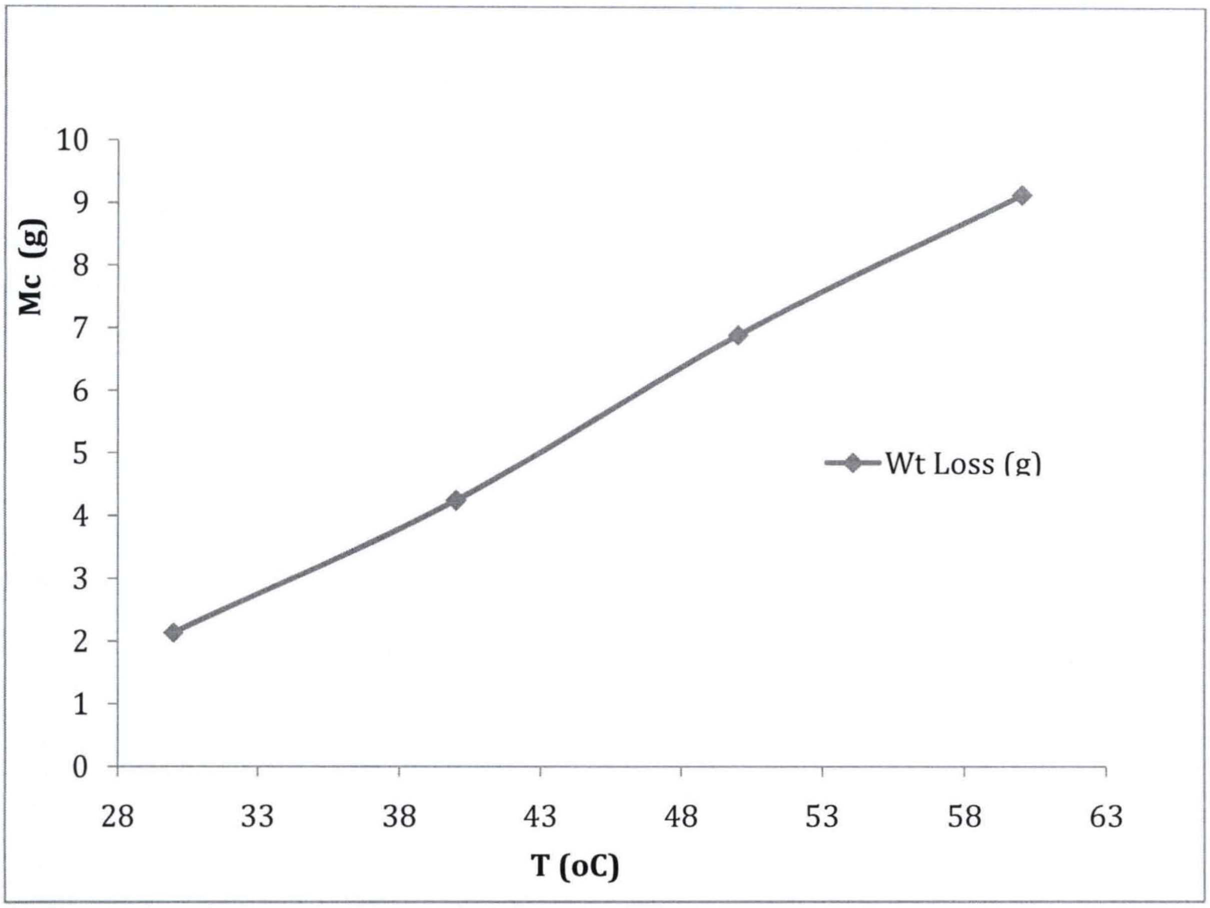


Figure 4.4: Variation of Weight Loss of Metal and Temperature for Corrosion in Cooling Water Pipeline at constant Fo = 1.9462; and Fs = 1.5; pH = 6.6 and P_{CO2} = 0.5 respectively.

4.2 Effects of Corrosion Scale on Corrosion Rate:

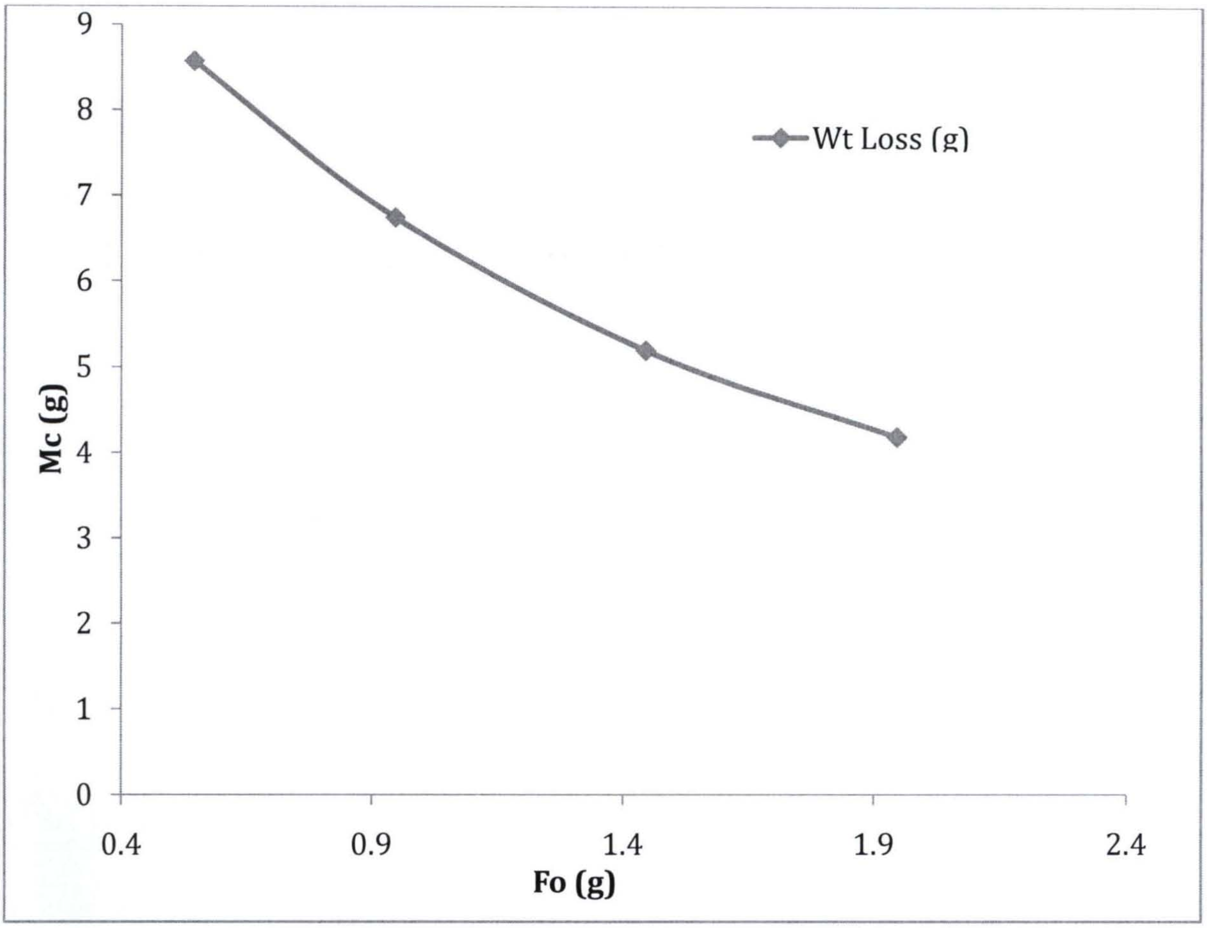


Figure 4.5: Variation of Weight Loss of Metal and Corrosion scale at 240days for Corrosion in Cooling Water Pipeline at constant T = 333K; Fs = 1.5; pH = 6.6 and P_{CO2} = 0.5 respectively

4.3 Effects of Iron (II) Contents on Corrosion Rate:

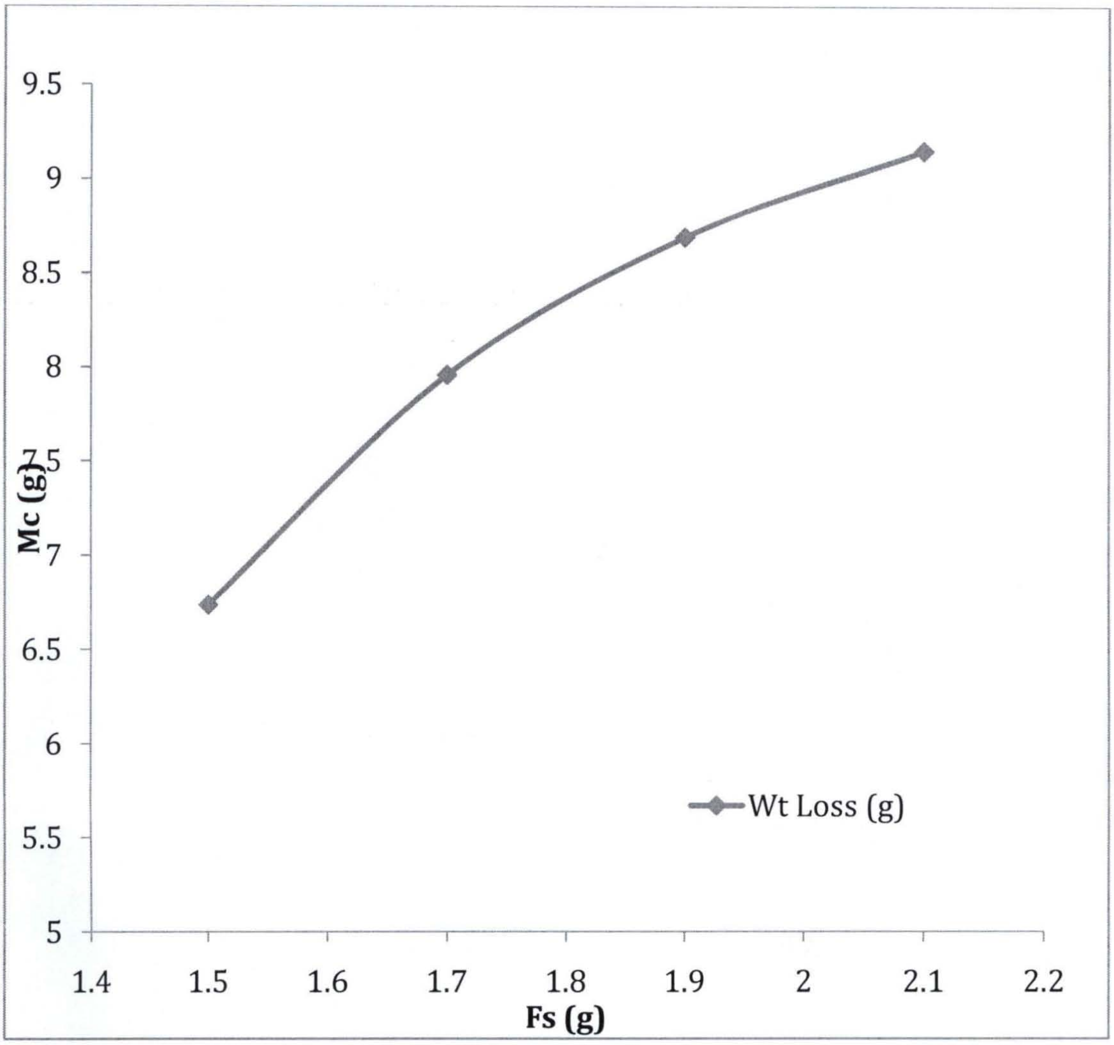


Figure 4.6: Variation of Weight Loss of Metal and Mineral Factor (Fe II content) at 240 days for Corrosion in Cooling Water Pipeline at constant T = 333K; Fo = 1.9462; pH = 6.6 and P_{CO2} = 0.5 respectively.

CHAPTER FIVE

5.0 DISCUSSION, CONCLUSION AND RECOMMENDATIONS

5.1 Discussion of Results

Mathematical model of corrosion rate (weight loss of crystal per time) in KRPC has been developed. This study focuses on the corrosion rate of mild steel in KRPC cooling water pipelines. The corrosion rate model equation as shown in equation 3.33 was simulated using MathCAD software (see Appendix A). The experimental and simulated results are presented on Tables 4.1 and 4.2 respectively while the results of statistical analyses are shown in Table 4.3.

The model equation 3.33 has been validated using Tables 4.1 and 4.2 as shown in Figures 4.1 and 4.2 respectively. The model has been applied to simulate the rate of general corrosion of carbon steel in KRPC cooling water system under different selected conditions that are contributing factors to corrosion problems in oil industries. The effects of these factors on the corrosion rate in cooling water system can be viewed in Appendices 'B', 'C' and 'D' respectively.

Figure 4.3 shows the variation of the mass of dissolved crystals of the corroded metal and the weight loss of the metal with respect to time at assumed conditions: temperature 'T' = 333K; corrosion scale 'Fo' = 1.9462; Iron (II) contents 'Fs' = 1.5 and at partial pressure 'P_{CO2}' = 0.5 respectively. It is seen that the mass of the corroded metal and the weight loss of the metal are directly proportional. That is, the residual mass of the corroded metal "Mc (g)" decreases as the weight loss of the metal due to corrosion "gi (g)" increases with time. Hence, the corrosion rate is time dependent. As corrosion continues, a time comes when the rate of weight loss "dgi/dt" becomes equal to the mass of the corroded metal left "dMc /dt" -half life. Beyond the half life point, the rate of corrosion increases astronomically. The point at which "Mc (g)" intercepts "gi (g)" is the signal point that the corrosion allowance of the pipe has been exceeded. Therefore, the integrity of the pipes cannot be guaranteed any longer. This intersection point under the prevailing conditions indicates the recommended time for the replacement of the pipes to ensure safety. This is due to the metal having lost useful resistance to corrosion hence its susceptibility to the corrosive environment is high. At this point, the metal must be changed as it will no longer carry on with its desired services. Below the half life point, good management could render the metal usable. For this reason, anticorrosion chemicals are required in the cooling water system to slow down the rate of corrosion. Since the variable growth or decay rate is proportional to its size, as shown in the experimental data results obtained, the corrosion rate in the cooling tower system increases with the years of exposure to corrosion agents. If the anticorrosion agent is present in the steel caring the cooling water, corrosion rate will be limited to the anticorrosion chemical present in the steel caring the cooling water.

Figure 4.4 shows the variation of weight loss of metal and temperature for corrosion in cooling water system. The condition was assumed to take place at various temperature ranges from 301K to 333K while every other factors contributing to corrosion rate were kept constant. This shows that corrosion rate increases with temperature. In other word, corrosion rate of metal increases with increase in temperature.

Figure 4.5 shows the variation of weight loss of metal and corrosion scale (Fo) for the corrosion in cooling water system. The condition was assumed to take place at different weight of corrosion scale while every other factors contributing to corrosion problems were kept constant. The result shows that weight loss of the metal decreases as corrosion scale increases. As scale on the mild steel surface increases, the corrosion rate reduces due to formation of strongly adhering black scale on the steel surfaces.

Figure 4.6 shows the variation of weight loss of metal against mineral factor (Fe II content) for corrosion in cooling water pipeline. The condition was assumed to take place at various Iron (II) content ranges while every other factors contributing to corrosion were kept constant. The result obtained shows that the weight loss increases as the mineral contents increases. This observation can be liked with the electrochemical processes of aqueous CO_2 corrosion of carbon steel involving the anodic dissolution of iron and the cathodic evolution of hydrogen shown in equation 2.44 of the chapter two of this thesis. This also shows that time variation scale dissolution is a function of specific surface of the mineral-fluid contact area. (Anderko and Young, 2002).

5.1.1 Effect of Temperature on corrosion rate

The MathCAD simulated results of the effect of temperature on corrosion rate from the developed equation are as shown under appendix 'B'. The condition was set to take place at varying temperature ranges; 303K, 313K, 323K and 333K respectively, while every other factors were kept constant at Mineral content (F_s) = 1.5 and Corrosion scale (F_o) = 1.9462. The results obtained for each varying temperature shows that the weight loss increased with increase in temperature as can be seen in Appendices 'B.1', 'B.2', 'B.3', and 'B.4' respectively. This shows that corrosion rate increases with temperature.

5.1.2 Effect of Corrosion Scale on corrosion rate

The MathCAD simulated results of the effect of corrosion scale on corrosion rate from the developed equation are as shown under appendix 'C'. The condition was set to take place at varying Corrosion scales: 0.5462g, 0.9462g, 1.4462g and 1.9642g respectively. Mineral content 'F_s' and temperature 'T' were kept constant at 1.5g and 313k respectively while every other factors were kept constant at their initial conditions. The results obtained for each varying corrosion scale shows that the weight loss decreased as corrosion scale increased as can be seen in Appendices 'C.1', 'C.2', 'C.3', and 'C.4' respectively. This shows that corrosion rate decreases with increasing corrosion scale. This actually agrees with the findings that corrosion rates reduces as scale on the mild steel surface increases, because of the formation of strongly adhering black scale on the mild steel surface (Anderko and Young, 2002). Under certain conditions surface layers can become very protective and reduce the rate of corrosion. In CO_2 corrosion when the concentrations of Fe^{2-} and CO_3^{2-} ions exceed the solubility limit, they form solid ferrous carbonate according to Sun, et al, 2009 as written in equation (2.54):

$$Fe^{2+} + CO_3^{2-} \xleftrightarrow{K_{sp(FeCO3)}} FeCO_{3(s)} \qquad (2.54)$$

Where,

$K_{sp(FeCO3)}$ Is the solubility product constant for ferrous carbonate. (Sun, et al, 2009)

The ferrous carbonate layer can slow down the corrosion process by presenting a diffusion barrier for the species involved in the corrosion process and thereby changing the conditions at the steel surface. The effective protectiveness of a solid ferrous carbonate layer depends on its porosity which hangs in the balance of the precipitation rate and the underlying corrosion rate. For high precipitation rates, and low corrosion rates, a dense and protective ferrous carbonate layer is obtained. (Sun and Nesic, (2008).

5.1.3 Effect of Iron (II) content on corrosion rate:

The MathCAD simulated results of the effect of iron (II) contents of the steel on corrosion rate from the developed equation are as shown under appendix 'D'. The condition was set at varying Fe (II) oxide contents (Fs): 1.5g, 1.7g, 1.9g and 2.1g respectively, while corrosion scale 'F_o' and temperature 'T' were maintained at initial condition 0.9462g and 313k respectively. Other parameters were also maintained constant at their initial condition. The results obtained for each varying corrosion scale shows that the weight loss decreased as corrosion scale increased as can be seen in Appendices 'D.1', 'D.2', 'D.3', and 'D.4' respectively. The result shows that the metal weight loss increased as the Fe (II) content of the metal increases. Hence, the corrosion rate increases with increase in mineral factor.

5.1.4 Model Prediction and Validation

It is mainly used in settings when the corrosion rate is worse, and to estimate how accurately this model will perform in any other cooling water facilities/pipelines both in the oil industry and in any other industry. To reduce variability, one round of cross-validation done was achieved by interpolating the data obtained from KRPC sample of data into complementary subsets to obtain the exact days that as it was in the original data that was used to first simulate the model, performing the analysis on one subset (called the *training set*), and validating the analysis on the other subset (called the *validation set* or *testing set*). Cross-validation is important in guarding against testing hypotheses suggested by the data (called Type III errors"), especially where further samples are hazardous, costly or unavailable.

Statistical parameters such as correlation coefficient, adjusted correlation coefficient, covariance and standard error were used to compare the result of the experiment to the simulation result.Table 4.3 shows the statistical precision analysis of the model equation being validated using experimental data obtained by Odigure et-al (2002). The correlation coefficient of obtained was 92.27% and the R-Square (adjusted coefficient of determination) value obtained was 85.13%, which is high suggesting that the relationship between the predictor and response variables is linear. The R-Square value of 85.13% implies that only 85.13% of the variability in the output could be captured and explained by this model. The co-variation and standard error in the model equation are 0.0213 and 0.0638 shows that the mathematical model is accurate. Finally, the low standard deviation of 0.1550 and the very low variance value of 0.0240 is a proof that the results are in agreement and the validation is correct.

It is assumed that no corrosion inhibitor was injected into the system and no pretreatment of the water. The pH of the system was kept constant at 6.6 and the effect on corrosion was neglected. Other variable factors responsible for corrosion were kept constant; temperature at constant 333K, Corrosion scale (F_o) at constant 1.9462, Mineral factor i. e. Fe II contents (F_s) at constant 1.5, and the P_{CO2} at a constant value 0.5. The plot obtained under these conditions as shown in Fig 4.3 shows that the weight losses of the metal increases with time while the mass of the metal decreases also with time respectively. This phenomenon explained that corrosion occurs with time even when every other factors responsible for corrosion were assumed constant. Hence, the mild steel loses weight with respect to time due to presence of CO_2 and water in the cooling system.

5.1.5 Findings and Discussions

The statistical data obtained from interview of some key personnel in KRPC are grouped as secondary data based on the subject question (see appendix 'F'). These data are tabulated as shown in Table 5.1, 5.2, 5.3 and 5.4 respectively. They are used to generate the pie charts shown in figures 5.1, 5.2, 5.3 and 5.4 respectively.

5.1.5.1 Rating the Performance of KRPC Production Plant: How do you rate KRPC plant performance?

Table 5.1 Statistical Rating of Performance of KRPC Production Plant

Answers	No of responses	Percentages
Good	4	10%
Fair	26	65%
Bad	8	20%
Do Not Know	2	5%
TOTAL	40	100%

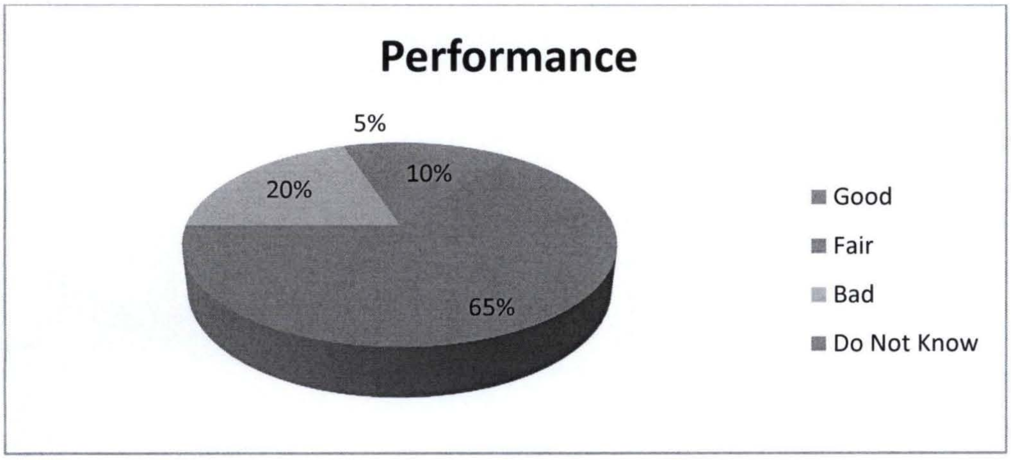


Fig 5.1 Pie Chat of Statistical rating of performance of KRPC production plant

5.1.5.2 Rating the Integrity of KRPC Equipments: How can you rate the integrity of the equipments in KRPC?

Table 5.2 Statistical Rating of Integrity of KRPC Equipments

Answers	No of responses	Percentages
Good	2	5%
Fair	20	50%
Bad	16	40%
Do Not Know	2	5%
TOTAL	40	100%

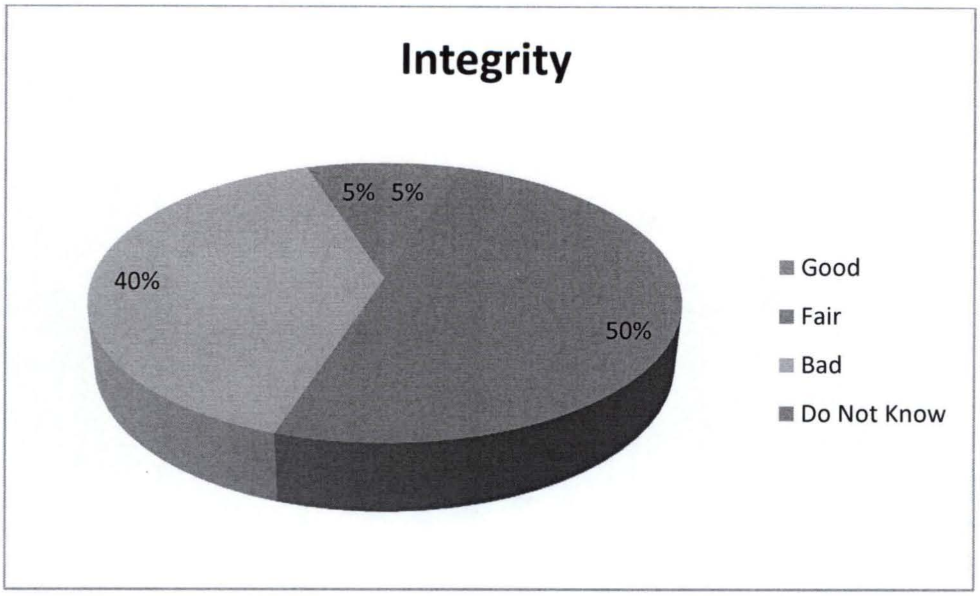


Fig 5.2 Pie Chat of statistical rating of integrity of KRPC equipments.

5.1.5.3 Rating of KRPC Turn Around Maintenance (TAM): How do you rate KRPC's TAM?

Table 5.3 Statistical Rating of KRPC Turn-Around-Maintenance

Answers	No of responses	Percentages
Good	4	10%
Fair	12	30%
Bad	20	50%
Do Not Know	4	10%
TOTAL	40	100%

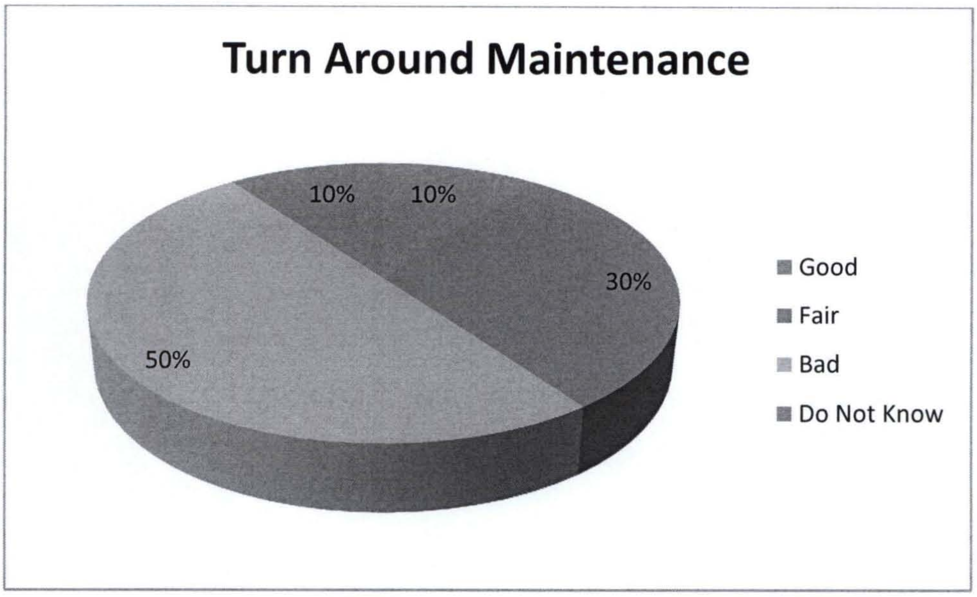


Fig 5.3 Pie Chat of statistical rating of KRPC Turn-Around-Maintenance.

5.1.5.4 General Assessment of Safety in KRPC Production Plant:

How do you rate the Safety in KRPC Production Plants in general?

Table 5.4 Statistical Rating of Safety in KRPC Production Plant

Answers	**No of responses**	**Percentages**
Good	6	15%
Fair	16	40%
Bad	16	40%
Do Not Know	2	5%
TOTAL	40	100%

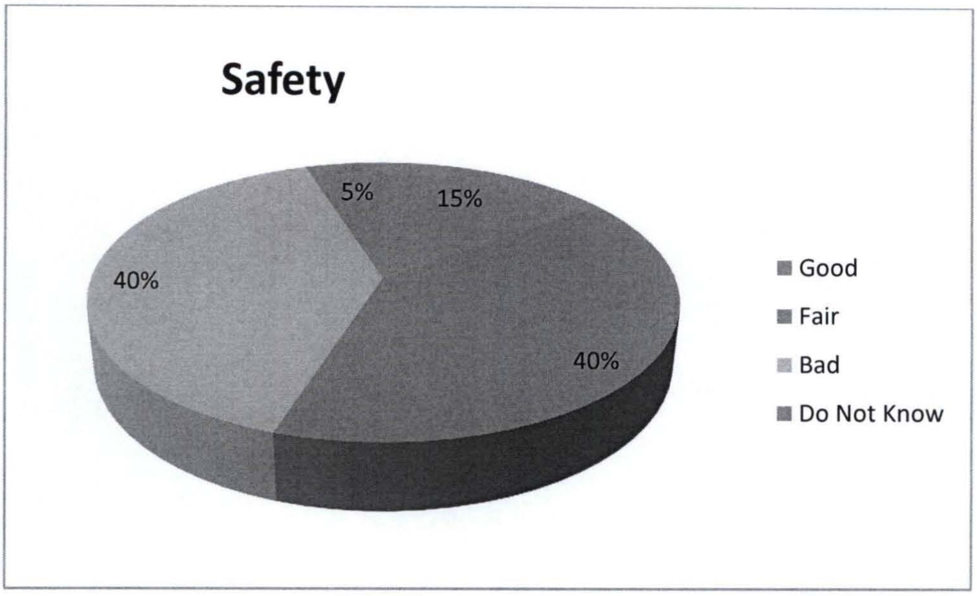


Fig.5.4 Pie Chat of statistical rating of safety in KRPC production plant.

5.1.6 Reasons for poor performance by KRPC

Many reasons were identified to be responsible for the delay in completing the in-house work scope as scheduled. Poor performance by KRPC is particularly due to the following reasons:

- Inadequate number of Plant Inspectors to perform prompt inspection on heat exchangers especially during hydro tests;
- Inadequate number of heavy duty equipment like tube bundle pullers and cranes to quickly pull out or re-install tube bundles.
- Excessive pitting corrosion identified during inspection of the equipment leading to severe leaks during hydro test;
- Shortage of fresh tubes in the Warehouse for the re-tubing of corroded, leaking tube bundles not stoppable by plugging.

5.1.7 Constraints to corrosion monitoring in KRPC

Following are the constraints to corrosion monitoring in KRPC: [Sources: staff response to questionnaire shared and one-on-one interview with selected staff of KRPC in 2009]

- Coupon tests have been limited due to lack of apparatus such as: coupons/coupon columns, hot air dryer, weighing balance, pH meter, agitating machine and reagents such as: corrosion inhibitors, Toluene, KURIZET S-204 and KURIZET T-225, etc.
- Corrater probes have not been used because at the time they were handed over at completion of plant construction project, there was no formal training of any inspector on how to use them. Lately, the measuring devices got burnt during the fire incident of ETSD caravan in 1993.
- Corrosion monitoring by thickness survey is hindered in some cases due largely to inadequate Ultrasonic Thickness Meters (UTM). Currently only two meters are functional. These meters use only cold probes. Hot probes are not available.
- Lack of training for plant inspectors to cope with modern methods of on-line corrosion monitoring.
- Non-release of vessels at the scheduled time for corrosion monitoring.
- Inaccessibility to current technical journals, codes, specifications and standards for updating knowledge and ease of references.
- Inadequate operational vehicles to cover entire plant equipment.
- Corrosion monitoring systems were completely absent for storage tanks.

5.2 Conclusions

The validation of the model developed in this work shows that there is a remarkable agreement between the experimental result and the model simulation result which shows that the model is valid for the equipment under study. This study also concludes that:

i. Corrosion rate increases with time; it increases with increase in temperature of the fluid passing through the pipe; and also increases with increase in mineral factor (Iron II content) of the mild steel pipe.

ii. Corrosion rate decreases with increase in corrosion scale

iii. Lack of proper maintenance and inadequate monitoring of equipment is responsible for high corrosion level in KRPC which if not attended to on time is a major threat and potential hazard to the safety of the plant; integrity of physical assets and risks to the environment.

5.3 Recommendations

Based on the analysis carried out the followings have been recommended:

1. The model should be modified to include effect of pH and free water on rust scale dissolution.

2 The model should be modified also to include effect of change in properties of the transportation fluid on rust scale dissolution

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www.onepetro.org

www.hsebooks.co.uk

www.mini-refineries.com

webmaster@nace.org

APPENDIX A

A.1 MODEL VALIDATION

The simulated data was validated by using statistical analysis to compare it to experimental (KRPC cooling water pipeline) data

The Experimental and Simulated Data are presented bleow:

data :=

	0	1	2
0	0	0	0
1	35	0.266	0.302
2	73	0.442	0.387
3	123	0.415	0.322
4	180	0.306	0.357
5	245	0.535	0.392

The matrix data used in this work is:

$X := \text{data}^{\langle 0 \rangle}$ $\quad Y := \text{data}^{\langle 1 \rangle}$ $\quad Y_1 := \text{data}^{\langle 1 \rangle}$ $\quad Y_2 := \text{data}^{\langle 2 \rangle}$

Number of data points:

Regression Statistics

Correlation coeff. $\text{corr}(Y_1, Y_2) = 0.9227$

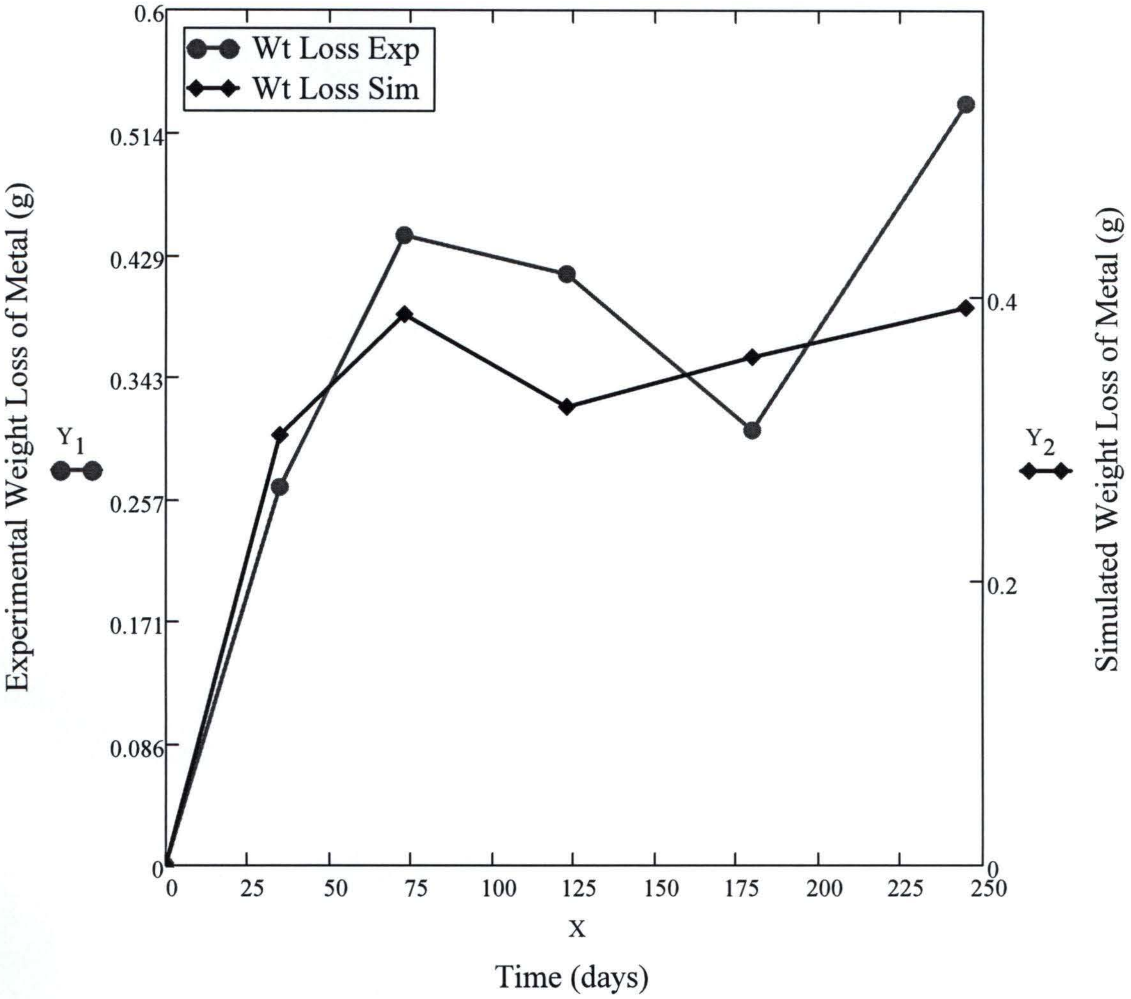
R² $\text{corr}(Y_1, Y_2)^2 = 0.8513$

Covariance $\text{cvar}(Y_1, Y_2) = 0.0213$

Standard Error $\text{stderr}(Y_1, Y_2) = 0.0638$

Standard Deviation $\text{stdev}(Y_1, Y_2) = 0.155$

Variance $\text{var}(Y_1, Y_2) = 0.024$


Wt Loss Exp
Wt Loss Sim
Experimental Weight Loss of Metal (g)
Simulated Weight Loss of Metal (g)
Y1
Y2
0.6
0.514
0.429
0.343
0.257
0.171
0.086
0
0.4
0.2
0
0
25
50
75
100
125
150
175
200
225
250
X
Time (days)

APPENDIX A

A.1b MODEL VALIDATION

The simulated data was validated by using statistical analysis to compare it to experimental (KRPC cooling water Return Line) data

The Experimental and Simulated Data are presented bleow:

data :=

	0	1	2
0	0	0	0
1	35	0.065	0.295
2	73	0.242	0.492
3	123	0.225	0.462
4	180	0.111	0.34
5	245	0.273	0.594

The matrix data used in this work is:

$X := data^{\langle 0 \rangle}$ $Y := data^{\langle 1 \rangle}$ $Y_1 := data^{\langle 1 \rangle}$ $Y_2 := data^{\langle 2 \rangle}$

Number of data points:

Regression Statistics

Correlation coeff. $\mathrm{corr}(Y_1, Y_2) = 0.9508$

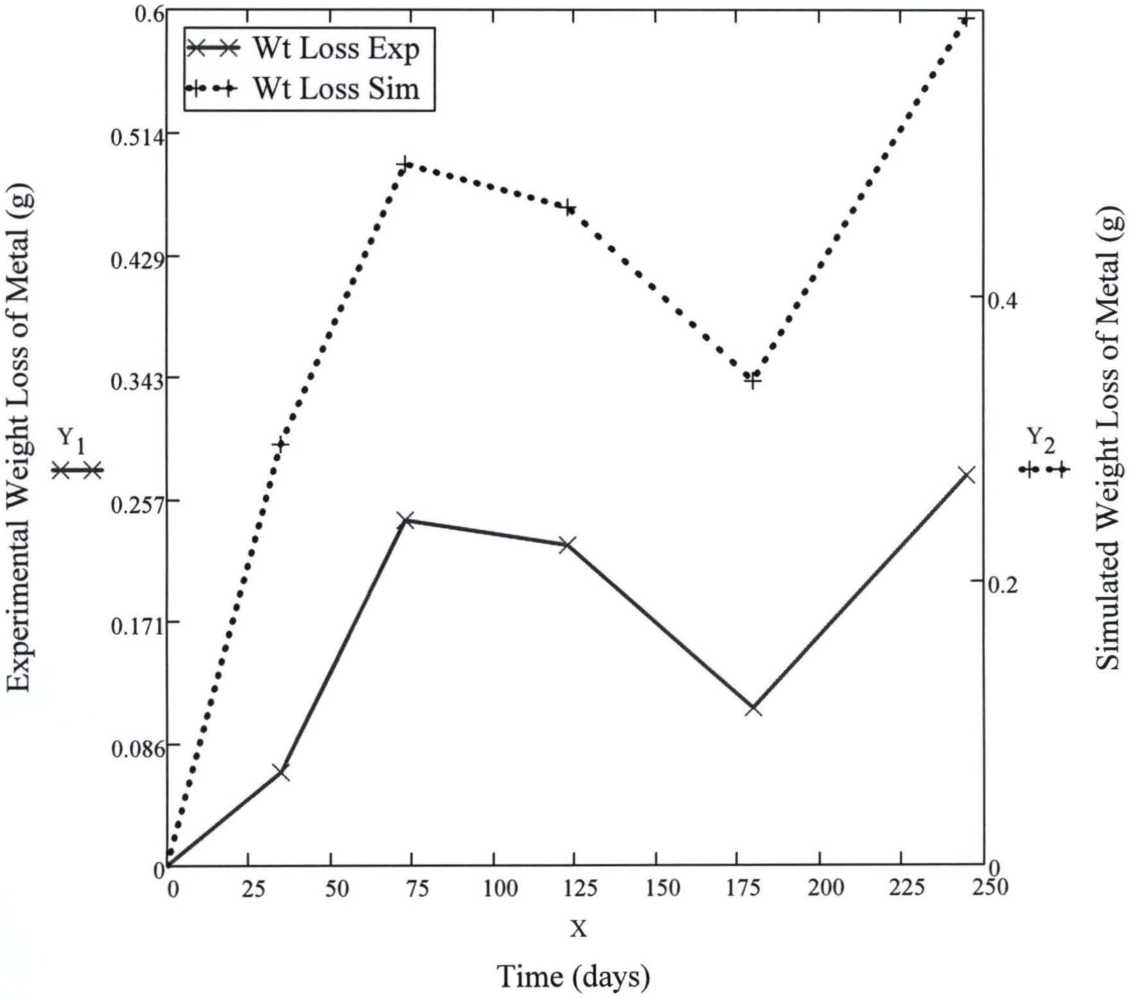
R² $\mathrm{corr}(Y_1, Y_2)^2 = 0.904$

Covariance $\mathrm{cvar}(Y_1, Y_2) = 0.0182$

Standard Error $\mathrm{stderr}(Y_1, Y_2) = 0.0721$

Standard Deviation $\mathrm{stdev}(Y_1, Y_2) = 0.1851$

Variance $\mathrm{var}(Y_1, Y_2) = 0.0343$



Wt Loss Exp
Wt Loss Sim
0.6
0.514
0.429
0.343
0.257
0.171
0.086
0
Experimental Weight Loss of Metal (g)
Y_1
Y_2
Simulated Weight Loss of Metal (g)
0.4
0.2
0
0
25
50
75
100
125
150
175
200
225
250
X
Time (days)

APPENDIX A

A.2 SIMULATION OF CORROSION RATE MODEL EQUATION DEVELOPED IN CHAPTER THREE:

The model equation developed in chapter three is simulated below using Mathcad.

The simulated results are also shown below the mathcad simulation algorithm.

This involves solving the following differential equation:

$$\frac{dm_c}{dt} = k_c \cdot m_c \cdot F_o \cdot (1 - F_s) \qquad k_{r(FeCO_3)} = e^{A_{(FeCO_3)} - \frac{B_{(FeCO_3)}}{RT_k}}$$

$$k_c = \exp\left(A - \frac{B}{R \cdot T}\right)$$

Defining the given data: $F_s := 1.5$ $A_c := 1$ $A_m := 3$

$A := 21.3$ $B := 64851.4$ $R := 8.314$ $T := 331$

The rate constant is: $k_c := \exp\left(A - \frac{B}{R \cdot T}\right)$ $F_o := 1.9462$

The initial condition is: $m_{c_0} := 10$ $n := 2$

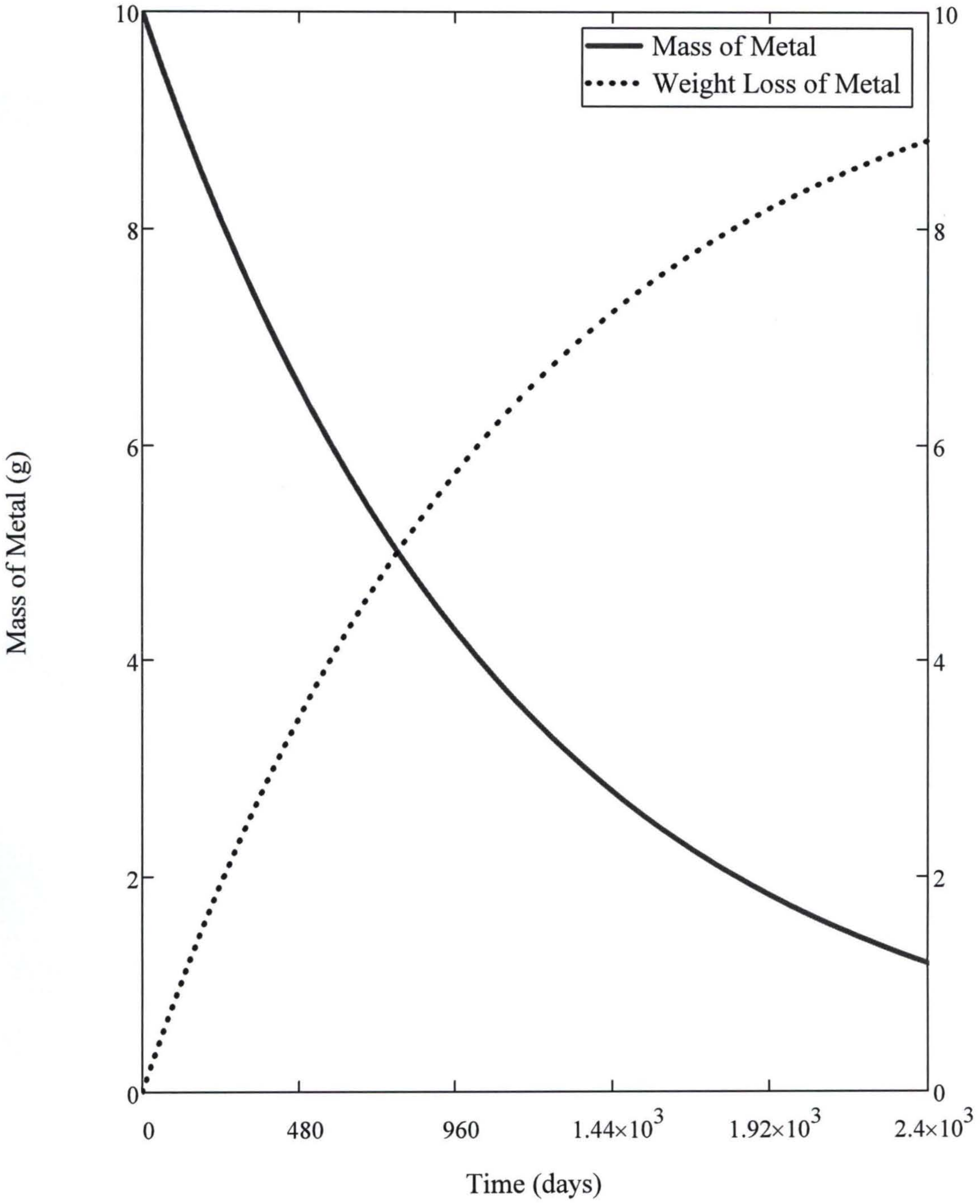
The differential function is: $D(t, m_c) := \left[k_c \cdot m_c \cdot \frac{1}{F_o} \cdot (1 - F_s)\right]$

Defining the period and steps: $T := 120$ $N := 120$

Setting up the integration variable: $Sol := \text{rkfixed}(m_c, 0, T, N, D)$

Plotting the solution: $i := 0..N$ $t_i := Sol_{i,0}$ $m_{c_i} := Sol_{i,1}$

$g_i := 10 - m_{c_i}$


Mass of Metal
Weight Loss of Metal
Mass of Metal (g)
Time (days)
0
2
4
6
8
10
0
480
960
1.44×10^3
1.92×10^3
2.4×10^3

m_{c_i} =	t_i =	g_i =
10	0	0
9.737	1	0.263
9.481	2	0.519
9.231	3	0.769
8.989	4	1.011
8.752	5	1.248
8.522	6	1.478
8.298	7	1.702
8.08	8	1.92
7.867	9	2.133
7.66	10	2.34
7.459	11	2.541
7.263	12	2.737
7.071	13	2.929
6.885	14	3.115
6.704	...	...
6.528		
6.356		
...		

APPENDIX B.1

B.1 EFFECT OF TEMPERATURE ON CORROSION RATE FROM THE DEVELOPED MODEL EQUATION

Temperature = 303 K

This involves solving the following differential equation:

$$\frac{dm_c}{dt} = k_c \cdot m_c \cdot F_o \cdot (1 - F_s) \qquad k_{r(FeCO_3)} = e^{A_{(FeCO_3)} - \frac{B_{(FeCO_3)}}{RT_k}}$$

$$k_c = \exp\left(A - \frac{B}{R \cdot T}\right)$$

Defining the given data: $F_s := 1.5$ $\quad A_c := 1$ $\quad A_m := 3$

$A := 21.3$ $\quad B := 64851.4$ $\quad R := 8.314$ $\quad T := 303$

The rate constant is: $k_c := \exp\left(A - \frac{B}{R \cdot T}\right)$ $\quad F_o := 1.9462$

The initial condition is: $m_{c_0} := 10$ $\quad n := 2$

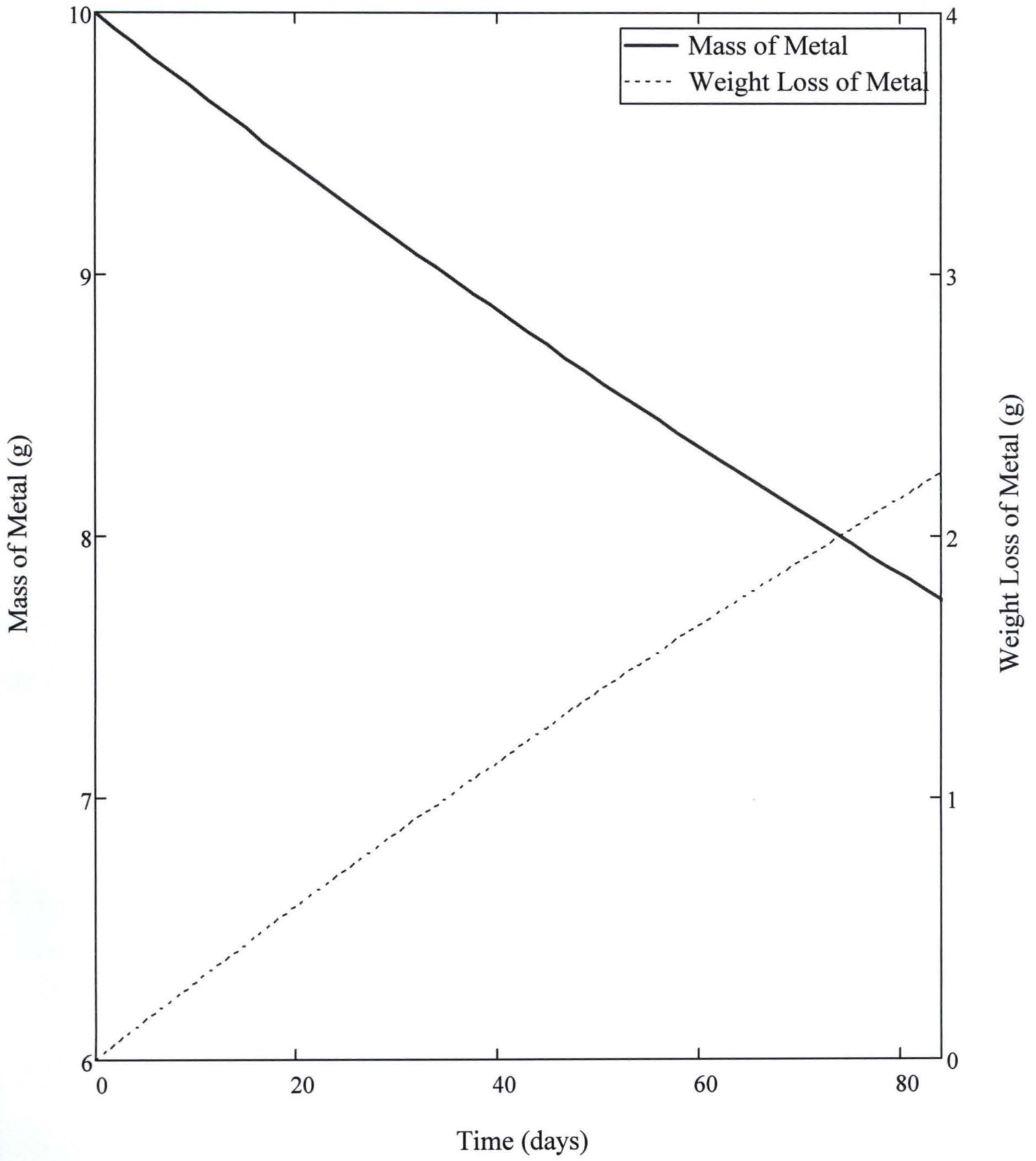
The differential function is: $D(t, m_c) := \left[k_c \cdot m_c \cdot \frac{1}{F_o} \cdot (1 - F_s)\right]$

Defining the period and steps: $T := 120$ $\quad N := 64$

Setting up the integration variable: $Sol := \text{rkfixed}(m_c, 0, T, N, D)$

Plotting the solution: $i := 0 .. N$ $\quad t_i := Sol_{i,0}$ $\quad m_{c_i} := Sol_{i,1}$

$$g_i := 10 - m_{c_i}$$


Mass of Metal
Weight Loss of Metal
Mass of Metal (g)
Weight Loss of Metal (g)
Time (days)
10
9
8
7
6
4
3
2
1
0
0
20
40
60
80

m_{c_i} =	t_i =	g_i =
10	0	0
9.944	2	0.056
9.887	4	0.113
9.832	6	0.168
9.776	8	0.224
9.721	9	0.279
9.666	11	0.334
9.611	13	0.389
9.557	15	0.443
9.503	17	0.497
9.449	19	0.551
9.396	21	0.604
9.343	23	0.657
9.29	24	0.71
9.238	26	0.762
9.186	...	...
9.134		
9.082		
...		

APPENDIX B.2

B.2 EFFECT OF TEMPERATURE ON CORROSION RATE FROM THE DEVELOPED MODEL EQUATION

Temperature = 313 K

This involves solving the following differential equation:

$$\frac{dm_c}{dt} = k_c \cdot m_c \cdot F_o \cdot (1 - F_s) \qquad k_{r(FeCO_3)} = e^{A_{(FeCO_3)} - \frac{B_{(FeCO_3)}}{RT_k}}$$

$$k_c = \exp\left(A - \frac{B}{R \cdot T}\right)$$

Defining the given data: $F_s := 1.5$ $A_c := 1$ $A_m := 3$

$A := 21.3$ $B := 64851.4$ $R := 8.314$ $T := 313$

The rate constant is: $k_c := \exp\left(A - \frac{B}{R \cdot T}\right)$ $F_o := 1.9462$

The initial condition is: $m_{c_0} := 10$ $n := 2$

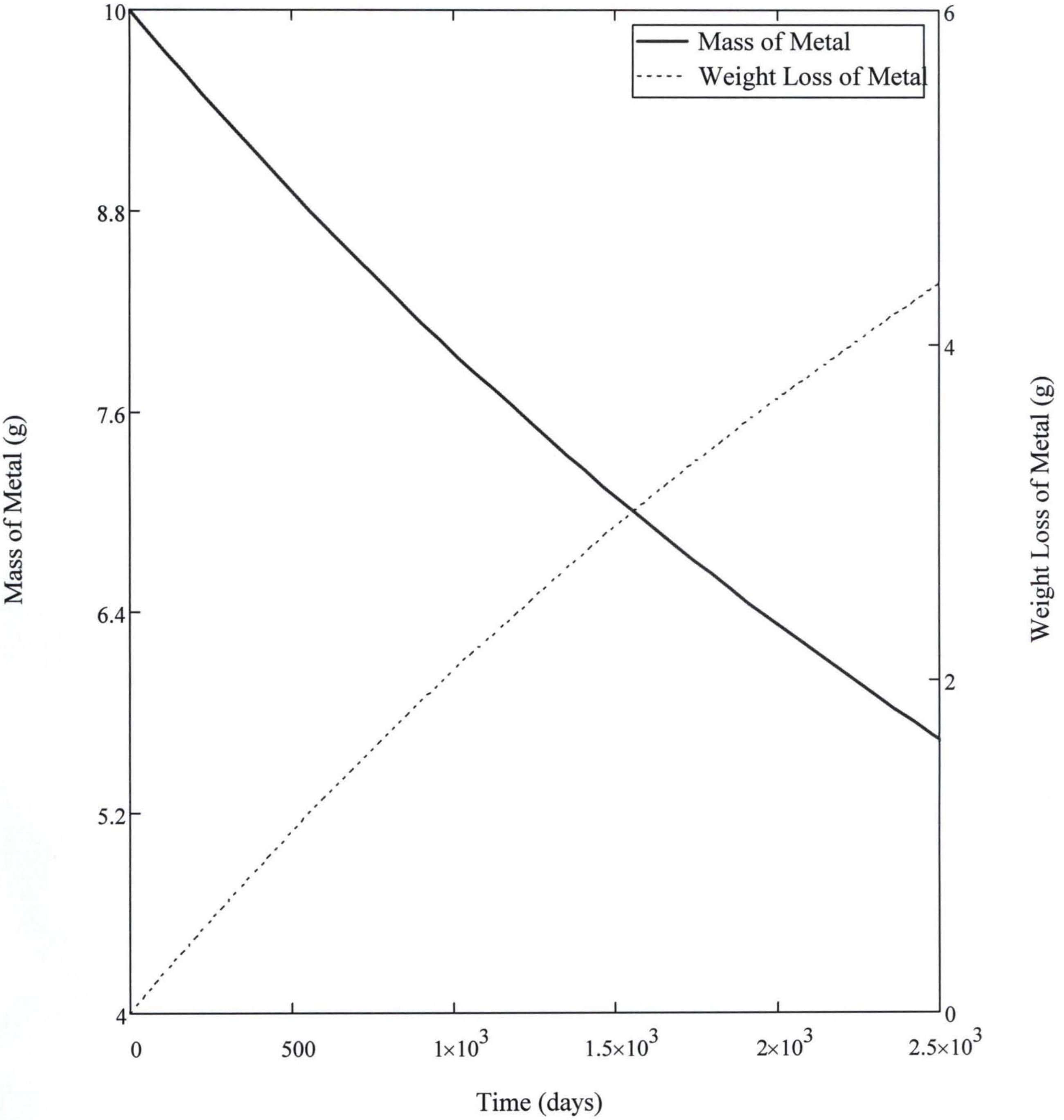
The differential function is: $D(t, m_c) := \left[k_c \cdot m_c \cdot \frac{1}{F_o} \cdot (1 - F_s)\right]$

Defining the period and steps: $T := 120$ $N := 64$

Setting up the integration variable: $Sol := \text{rkfixed}(m_c, 0, T, N, D)$

Plotting the solution: $i := 0..N$ $t_i := Sol_{i,0}$ $m_{c_i} := Sol_{i,1}$

$g_i := 10 - m_{c_i}$


Mass of Metal
Weight Loss of Metal
Mass of Metal (g)
Weight Loss of Metal (g)
Time (days)
10
8.8
7.6
6.4
5.2
4
6
4
2
0
0
500
1×10^3
1.5×10^3
2×10^3
2.5×10^3

$m_{c_i} =$

10
9.872
9.746
9.621
9.498
9.376
9.256
9.137
9.02
8.905
8.791
8.678
8.567
8.457
8.349
8.242
8.137
8.032
...

$t_i =$

0
2
4
6
8
9
11
13
15
17
19
21
23
24
26
...

$g_i =$

0
0.128
0.254
0.379
0.502
0.624
0.744
0.863
0.98
1.095
1.209
1.322
1.433
1.543
1.651
...

APPENDIX B.3

B.3 EFFECT OF TEMPERATURE ON CORROSION RATE FROM THE DEVELOPED MODEL EQUATION

Temperature = 323 K

This involves solving the following differential equation:

$$\frac{dm_c}{dt} = k_c \cdot m_c \cdot F_o \cdot \left(1 - F_s\right) \qquad k_{r(FeCO_3)} = e^{A_{(FeCO_3)} - \frac{B_{(FeCO_3)}}{RT_k}}$$

$$k_c = \exp\left(A - \frac{B}{R \cdot T}\right)$$

Defining the given data: $F_s := 1.5$ $\quad A_c := 1$ $\quad A_m := 3$

$A := 21.3$ $\quad B := 64851.4$ $\quad R := 8.314$ $\quad T := 323$

The rate constant is: $k_c := \exp\left(A - \frac{B}{R \cdot T}\right)$ $\quad F_o := 1.9462$

The initial condition is: $m_{c_0} := 10$ $\quad n := 2$

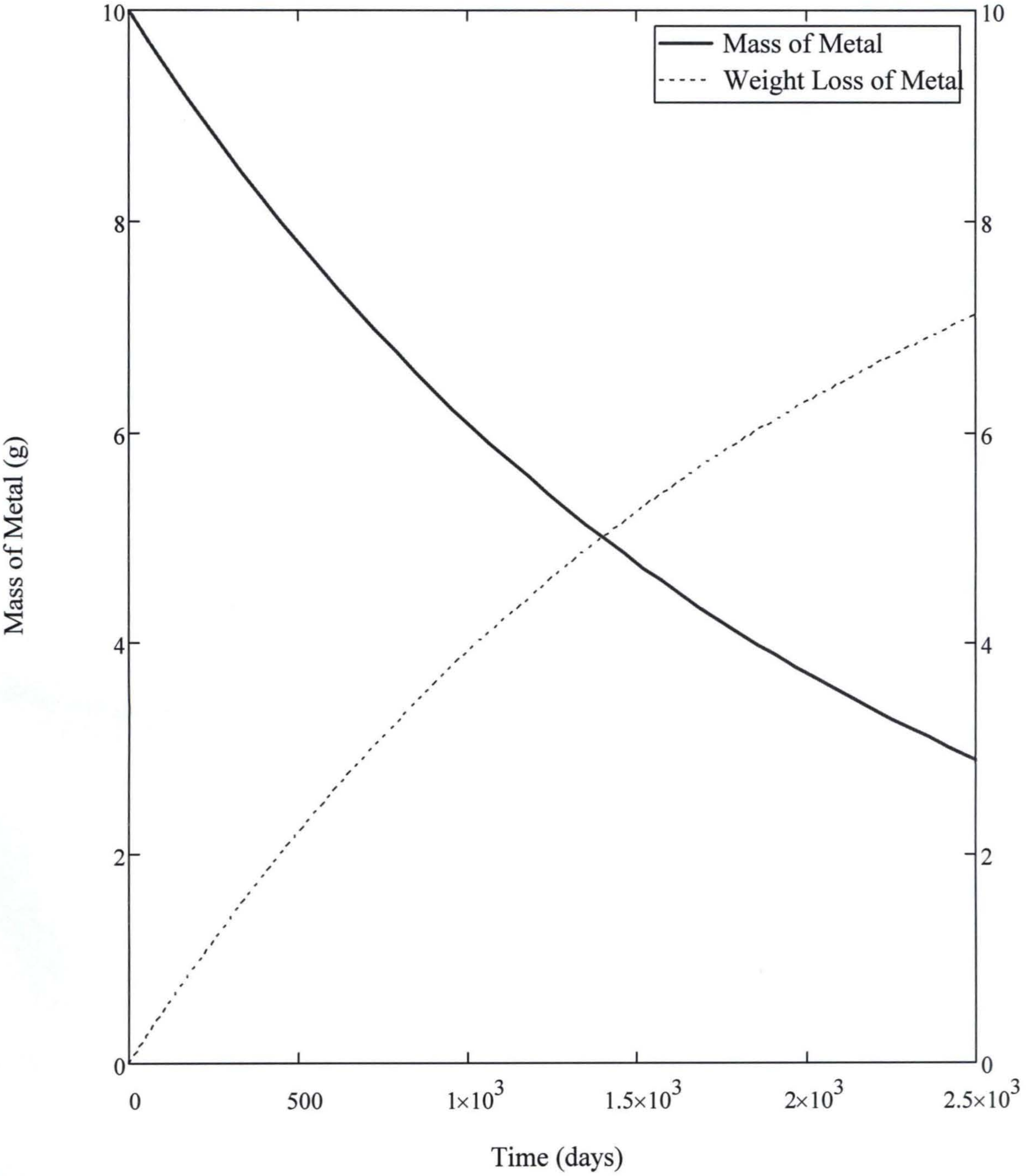
The differential function is: $D\left(t, m_c\right) := \left[k_c \cdot m_c \cdot \frac{1}{F_o} \cdot \left(1 - F_s\right)\right]$

Defining the period and steps: $T := 120$ $\quad N := 64$

Setting up the integration variable: $Sol := \text{rkfixed}\left(m_c, 0, T, N, D\right)$

Plotting the solution: $i := 0..N$ $\quad t_i := Sol_{i,0}$ $\quad m_{c_i} := Sol_{i,1}$

$g_i := 10 - m_{c_i}$


Mass of Metal
Weight Loss of Metal
Mass of Metal (g)
Weight Loss of Metal (g)
Time (days)
0
2
4
6
8
10
0
500
1×10^3
1.5×10^3
2×10^3
2.5×10^3

$m_{c_i} =$	$t_i =$	$g_i =$
10	0	0
9.725	2	0.275
9.458	4	0.542
9.198	6	0.802
8.945	8	1.055
8.699	9	1.301
8.46	11	1.54
8.227	13	1.773
8.001	15	1.999
7.781	17	2.219
7.567	19	2.433
7.359	21	2.641
7.157	23	2.843
6.96	24	3.04
6.768	26	3.232
6.582	...	...
6.401		
6.225		
...		

APPENDIX B.4

B.4 EFFECT OF TEMPERATURE ON CORROSION RATE FROM THE DEVELOPED MODEL EQUATION

Temperature = 333 K

This involves solving the following differential equation:

$$\frac{dm_c}{dt} = k_c \cdot m_c \cdot F_o \cdot \left(1 - F_s\right) \qquad k_{r(FeCO_3)} = e^{A_{(FeCO_3)} - \frac{B_{(FeCO_3)}}{RT_k}}$$

$$k_c = \exp\left(A - \frac{B}{R \cdot T}\right)$$

Defining the given data: $F_s := 1.5$ $A_c := 1$ $A_m := 3$

$A := 21.3$ $B := 64851.4$ $R := 8.314$ $T := 333$

The rate constant is: $k_c := \exp\left(A - \frac{B}{R \cdot T}\right)$ $F_o := 1.9462$

The initial condition is: $m_{c_0} := 10$ $n := 2$

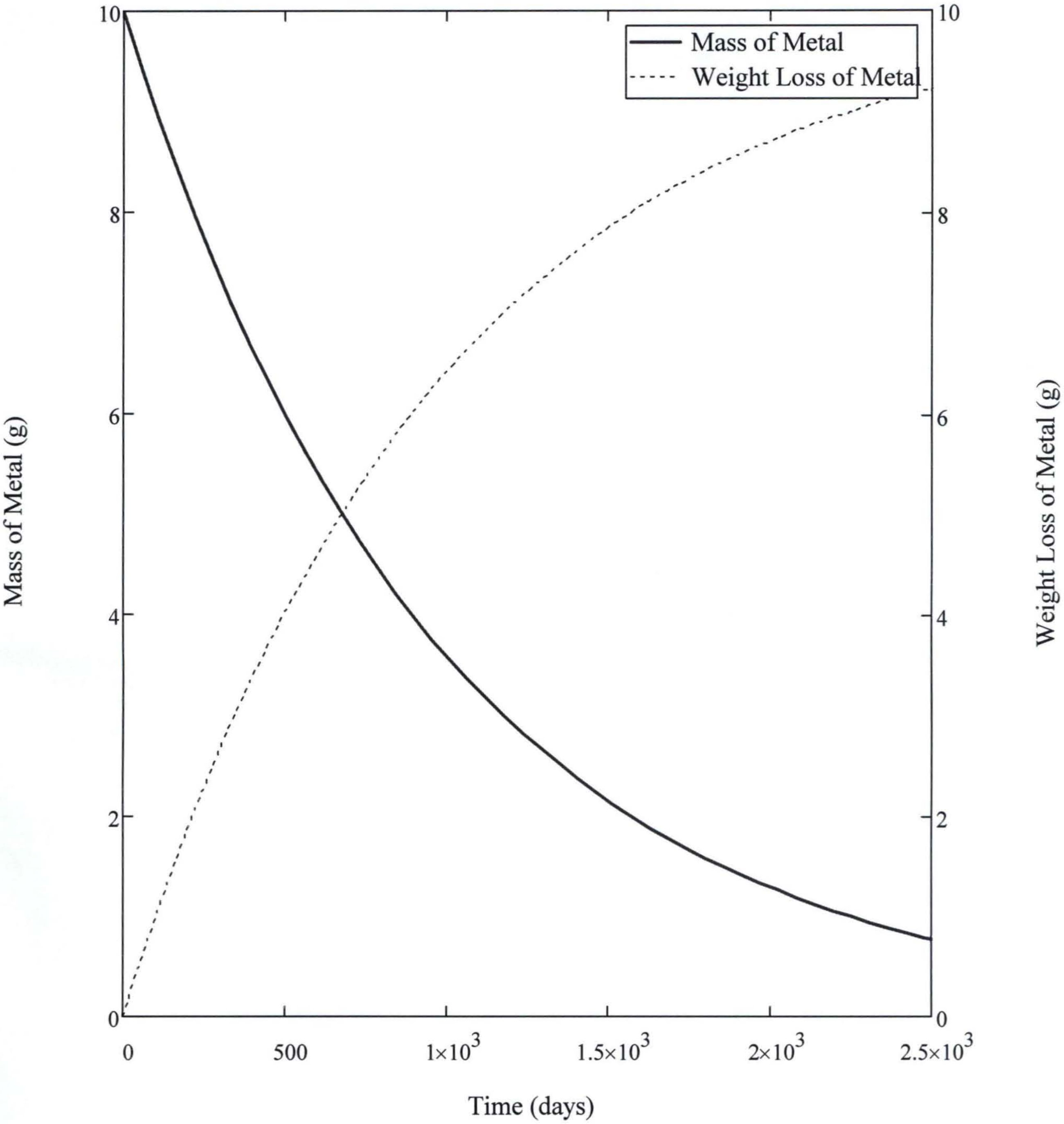
The differential function is: $D\left(t, m_c\right) := \left[k_c \cdot m_c \cdot \frac{1}{F_o} \cdot \left(1 - F_s\right)\right]$

Defining the period and steps: $T := 120$ $N := 64$

Setting up the integration variable: $Sol := \text{rkfixed}\left(m_c, 0, T, N, D\right)$

Plotting the solution: $i := 0 .. N$ $t_i := Sol_{i,0}$ $m_{c_i} := Sol_{i,1}$

$g_i := 10 - m_{c_i}$


Mass of Metal
Weight Loss of Metal
Mass of Metal (g)
Weight Loss of Metal (g)
Time (days)
0
2
4
6
8
10
0
500
1×10^3
1.5×10^3
2×10^3
2.5×10^3

$m_{c_i} =$
10
9.44
8.912
8.414
7.943
7.498
7.079
6.683
6.309
5.956
5.623
5.308
5.011
4.731
4.466
4.216
3.98
3.758
...

$t_i =$
0
2
4
6
8
9
11
13
15
17
19
21
23
24
26
...

$g_i =$
0
0.56
1.088
1.586
2.057
2.502
2.921
3.317
3.691
4.044
4.377
4.692
4.989
5.269
5.534
...

APPENDIX C.1

C.1 EFFECT OF CORROSION SCALE ON CORROSION RATE FROM THE DEVELOPED MODEL EQUATION

Corrosion scale = 0.5462g

This involves solving the following differential equation:

$$\frac{dm_c}{dt} = k_c \cdot m_c \cdot F_o \cdot (1 - F_s) \qquad k_{r(FeCO_3)} = e^{A_{(FeCO_3)} - \frac{B_{(FeCO_3)}}{RT_k}}$$

$$k_c = \exp\left(A - \frac{B}{R \cdot T}\right)$$

Defining the given data: $F_s := 1.5$ $A_c := 1$ $A_m := 3$

$A := 21.3$ $B := 64851.4$ $R := 8.314$ $T := 313$

The rate constant is: $k_c := \exp\left(A - \frac{B}{R \cdot T}\right)$ $F_o := 0.5462$

The initial condition is: $m_{c_0} := 10$ $n := 2$

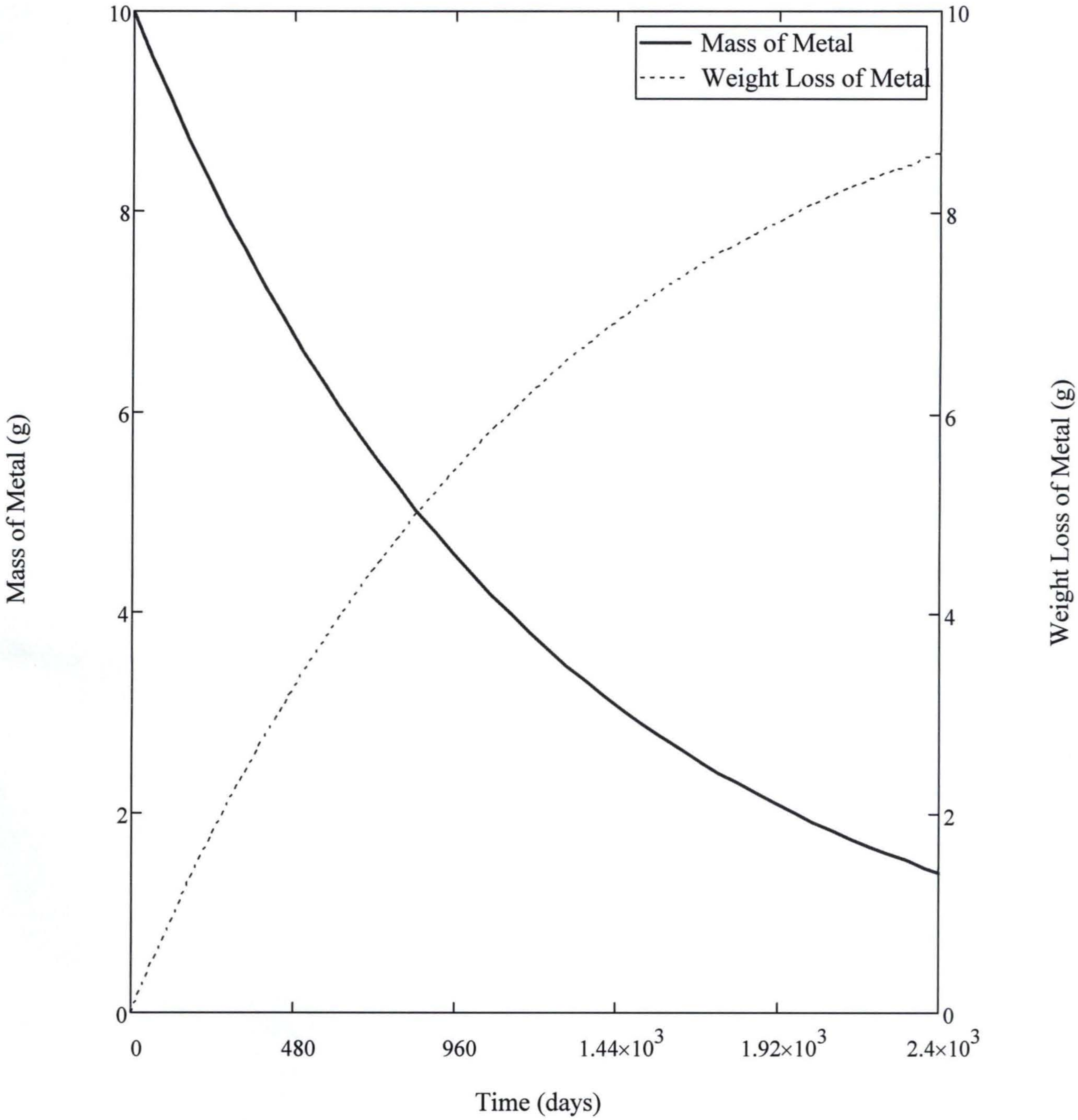
The differential function is: $D(t, m_c) := \left[k_c \cdot m_c \cdot \frac{1}{F_o} \cdot (1 - F_s)\right]$

Defining the period and steps: $T := 120$ $N := 64$

Setting up the integration variable: $Sol := rkfixed(m_c, 0, T, N, D)$

Plotting the solution: $i := 0 .. N$ $t_i := Sol_{i,0}$ $m_{c_i} := Sol_{i,1}$

$g_i := 10 - m_{c_i}$


Mass of Metal
Weight Loss of Metal
Mass of Metal (g)
Weight Loss of Metal (g)
Time (days)
0
480
960
1.44×10^3
1.92×10^3
2.4×10^3
0
2
4
6
8
10

$m_{c_i} =$	$t_i =$	$g_i =$
10	0	0
9.551	2	0.449
9.122	4	0.878
8.713	6	1.287
8.322	8	1.678
7.948	9	2.052
7.592	11	2.408
7.251	13	2.749
6.925	15	3.075
6.614	17	3.386
6.318	19	3.682
6.034	21	3.966
5.763	23	4.237
5.504	24	4.496
5.257	26	4.743
5.021	...	...
4.796		
4.581		
...		

APPENDIX C.2

C.2 EFFECT OF CORROSION SCALE ON CORROSION RATE FROM THE DEVELOPED MODEL EQUATION

Corrosion scale (F_0) = 0.9462g

This involves solving the following differential equation:

$$\frac{dm_c}{dt} = k_c \cdot m_c \cdot F_o \cdot (1 - F_s) \qquad k_{r(FeCO_3)} = e^{A_{(FeCO_3)} - \frac{B_{(FeCO_3)}}{RT_k}}$$

$$k_c = \exp\left(A - \frac{B}{R \cdot T}\right)$$

Defining the given data: $F_s := 1.5$ $\quad A_c := 1$ $\quad A_m := 3$

$A := 21.3$ $\quad B := 64851.4$ $\quad R := 8.314$ $\quad T := 313$

The rate constant is: $k_c := \exp\left(A - \frac{B}{R \cdot T}\right)$ $\quad F_o := 0.9462$

The initial condition is: $m_{c_0} := 10$ $\quad n := 2$

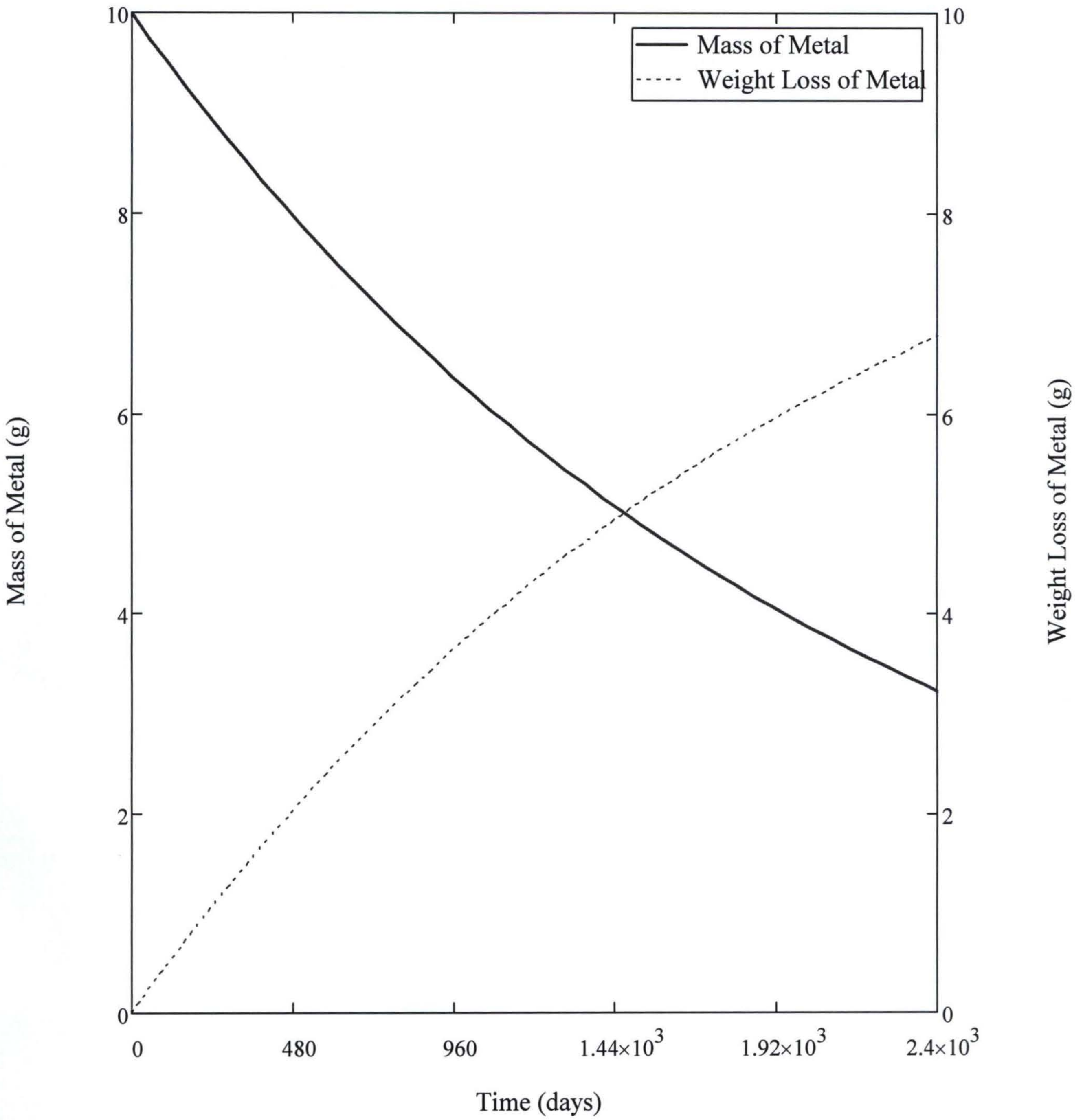
The differential function is: $D(t, m_c) := \left[k_c \cdot m_c \cdot \frac{1}{F_o} \cdot (1 - F_s)\right]$

Defining the period and steps: $T := 120$ $\quad N := 64$

Setting up the integration variable: $Sol := \mathrm{rkfixed}(m_c, 0, T, N, D)$

Plotting the solution: $i := 0 .. N$ $\quad t_i := Sol_{i,0}$ $\quad m_{c_i} := Sol_{i,1}$

$g_i := 10 - m_{c_i}$


Mass of Metal
Weight Loss of Metal
Mass of Metal (g)
Weight Loss of Metal (g)
Time (days)
0
2
4
6
8
10
0
480
960
1.44×10^3
1.92×10^3
2.4×10^3

$m_{c_i} =$	$t_i =$	$g_i =$
10	0	0
9.738	2	0.262
9.484	4	0.516
9.235	6	0.765
8.994	8	1.006
8.759	9	1.241
8.529	11	1.471
8.306	13	1.694
8.089	15	1.911
7.877	17	2.123
7.671	19	2.329
7.471	21	2.529
7.275	23	2.725
7.085	24	2.915
6.899	26	3.101
6.719	28	3.281
6.543	30	3.457
6.372	32	3.628
6.205	34	3.795
6.043	36	3.957
5.885	38	4.115
5.731	39	4.269
5.581	41	4.419
5.435	43	4.565
5.293	45	4.707
5.154	47	4.846
5.019	49	4.981
4.888	51	5.112
4.76	53	5.24
4.636	54	5.364
4.514	56	5.486
4.396	58	5.604
4.281	60	5.719
...	...	...

APPENDIX C.3

C.3 EFFECT OF CORROSION SCALE ON CORROSION RATE FROM THE DEVELOPED MODEL EQUATION

Corrosion scale (F_0) = 1.4462g

This involves solving the following differential equation:

$$\frac{dm_c}{dt} = k_c \cdot m_c \cdot F_o \cdot (1 - F_s) \qquad k_{r(FeCO_3)} = e^{A_{(FeCO_3)} - \frac{B_{(FeCO_3)}}{RT_k}}$$

$$k_c = \exp\left(A - \frac{B}{R \cdot T}\right)$$

Defining the given data: $F_s := 1.5$ $\quad A_c := 1$ $\quad A_m := 3$

$A := 21.3$ $\quad B := 64851.4$ $\quad R := 8.314$ $\quad T := 313$

The rate constant is: $k_c := \exp\left(A - \frac{B}{R \cdot T}\right)$ $\quad F_o := 1.4462$

The initial condition is: $m_{c_0} := 10$ $\quad n := 2$

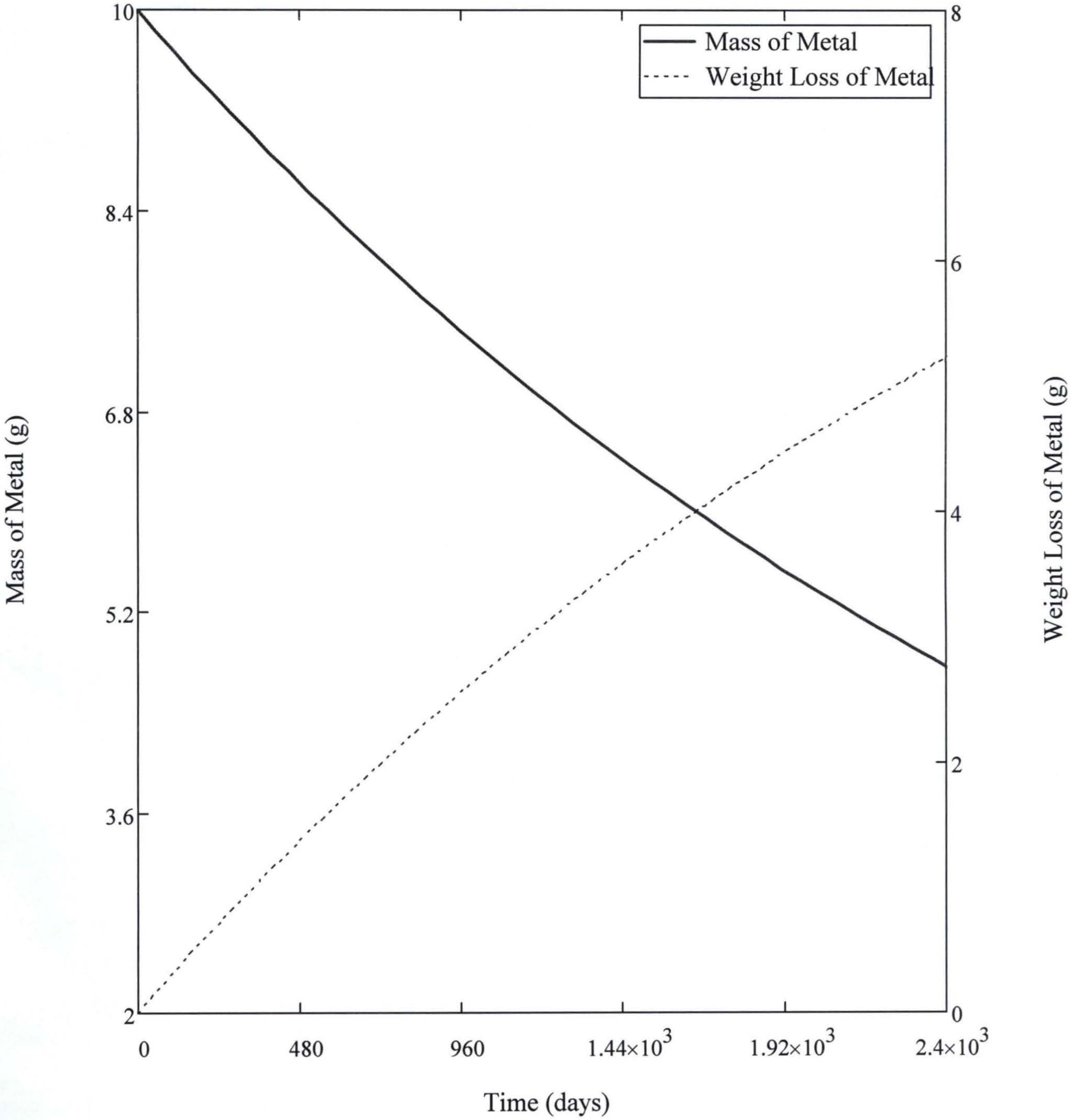
The differential function is: $D(t, m_c) := \left[k_c \cdot m_c \cdot \frac{1}{F_o} \cdot (1 - F_s)\right]$

Defining the period and steps: $T := 120$ $\quad N := 64$

Setting up the integration variable: $Sol := \text{rkfixed}(m_c, 0, T, N, D)$

Plotting the solution: $i := 0..N$ $\quad t_i := Sol_{i,0}$ $\quad m_{c_i} := Sol_{i,1}$

$g_i := 10 - m_{c_i}$


Mass of Metal
Weight Loss of Metal
10
8.4
6.8
5.2
3.6
2
8
6
4
2
0
0
480
960
1.44×10^3
1.92×10^3
2.4×10^3
Time (days)
Mass of Metal (g)
Weight Loss of Metal (g)

$m_{c_i} =$	$t_i =$	$g_i =$
10	0	0
9.828	2	0.172
9.659	4	0.341
9.493	6	0.507
9.33	8	0.67
9.169	9	0.831
9.012	11	0.988
8.857	13	1.143
8.704	15	1.296
8.555	17	1.445
8.408	19	1.592
8.263	21	1.737
8.121	23	1.879
7.981	24	2.019
7.844	26	2.156
7.709	28	2.291
7.577	30	2.423
7.446	32	2.554
7.318	34	2.682
7.192	36	2.808
7.069	38	2.931
6.947	39	3.053
6.828	41	3.172
6.71	43	3.29
6.595	45	3.405
6.482	47	3.518
6.37	49	3.63
6.261	51	3.739
6.153	53	3.847
6.047	54	3.953
5.943	56	4.057
5.841	58	4.159
5.74	60	4.26
...	...	...

APPENDIX C.4

C.4 EFFECT OF CORROSION SCALE ON CORROSION RATE FROM THE DEVELOPED MODEL EQUATION

Corrosion scale (F_0) = 1.9462g

This involves solving the following differential equation:

$$\frac{dm_c}{dt} = k_c \cdot m_c \cdot F_o \cdot (1 - F_s) \qquad k_{r(FeCO_3)} = e^{A_{(FeCO_3)} - \frac{B_{(FeCO_3)}}{RT_k}}$$

$$k_c = \exp\left(A - \frac{B}{R \cdot T}\right)$$

Defining the given data: $F_s := 1.5$ $\quad A_c := 1$ $\quad A_m := 3$

$A := 21.3$ $\quad B := 64851.4$ $\quad R := 8.314$ $\quad T := 313$

The rate constant is: $k_c := \exp\left(A - \frac{B}{R \cdot T}\right)$ $\quad F_o := 1.9462$

The initial condition is: $m_{c_0} := 10$ $\quad n := 2$

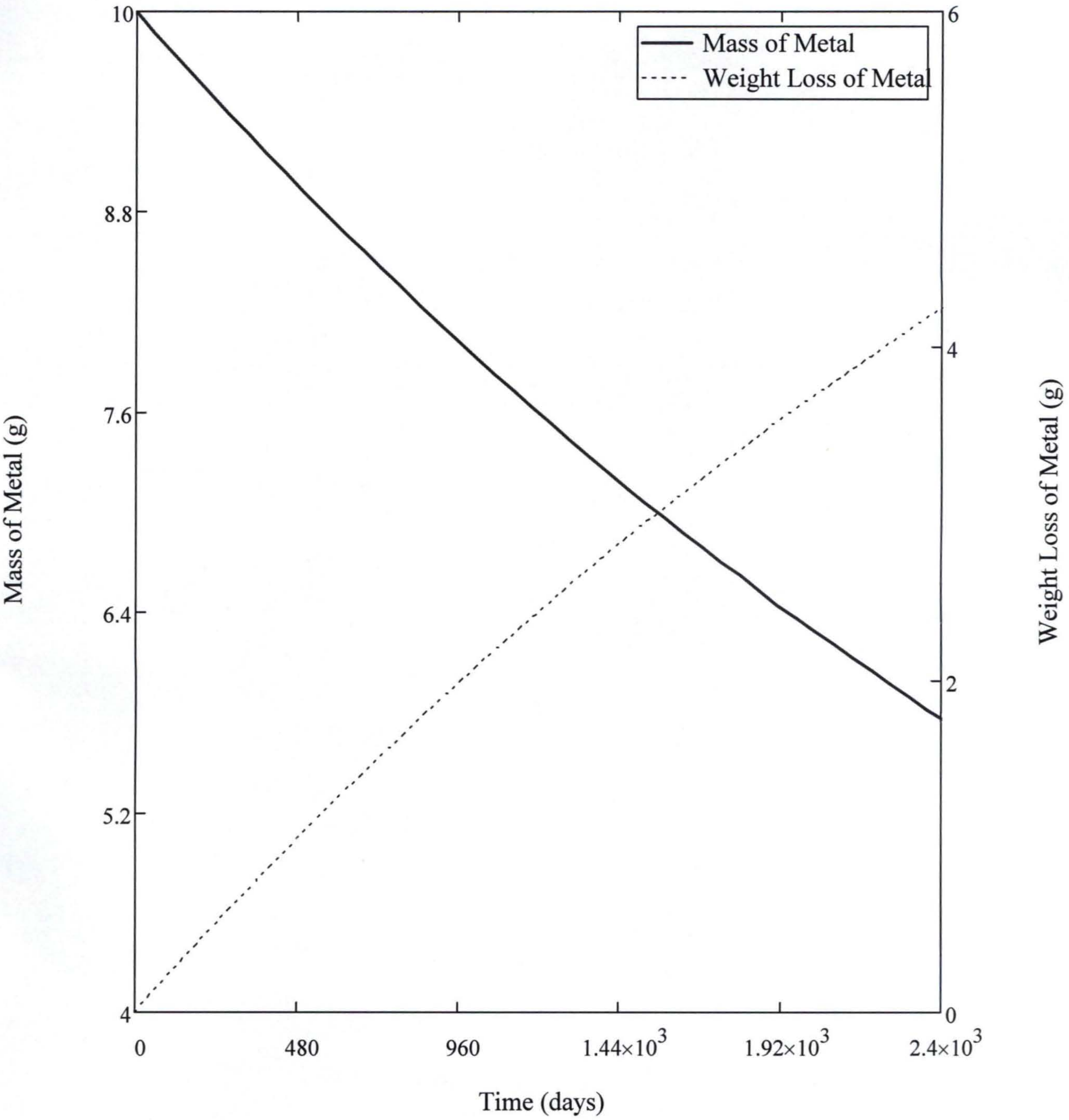
The differential function is: $D(t, m_c) := \left[k_c \cdot m_c \cdot \frac{1}{F_o} \cdot (1 - F_s)\right]$

Defining the period and steps: $T := 120$ $\quad N := 64$

Setting up the integration variable: $Sol := \text{rkfixed}(m_c, 0, T, N, D)$

Plotting the solution: $i := 0..N$ $\quad t_i := Sol_{i,0}$ $\quad m_{c_i} := Sol_{i,1}$

$g_i := 10 - m_{c_i}$



Mass of Metal
Weight Loss of Metal
10
8.8
7.6
6.4
5.2
4
6
4
2
0
0
480
960
1.44×10^3
1.92×10^3
2.4×10^3
Mass of Metal (g)
Weight Loss of Metal (g)
Time (days)

m_{c_i} =	t_i =	g_i =
10	0	0
9.872	2	0.128
9.746	4	0.254
9.621	6	0.379
9.498	8	0.502
9.376	9	0.624
9.256	11	0.744
9.137	13	0.863
9.02	15	0.98
8.905	17	1.095
8.791	19	1.209
8.678	21	1.322
8.567	23	1.433
8.457	24	1.543
8.349	26	1.651
8.242	28	1.758
8.137	30	1.863
8.032	32	1.968
7.929	34	2.071
7.828	36	2.172
7.728	38	2.272
7.629	39	2.371
7.531	41	2.469
7.435	43	2.565
7.339	45	2.661
7.245	47	2.755
7.153	49	2.847
7.061	51	2.939
6.971	53	3.029
6.881	54	3.119
6.793	56	3.207
6.706	58	3.294
6.62	60	3.38
...	...	...

APPENDIX D.1

D.1 EFFECT OF MINERAL FACTOR (IRON II OXIDE CONTENT OF MILD STEEL) ON CORROSION RATE FROM THE DEVELOPED MODEL EQUATION

Mineral Factor (Fe II content of the Mild steel): $(F_S) = 1.5$g

This involves solving the following differential equation:

$$\frac{dm_c}{dt} = k_c \cdot m_c \cdot F_o \cdot (1 - F_s) \qquad k_{r(FeCO_3)} = e^{A_{(FeCO_3)} - \frac{B_{(FeCO_3)}}{RT_k}}$$

$$k_c = \exp\left(A - \frac{B}{R \cdot T}\right)$$

Defining the given data: $F_s := 1.5 \qquad A_c := 1 \qquad A_m := 3$

$$A := 21.3 \qquad B := 64851.4 \qquad R := 8.314 \qquad T := 313$$

The rate constant is: $k_c := \exp\left(A - \frac{B}{R \cdot T}\right) \qquad F_o := 0.9462$

The initial condition is: $m_{c_0} := 10 \qquad n := 2$

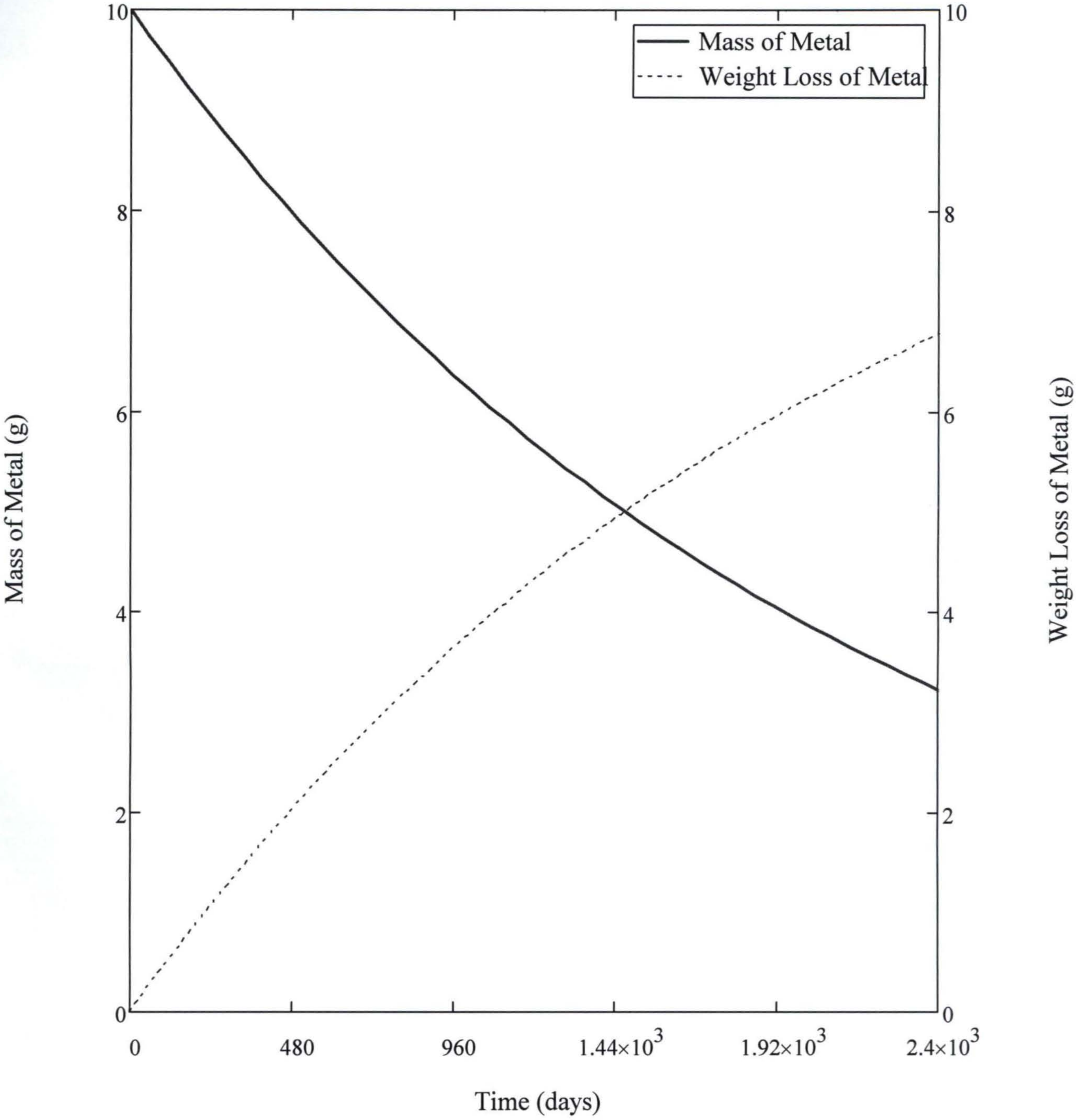
The differential function is: $D(t, m_c) := \left[k_c \cdot m_c \cdot \frac{1}{F_o} \cdot (1 - F_s)\right]$

Defining the period and steps: $T := 120 \qquad N := 64$

Setting up the integration variable: $Sol := \text{rkfixed}(m_c, 0, T, N, D)$

Plotting the solution: $i := 0..N \qquad t_i := Sol_{i,0} \qquad m_{c_i} := Sol_{i,1}$

$$g_i := 10 - m_{c_i}$$


Mass of Metal
Weight Loss of Metal
Mass of Metal (g)
Weight Loss of Metal (g)
Time (days)
0
2
4
6
8
10
0
480
960
1.44×10^3
1.92×10^3
2.4×10^3

$m_{c_i} =$	$t_i =$	$g_i =$
10	0	0
9.738	2	0.262
9.484	4	0.516
9.235	6	0.765
8.994	8	1.006
8.759	9	1.241
8.529	11	1.471
8.306	13	1.694
8.089	15	1.911
7.877	17	2.123
7.671	19	2.329
7.471	21	2.529
7.275	23	2.725
7.085	24	2.915
6.899	26	3.101
6.719	28	3.281
6.543	30	3.457
6.372	32	3.628
6.205	34	3.795
6.043	36	3.957
5.885	38	4.115
5.731	39	4.269
5.581	41	4.419
5.435	43	4.565
5.293	45	4.707
5.154	47	4.846
5.019	49	4.981
4.888	51	5.112
4.76	53	5.24
4.636	54	5.364
4.514	56	5.486
4.396	58	5.604
4.281	60	5.719
...	...	...

APPENDIX D.2

D.2 EFFECT OF MINERAL FACTOR (IRON II OXIDE CONTENT OF MILD STEEL) ON CORROSION RATE FROM THE DEVELOPED MODEL EQUATION

Mineral Factor (Fe II content of the Mild steel): $(F_S) = 1.7\text{g}$

This involves solving the following differential equation:

$$\frac{dm_c}{dt} = k_c \cdot m_c \cdot F_o \cdot (1 - F_s) \qquad k_{r(FeCO_3)} = e^{A_{(FeCO_3)} - \frac{B_{(FeCO_3)}}{RT_k}}$$

$$k_c = \exp\left(A - \frac{B}{R \cdot T}\right)$$

Defining the given data: $F_s := 1.7$ $A_c := 1$ $A_m := 3$

$A := 21.3$ $B := 64851.4$ $R := 8.314$ $T := 313$

The rate constant is: $k_c := \exp\left(A - \frac{B}{R \cdot T}\right)$ $F_o := 0.9462$

The initial condition is: $m_{c_0} := 10$ $n := 2$

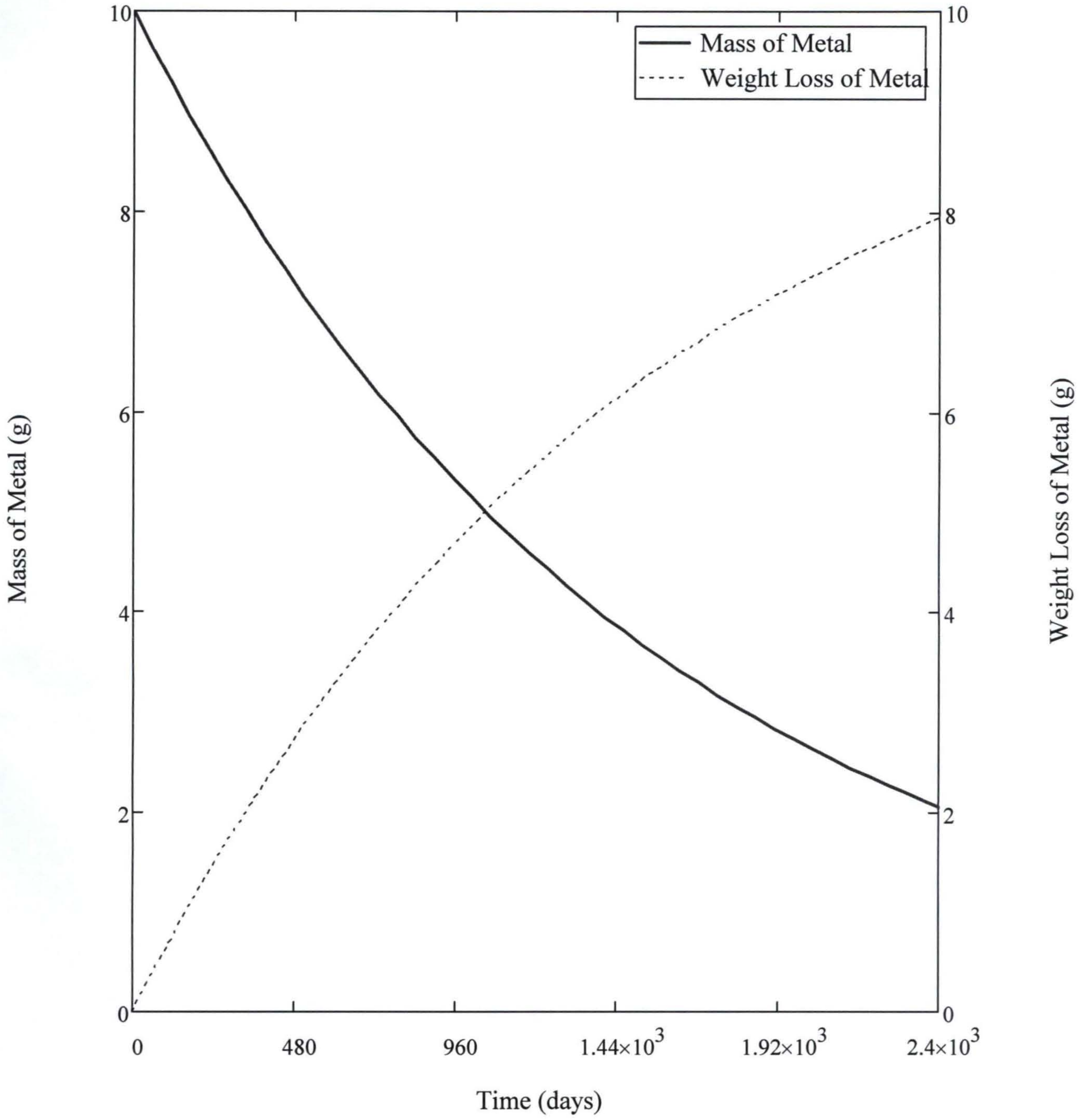
The differential function is: $D(t, m_c) := \left[k_c \cdot m_c \cdot \frac{1}{F_o} \cdot (1 - F_s)\right]$

Defining the period and steps: $T := 120$ $N := 64$

Setting up the integration variable: $Sol := \text{rkfixed}(m_c, 0, T, N, D)$

Plotting the solution: $i := 0..N$ $t_i := Sol_{i,0}$ $m_{c_i} := Sol_{i,1}$

$g_i := 10 - m_{c_i}$


Mass of Metal
Weight Loss of Metal
Mass of Metal (g)
Weight Loss of Metal (g)
Time (days)
0
480
960
1.44×10^3
1.92×10^3
2.4×10^3
0
2
4
6
8
10

$m_{c_i} =$	$t_i =$	$g_i =$
10	0	0
9.636	2	0.364
9.285	4	0.715
8.946	6	1.054
8.62	8	1.38
8.306	9	1.694
8.004	11	1.996
7.712	13	2.288
7.431	15	2.569
7.16	17	2.84
6.899	19	3.101
6.648	21	3.352
6.406	23	3.594
6.172	24	3.828
5.948	26	4.052
5.731	28	4.269
5.522	30	4.478
5.321	32	4.679
5.127	34	4.873
4.94	36	5.06
4.76	38	5.24
4.587	39	5.413
4.42	41	5.58
4.259	43	5.741
4.103	45	5.897
3.954	47	6.046
3.81	49	6.19
3.671	51	6.329
3.537	53	6.463
3.408	54	6.592
3.284	56	6.716
3.165	58	6.835
3.049	60	6.951
...	...	...

APPENDIX D.3

D.3 EFFECT OF MINERAL FACTOR (IRON II OXIDE CONTENT OF MILD STEEL) ON CORROSION RATE FROM THE DEVELOPED MODEL EQUATION

Mineral Factor (Fe II content of the Mild steel): $(F_S) = 1.9g$

This involves solving the following differential equation:

$$\frac{dm_c}{dt} = k_c \cdot m_c \cdot F_o \cdot (1 - F_s) \qquad k_{r(FeCO_3)} = e^{A_{(FeCO_3)} - \frac{B_{(FeCO_3)}}{RT_k}}$$

$$k_c = \exp\left(A - \frac{B}{R \cdot T}\right)$$

Defining the given data: $F_s := 1.9$ $\quad A_c := 1$ $\quad A_m := 3$

$A := 21.3$ $\quad B := 64851.4$ $\quad R := 8.314$ $\quad T := 313$

The rate constant is: $k_c := \exp\left(A - \frac{B}{R \cdot T}\right)$ $\quad F_o := 0.9462$

The initial condition is: $m_{c_0} := 10$ $\quad n := 2$

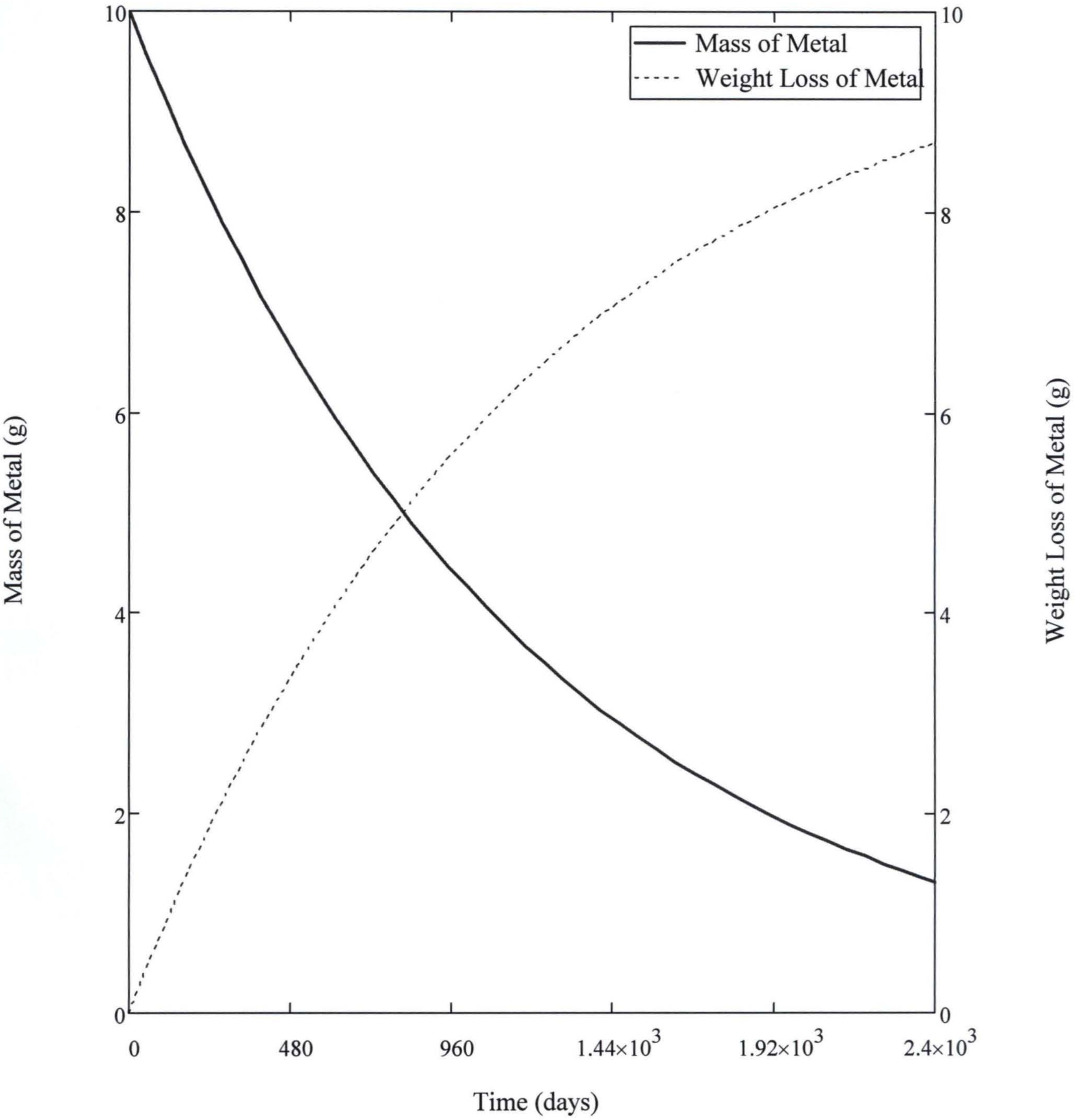
The differential function is: $D(t, m_c) := \left[k_c \cdot m_c \cdot \frac{1}{F_o} \cdot (1 - F_s)\right]$

Defining the period and steps: $T := 120$ $\quad N := 64$

Setting up the integration variable: $Sol := \mathrm{rkfixed}(m_c, 0, T, N, D)$

Plotting the solution: $i := 0..N$ $\quad t_i := Sol_{i,0}$ $\quad m_{c_i} := Sol_{i,1}$

$g_i := 10 - m_{c_i}$


Mass of Metal
Weight Loss of Metal
Mass of Metal (g)
Weight Loss of Metal (g)
Time (days)
0
2
4
6
8
10
0
480
960
1.44×10^3
1.92×10^3
2.4×10^3

$m_{c_i} =$	$t_i =$	$g_i =$
10	0	0
9.534	2	0.466
9.09	4	0.91
8.666	6	1.334
8.262	8	1.738
7.877	9	2.123
7.51	11	2.49
7.16	13	2.84
6.827	15	3.173
6.509	17	3.491
6.205	19	3.795
5.916	21	4.084
5.64	23	4.36
5.378	24	4.622
5.127	26	4.873
4.888	28	5.112
4.66	30	5.34
4.443	32	5.557
4.236	34	5.764
4.039	36	5.961
3.851	38	6.149
3.671	39	6.329
3.5	41	6.5
3.337	43	6.663
3.181	45	6.819
3.033	47	6.967
2.892	49	7.108
2.757	51	7.243
2.629	53	7.371
2.506	54	7.494
2.389	56	7.611
2.278	58	7.722
2.172	60	7.828
...	...	...

APPENDIX D.4

D.4 EFFECT OF MINERAL FACTOR (IRON II OXIDE CONTENT OF MILD STEEL) ON CORROSION RATE FROM THE DEVELOPED MODEL EQUATION

Mineral Factor (Fe II content of the Mild steel): $(F_S) = 2.1g$

This involves solving the following differential equation:

$$\frac{dm_c}{dt} = k_c \cdot m_c \cdot F_o \cdot \left(1 - F_s\right) \qquad k_{r(FeCO_3)} = e^{A_{(FeCO_3)} - \frac{B_{(FeCO_3)}}{RT_k}}$$

$$k_c = \exp\left(A - \frac{B}{R \cdot T}\right)$$

Defining the given data: $F_s := 2.1$ $\quad A_c := 1$ $\quad A_m := 3$

$A := 21.3$ $\quad B := 64851.4$ $\quad R := 8.314$ $\quad T := 313$

The rate constant is: $k_c := \exp\left(A - \frac{B}{R \cdot T}\right)$ $\quad F_o := 0.9462$

The initial condition is: $m_{c_0} := 10$ $\quad n := 2$

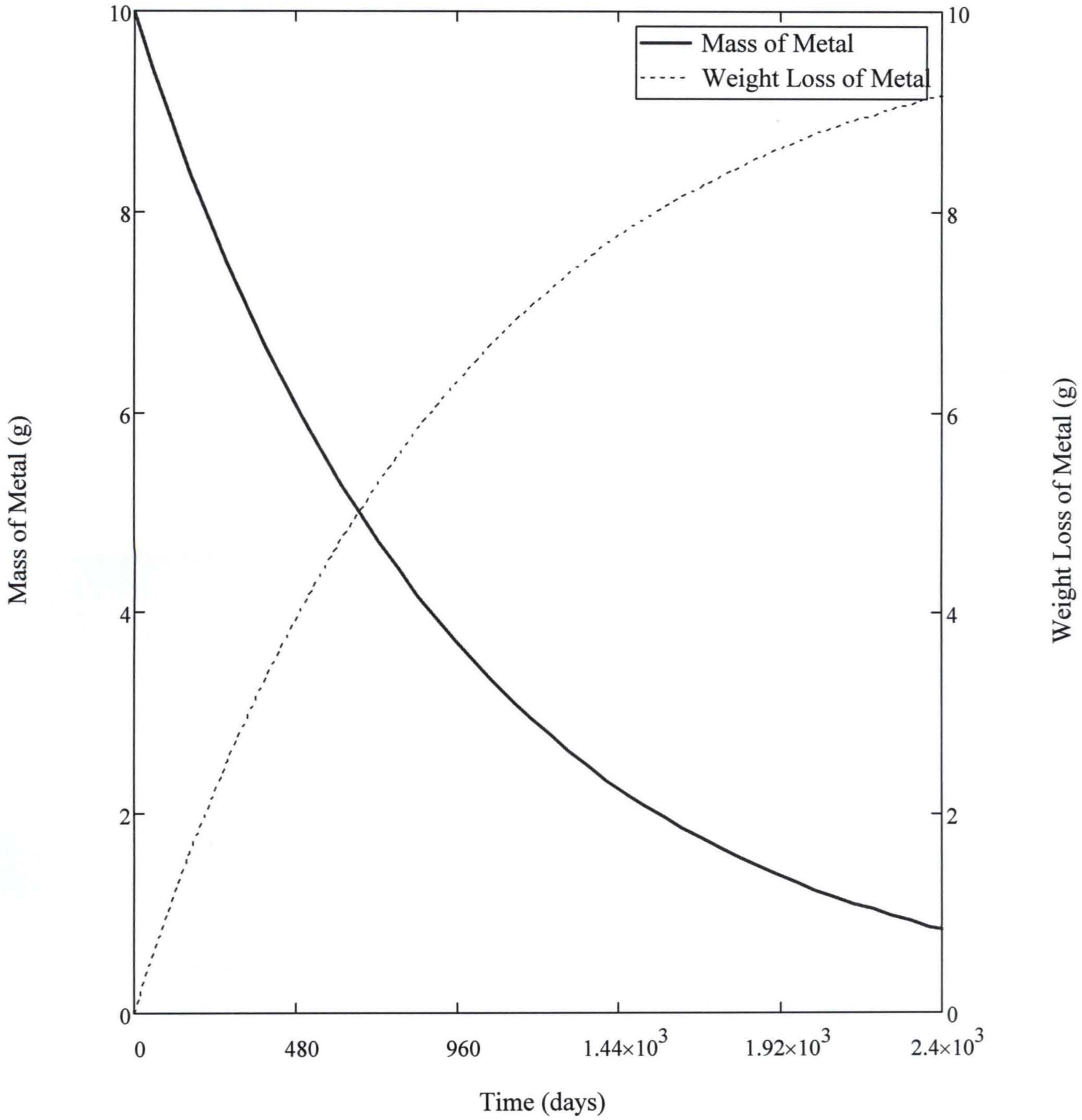
The differential function is: $D\left(t, m_c\right) := \left[k_c \cdot m_c \cdot \frac{1}{F_o} \cdot \left(1 - F_s\right)\right]$

Defining the period and steps: $T := 120$ $\quad N := 64$

Setting up the integration variable: $Sol := \mathrm{rkfixed}\left(m_c, 0, T, N, D\right)$

Plotting the solution: $i := 0..N$ $\quad t_i := Sol_{i,0}$ $\quad m_{c_i} := Sol_{i,1}$

$g_i := 10 - m_{c_i}$


Mass of Metal
Weight Loss of Metal
Mass of Metal (g)
Weight Loss of Metal (g)
0
2
4
6
8
10
0
480
960
1.44×10³
1.92×10³
2.4×10³
Time (days)

m_{c_i} =	t_i =	g_i =
10	0	0
9.433	2	0.567
8.899	4	1.101
8.395	6	1.605
7.919	8	2.081
7.471	9	2.529
7.047	11	2.953
6.648	13	3.352
6.271	15	3.729
5.916	17	4.084
5.581	19	4.419
5.265	21	4.735
4.966	23	5.034
4.685	24	5.315
4.42	26	5.58
4.169	28	5.831
3.933	30	6.067
3.71	32	6.29
3.5	34	6.5
3.302	36	6.698
3.115	38	6.885
2.938	39	7.062
2.772	41	7.228
2.615	43	7.385
2.467	45	7.533
2.327	47	7.673
2.195	49	7.805
2.071	51	7.929
1.953	53	8.047
1.843	54	8.157
1.738	56	8.262
1.64	58	8.36
1.547	60	8.453
...	...	...

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INSPECTION REPORT

DATE:	14^{TH} SEPTEMBER 2007.	REPORT NO. 1253
AREA:	PPU (EA)	
UNIT:	74 (COOLING TOWER)	
ITEM:	COOLING WATER RETURN LINE	
SERVICE:	COOLING WATER	
SUBJECT:	**CORROSION TEST COUPONS WEIGHT-LOSS EVALUATION**	

1.0 PREAMBLE

The corrosion rate of cooling water was evaluated by inserting three marked coupons in the column provided on the cooling water return line and analyzed after 60 days of immersion period.

2.0 OBSERVATIONS

2.1 On withdrawal of coupons, little brownish deposits were observed on part of the coupons' surfaces.

2.2 After cleaning and pickling, corrosion was observed on the coupons.

2.3 Water flow was approximately 1m/sec throughout the period of coupon insertion.

3.0 EVALUATION

S/N	COUPON NO.	INITIAL WEIGHT (gm) W_{t1}	FINAL WEIGHT (gm) W_{t2}	SURFACE AREA, A (dm^2)	LOSS IN WEIGHT (gm)	RESIDENT TIME, D (days)	CORROSION RATE (MDD)
1.	008	11.3698	11.3394	0.31	0.0004	60	0.0215
2.	041	11.4102	11.3874	0.31	0.0228	60	1.2258
3.	068	11.5108	11.4764	0.31	0.0344	60	1.8495

$$\text{Corrosion Rate, MD} = \frac{(W_{t1} - W_{t2}) * 10^3}{A * D}$$

Average corrosion Rate = 1.0323MDD

ACCEPTABLE KURITA STANDARD

0	-	10MDD	-	Very Good
10	-	20MDD	-	Good
21	-	Above	-	Not satisfactory

4.0 CONCLUSION

The average corrosion rate of 1.0323MDD shows that the cooling water treatment programme is VERY GOOD going be KURITA Standard.

5.0 RECOMMENDATION

The current cooling water treatment programme should be maintained.

INSPECTORS
U.P. AKOGUN
R.A. ADEWARA

M. HAYATUDEEN
SUPT., PPU/OFFSITE

A. R SHEHU
DM, I&T

CC: EDO, METSD, MMTCE, MPPU, MFSE

APPENDIX 'F'

(α)

KRPC - The pride of the

INSPECTION REPORT

ATE: 13TH NOVEMBER 2007. REPORT NO. 1311
REA: PPU (EA)
NIT: 74 (COOLING TOWER)
EM: COOLING WATER RETURN LINE
RVICE: COOLING WATER
BJECT: CORROSION TEST COUPONS WEIGHT-LOSS EVALUATION

.0 PREAMBLE

The corrosion rate of cooling water was evaluated by inserting three marked coupons in the column provided on the cooling water return line and analyzed after 60 days of immersion period.

.0 OBSERVATIONS

2.1 On withdrawal of coupons, brownish deposits were observed on part of the coupons' surfaces.
2.2 After cleaning and pickling, corrosion was observed on the coupons.
2.3 Water flow was approximately 1m/sec throughout the period of coupon insertion.

EVALUATION

COUPON NO.	INITIAL WEIGHT (gm) W_{t1}	FINAL WEIGHT (gm) W_{t2}	SURFACE AREA, A (dm^2)	LOSS IN WEIGHT (gm)	RESIDENT TIME, D (days)	CORROSION RATE (MDD)
019	11.3585	11.2997	0.31	0.0588	60	3.1613
057	11.5171	11.4592	0.31	0.0579	60	3.1129
070	11.3789	11.1919	0.31	O.187	60	10.0538

$$\text{Corrosion Rate, MDD} = \frac{(W_{t1} - W_{t2}) * 10^3}{A * D}$$

Average corrosion Rate = 5.4427MDD

ACCEPTABLE KURITA STANDARD

0	-	10MDD	-	Very Good
10	-	20MDD	-	Good
21	-	Above	-	Not satisfactory

.0 CONCLUSION

The average corrosion rate of 5.4427MDD shows that the cooling water treatment programme is VERY GOOD going by KURITA Standard.

.0 RECOMMENDATION

The current cooling water treatment programme should be maintained.

INSPECTORS
F. AKOGUN
ADEWARA

S.O. AYENI
CHIEF INSPECTOR

A.R. SHEHU
DM, I&T

FDO, METSD, MMTCE, MPPU, MFSE

APPENDIX 'E1'

KRPC - The pride of the

INSPECTION REPORT

DATE: 16TH JANUARY 2008. REPORT NO. 1383
AREA: PPU (EA)
UNIT: 74 (COOLING TOWER)
ITEM: COOLING WATER RETURN LINE
SERVICE: COOLING WATER
SUBJECT: **CORROSION TEST COUPONS WEIGHT-LOSS EVALUATION**

1.0 PREAMBLE

The corrosion rate of cooling water was evaluated by inserting three marked coupons in the column provided on the cooling water return line and analyzed after 64 days of immersion period.

2.0 OBSERVATIONS

2.1 On withdrawal of coupons, slight brownish deposits were observed on part of the coupons' surfaces.
2.2 After cleaning and pickling, minor corrosion was observed on the coupons.
2.3 Water flow was approximately 1m/sec throughout the period of coupon insertion.

3.0 EVALUATION

S/N	COUPON NO.	INITIAL WEIGHT (gm) W_{t1}	FINAL WEIGHT (gm) W_{t2}	SURFACE AREA, A (dm^2)	LOSS IN WEIGHT (gm)	RESIDENT TIME, D (days)	CORROSION RATE (MDD)
1.	001	11.5148	11.5122	0.31	0.0026	64	0.131
2.	027	11.5182	11.5147	0.31	0.0035	64	0.1764
3.	060	11.4175	11.4147	0.31	O.0028	64	0.1411

$$\text{Corrosion Rate, MDD} = \frac{(W_{t1} - W_{t2}) * 10^3}{A * D}$$

Average corrosion Rate = 0.1495MDD

ACCEPTABLE KURITA STANDARD

0 - 10MDD - Very Good
10 - 20MDD - Good
21 - Above - Not satisfactory

4.0 CONCLUSION

The average corrosion rate of **0.1495MDD** shows that the cooling water treatment programme is VERY GOOD going by KURITA Standard.

5.0 RECOMMENDATION

The current cooling water treatment programme should be maintained.

U.P. AKOGUN
INSPECTOR

S.O. AYENI
CHIEF INSPECTOR

J.A. AMWE
Ag. DM, I&T

CC: EDO, METSD, MMTCE, MPPU, MFSE

APPENDIX F2

KRPC - The pride of the

INSPECTION REPORT

DATE:	17TH MARCH 2008.	REPORT NO. 1510
AREA:	PPU (EA)	
UNIT:	74 (COOLING TOWER)	
ITEM:	COOLING WATER RETURN LINE	
SERVICE:	COOLING WATER	
SUBJECT:	CORROSION TEST COUPONS WEIGHT-LOSS EVALUATION	

1.0 PREAMBLE

The corrosion rate of cooling water was evaluated by inserting three marked coupons in the column provided on the cooling water return line and analyzed after 60 days of immersion period.

2.0 OBSERVATIONS

2.1 On withdrawal of coupons, brownish deposits were observed on part of the coupon's surfaces.

2.2 After cleaning and pickling, corrosion was observed on the coupons.

2.3 The water flow was not interrupted throughout the 60 days duration.

3.0 EVALUATION OF DATA

S/N	COUPON NO.	INITIAL WEIGHT (gm) Wt_1	FINAL WEIGHT (gm) Wt_2	SURFACE AREA, A $(dm)^2$	LOSS IN WEIGHT (gm)	RESIDENT TIME, D (days)	CORROSION RATE (MDD)
1.	022	11.3927	11.1742	0.31	0.2185	60	11.7473
2.	055	11.4827	11.2686	0.31	0.2141	60	11.5107
3.	059	11.4987	11.2721	0.31	0.2266	60	12.1827

$$\text{Corrosion Rate, MDD} = \frac{(Wt_1 \,.\, Wt_2) \times 10^3}{A \times D}$$

Average Corrosion Rate = 11.81MDD

ACCEPTABLE KURITA STANDARD

0	-	10MDD -	Very Good
11	-	20MDD -	Good
21	-	Above -	Not Satisfactory

4.0 CONCLUSION

The average corrosion rate of 11.81MDD shows that the cooling water treatment programme is good going by KURITA standard

5.0 RECOMMENDATIONS

5.1 The water flow should not be interrupted during the resident period of coupons.

5.2 The current cooling water treatment programme can be improved upon..

INSPECTORS
C.P. AKOGUN
R.A. ADEWARA

A.R. SHEHU
DM. I&T

CC: EDO, METSD, MMTCE, MPPU, MFSE

KRPC - The pride of the Nation

INSPECTION REPORT

DATE: 23RD JULY, 2008. REPORT NO. 1840
AREA: PPU (EA)
UNIT: 74- (COOLING TOWER)
ITEM: COOLING WATER RETURN LINE
SERVICE: COOLING WATER
SUBJECT: **CORROSION TEST COUPONS' WEIGHT LOSS EVALUATION**

1.0 INTRODCTION

The corrosion rate of cooling water was evaluated by inserting three marked coupons in the column provided on the coling water return line and analyzed after 68 days of immersion period.

2.0 OBSERVATIONS.

2.1 On withdrawal of coupons, brownish deposits were observed on the coupons' surfaces.
2.1 After cleaning and pickling, corrosion was observed on the coupons.
2.3 Water flow was approximately 1m/sec throughout the period of coupon insertion.

3.0 EVALUATION

COUPON NO	INITIAL WEIGHT (W1)	FINAL WEIGHT (W2)	SURFACE AREA (A)	LOSS IN WEIGHT	RESIDENT TIME (D)	CORROSION RATE (MDD)
008	11.3411	10.9345	0.31	0.4066	68	19.28842505
041	11.3877	11.0019	0.31	0.3858	68	18.3017[illegible]
068	11.4769	11.0717	0.31	0.4052	68	19[illegible]
		AVERAGE CORROSION RATE (MDD) =				18.9373814

Corrosion Rate = [(W1 -W2)*10^3]/ (A*D)

ACCEPTABLE KURITA STANDARD

0 - 10MDD	VERY GOOD
10 - 20MDD	GOOD
21 - ABOVE	NOT SATISFACTORY

4.0 CONCLUSION

The average corrosion rate of **18.9374MDD** shows that the cooling water treatment is **GOOD** going by KURITA standard.

5.0 RECOMMENDATIONS

5.1 The current cooling water treatment programme should be improved upon.
5.2 KURITA should make corroison coupons available.

U.P. AKOGUN	**M. HAYATUDEEN**	**A.R. SHEHU**
PLANT INSPECOR	SUPT. PPU/OFFSITE	DM, I&T

Cc: EDO, METSD, MMTCE, MPPU, MFSE

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INSPECTION REPORT

DATE: 23rd October 2008. REPORT NO. 1946

AREA: III

UNIT: 16 - FCCU

ITEM: 24" – P – 16077 – B11N

SERVICE: HYDROCARBON VAPOUR LINE FROM 16E01B – 16D03

SUBJECT: **ULTRASONIC THICKNESS MEASUREMENT (U. T. M.) SURVEY ON 24" – P – 16077 – B11N HYDROCARBON VAPOUR FROM 16E01B – 16D03**

1.0 INTRODUCTION

As part of the intensive thickness survey being carried out on the process piping in the FCCU, Ultrasonic Thickness Measurement (U. T. M.) survey was carried out on 24" – P – 16077 – B11N Hydrocarbon Vapour Line from 16E01B – 16D03. The results obtained are as shown in the table below:

2.0 DESIGN PARAMETERS

The original thickness of the line is 9.52mm and the Corrosion Allowance is 2.52mm.

3.0 U.T.M. RESULTS

	Actual Readings (mm)						
Ref.	1	2*	3	4	5*	6	7
A	7.5	7.1	7.1	6.8	7.0	7.7	7.4
B	6.8	7.1	6.5	6.5	7.0	6.8	7.2
C	7.4	5.9	6.0	6.4	7.0	6.9	
D	7.7	7.5	7.1	7.4	7.2	7.1	7.7

* indicates elbow points

Excessive metal loss was observed on some sections of the line.

4.0 RECOMMENDATION

Schedule the 24" – P – 16077 – B11N Hydrocarbon Vapour Line from 16E01B – 16D03 for replacement.

I. O. FAFIOLU
Plant Inspector (WRPC)

P. N. TWAKI
Chief Inspector, Fuels

J. A. AMWE
DM, I & T.

cc: EDO, METSD, MMTCE, MPROD, MFSE

APPENDIX E

KRPC - The pride of the Nation

INSPECTION REPORT

DATE: 17TH MARCH, 2010. REPORT NO. 321
AREA: PPU (EA)
UNIT: 74- (COOLING TOWER)
ITEM: COOLING WATER RETURN LINE
SERVICE: COOLING WATER
SUBJECT: **CORROSION TEST COUPONS' WEIGHT LOSS EVALUATION**

1.0 INTRODCTION

The corrosion rate of cooling water was evaluated by inserting three marked coupons in the column provided on the coling water return line and analyzed after 90 days of immersion period.

2.0 OBSERVATIONS.

2.1 On withdrawal of coupons, brownish deposits were observed on the coupons' surfaces.
2.1 After cleaning and pickling, corrosion was observed on the coupons.
2.3 Water flow was approximately 1m/sec throughout the period of coupon insertion.
2.4 Two bolts & nuts in one of the flanges of the column housing the coupons are bad

3.0 EVALUATION

COUPON NO	INITIAL WEIGHT (W1)	FINAL WEIGHT (W2)	SURFACE AREA (A)	LOSS IN WEIGHT	RESIDENT TIME (D)	CORROSION RATE (MDD)
2731	8.7202	8.5561	0.174	0.1641	90	10.4789272
2732	8.6999	8.551	0.174	0.1489	90	9.508301405
2733	8.709	8.5489	0.174	0.1601	90	10.22349936
		AVERAGE CORROSION RATE (MDD) =				10.07024266

Corrosion Rate = [(Wt1 -Wt2)*10^3]/ (A*D)

ACCEPTABLE KURITA STANDARD

0 - 10MDD	VERY GOOD
10 - 20MDD	GOOD
21 - ABOVE	NOT SATISFACTORY

4.0 CONCLUSION

The average corrosion rate of **10.07024MDD** shows that the cooling water treatment is **GOOD** going by KURITA standard.

5.0 RECOMMENDATIONS

5.1 Replace the bad bolts and nuts in one of the flanges of the column housing the coupons.
5.2 The current cooling water treatment programme should be improved upon.

U.P. AKOGUN	**M. HAYATUDEEN**	**A.R. SHEHU**
PLANT INSPECOR	SUPT. PPU/OFFSITE	DM, I&T

Cc: EDO, METSD, MMTCE, MPPU, MFSE

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INSPECTION REPORT

DATE: 19TH MAY, 2010. REPORT NO. 331
AREA: PPU (EA)
UNIT: 74- (COOLING TOWER)
ITEM: COOLING WATER RETURN LINE
SERVICE: COOLING WATER
SUBJECT: **CORROSION TEST COUPONS' WEIGHT LOSS EVALUATION**

1.0 INTRODCTION

The corrosion rate of cooling water was evaluated by inserting three marked coupons in the colum provided on the coling water return line and analyzed after 62 days of immersion period.

2.0 OBSERVATIONS.

2.1 On withdrawal of coupons, brownish deposits were observed on the coupons' surfaces.
2.1 After cleaning and pickling, corrosion was observed on the coupons.
2.3 Water flow was approximately 1m/sec throughout the period of coupon insertion.
2.4 Two bolts & nuts in one of the flanges of the column housing the coupons are bad

3.0 EVALUATION

COUPON NO	INITIAL WEIGHT (W1)	FINAL WEIGHT (W2)	SURFACE AREA (A)	LOSS IN WEIGHT	RESIDENT TIME (D)	CORROSION RATE (MDD)
2586	8.6581	8.348	0.174	0.3101	62	28.74490174
2587	8.6544	8.3662	0.174	0.2882	62	26.71486837
2588	8.6665	8.4439	0.174	0.2226	62	20.634[illegible]
AVERAGE CORROSION RATE (MDD) =						25.36[illegible]264

Corrosion Rate = ((W1 - W2)*10^3)/(A*D)

ACCEPTABLE KURITA STANDARD

0 - 10MDD	VERY GOOD
10 - 20MDD	GOOD
21 - ABOVE	NOT SATISFACTORY

4.0 CONCLUSION

The average corrosion rate of **25.3646MDD** shows that the cooling water treatment is **NOT SATISFACTORY** going by KURITA standard.

5.0 RECOMMENDATIONS

5.1 Replace the bad bolts and nuts in one of the flanges of the column housing the coupons.
5.2 The current cooling water treatment programme should be improved upon.

INSPECTORS
S.O. AYENI
U.P. AKOGUN
K.C. ANYABOLU

M. HAYATUDEEN
SUPT. PPU/OFFSITE

A.R. SHEHU
DM, I&T

Cc: EDO, METSD, MMTCE, MPPU, MFSE

APPENDIX 'F'

FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA.

DEPARTMENT OF CHEMICAL ENGINEERING

QUESTIONNARE ON THE TOPIC:-

SAFETY ASSESSMENT OF PRODUCTION PLANT IN NIGERIA; A CASE STUDY OF KADUNA REFINERY PETROCHEMICAL COMPANY (KRPC); CORROSION DEVELOPMENT MECHANISM.

28TH MAY, 2008

Dear respondent,

You are kindly requested to complete this questionnaire that is designed to elicit information on "Safety Assessment of Kaduna Refinery Petrochemical company" (KRPC)

You are one of the few ones selected for the purpose of this study, therefore, sincere responses are thus required.

Section A: [Personal Data]

[Please fill the gaps in this section]

1. Name of your Department in the Company..
2. Sex..
3. Job designation...
4. Your years of working experience in the KRPC...

Section B: [Personal observations]

[Please respond appropriately to the following items by fill in the space provided]

5. What are the most commonly used corrosion monitoring system in KRPC?
   ....
   ....
   ....
6. What are the constraints to corrosion monitoring in KRPC?
   ....
   ....
   ....

....

....

....

....

7. How many times has accident occurred in KRPC as a result of equipment failure in the past five years?

   ....

8. How often do they do Turn-Around-Maintenance [TAM] in KRPC?

   ....

   ....

9. What were the reasons for poor performance by KRPC in the execution of TAM '98 project?

   ....

   ....

   ....

   ....

Section C: [Personal Assessment]

[Please respond appropriately to the items below by putting a tick [X] in any of the three columns as the alternative that best represent your assessment and evaluation to each request]

	GOOD	FAIR	BAD	DO Not KNOW
10. How do you rate KRPC Performance?				
11. How do you rate KRPC Turn-Around-Maintenance?				
12. How can you rate the integrity of equipments in KRPC?				
13. To what extent can you assess the safety of production Plants in KRPC?				