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An Experimental Investigation Into Corrossion Problems At Kaduna Refinery And Petrochemicals Plant Kaduna, Nigeria, Using Local Crude Oil Blend

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Abstract: ***Corrosion problem in Refinery operation has led to serious economic waste. The Kaduna Refinery and Petrochemical Company Limited is one of the four Refineries established by the Federal Government of Nigeria through the Nigerian National Petroleum Co-operation (NNPC). The Kaduna Refinery from its inception was designed to process heavy crude oil for the production of lubricants and since the Nigerian crude oil are in the majority of cases light, importation of the crude from abroad was the only option. Recent research on blending of crude from different fields in Nigeria to achieve the same characteristics as the imported crude has given some positive results. Then there is need to investigate the corrosiveness of the blend to ensure a trouble free operation during the trail run.***

Samples from various oil fields in Nigeria were blended which formed medium A, and an inhibitor was added to the blend to form medium B, and finally Arabian light was obtained from NNPC (Department of Petroleum Resources), which formed medium C, a coupon of 40mm made of 5Cr. ½ Mo was prepared (six in number). The coupons were tested in the different media for corrosion effect under varying temperature of the range of 230^{o}C – 400^{o}C; prolonged effect on the coupon was also observed.

From the analysis of the observation, it was noted that the corrosion rate of the Nigerian crude blend increased slightly with temperature in steps of 230^{o}C up to 400^{o}C and 480^{o}C maximum in some cases.

A comparative analysis between the corrosion rates measured by medium A and B at the same temperature limit indicated a reduction in corrosion rate in favor of Medium B. the corrosion rate measured by medium C is higher than that of medium B. Hence, from the experimental analysis, it was deduced that blending Nigerian local crude oil to achieve the desired characteristics of the imported crude to feed the aforesaid plant was economically feasible and sustainable.

Keywords: Background of Study, Literature Review, Experimental Estimation of Corrosion Rate, Results, Analysis and Discussion, Summary, Conclusion and Recommendations.

I. INTRODUCTION

A. BACKGROUND OF STUDY

Petroleum refining has evolved continuously in response to changing consumer demand for better and different products. Refining is the processing of the complex mixture of hydrocarbons into a number of other complex mixtures of hydrocarbons. The original requirement was to produce kerosene as a cheaper and better source of light.

The development of the internal combustion engine led to the production of gasoline and diesel fuels, the evolution of the airplane created a need first for high-octane aviation gasoline and then for fuel, a sophisticated form of the original product, kerosene. Present day refineries produce a variety of products, including many required as feedstock for the petrochemical industry, and asphalts for road construction etc. which gave rise to the construction of Kaduna Refinery and Petrochemical Company in the northern part of the country (Nigeria).

The Kaduna Refinery and petrochemical Limited is one of the four refineries established by the Government of Nigeria through the Nigerian National Petroleum Co-operation (NNPC). The Kaduna Refinery from its inception was designed to process heavy crudes for the production of lubricants and since the Nigerian crude's are in the majority of cases light, importation of the crude from abroad was the only option. Recent research on blending of crudes (which is the process of mixing and combining hydrocarbon fractions, additives, and other components to produce finished products with specific performance properties) from different fields in Nigeria to achieve the same characteristics as the imported crude has given some positive results. Then is therefore the need to investigate the corrosiveness of the blend to ensure a trouble free operation during the trial run or field operation.

B. STATEMENT OF THE PROBLEM

Recently, research proposals on the investigation into corrosion problems in Kaduna Refinery and petrochemical company (KRPC) using Nigeria crude blend have been presented by different Engineers and Scientists, but the value and reliability of the data to be obtained depends on details involved in the test.

Since the refinery was designed to process heavy crudes for the production of lubricants and since the Nigerian crude are in the majority of cases light, important of the crude from abroad was the only option. Recent research on blending of crudes from different fields in Nigeria to achieve the same characteristics as the imported crude has given some positive results. Then, there is need to investigate the corrosiveness of the blend to ensure a trouble free operation during the trial run.

C. OBJECTIVE OF THE STUDY

Controlling and manipulating all the rate factors affecting corrosion in a process plant are very difficult. Simulating actual refinery operation in a laboratory test is of considerable importance in obtaining reliable and reproducible results.

Therefore, the main objective of this is to design an adequate experimental technique to carry out the following functions:-

- ✓ Determine the appropriate blend ratio to yield the characteristics of the desired crude (imported),
- ✓ To test and prove operational reliability of the blended crude,
- ✓ Determination of penetration (corrosion) rate and estimation of probable retirement rate, by the weight loss method,
- ✓ Correlation of unexpected changes of process environment to operation variables,
- ✓ Process control, inhibition, anodic and cathodic protection,
- ✓ Material assessment and selection.

II. LITERATURE REVIEW

A. CONCEPT OF CORROSION

Corrosion is a common phenomenon in petroleum refining environment; its effects are so detrimental that various methods of preventing and controlling it have been put forward by engineers.

Corrosion mechanism can be described as an electrochemical process, as a result of observations on the behavior of iron in aqueous media. For this process to occur, three requirements must be fulfilled.

- ✓ An electromotive force or potential difference must be present, i.e. anode and cathode areas.
- ✓ There must be an electrical or couple established between the anode and the cathode.
- ✓ The anode and cathode, electrically connected, must be in contact with the test fluid that will conduct current (as electrolyte).

For corrosion to occur at a significant rate, some means of cathodic depolarization must be active. In other words, in the absence of the cathodic depolarization agents, such as oxygen or thermally degraded components, the system soon results in a drastic reduction of the corrosion rate. If the corrosion continues and more metal loss is evident, an effective cathodic depolarization mechanism is present.

The electrochemical phenomena of corrosion can be discussed as follows: On the system vessel, there is an anode and a cathode; the metal at the anode loses two electrons which flows through the metal pipe to the cathode. The surface reaction is as follows:

$Fe \longrightarrow Fe^{++} + 2e$ ---------------------------------2.1.1

The rate of this reaction is found to be dependent upon the rate of the cathode reaction; hence, the corrosion rate is "cathodically controlled". The iron ion, Fe^{++}, enters the solution as a positively charged soluble particle of ion. The cathode, being negatively charged, attracts hydrogen ions (H^+) which arise from the dissociation or ionization of water.

$H_2O \longrightarrow H^+ + OH^-$ -----------------------2.1.2

At the cathode, hydrogen ions accept electrons and become atom of hydrogen.

$2H^+ + 2e \longrightarrow 2H$ ------------------------------2.1.3

Since the electrolyte must remain electrically neutral, the positively charged ferrous ions (Fe^{++}) often are oxidized to ferric ions (Fe^{+++}) which react with the negatively charged hydroxyl ions to form ferric hydroxide or rust.

$Fe^{++} + 3H_2O \longrightarrow Fe^{+++} + 3OH \longrightarrow Fe(OH)_3$ rust $+ 3H^+$--2.1.4

If enough hydrogen accumulates at the cathode, it becomes polarized; i.e. a very thin film of hydrogen will cover the metal surface which prevents direct contact between the electrons and the cathode. It behaves as a non-ferrous coating membrane. The corrosion severity is a function of the membrane permeability.

a. CHEMICAL THEORY

The chemical corrosion mechanism is one of the corrosion processes which depend on the nature of the surrounding media with which the metal reacts. Corrosion at high temperature in the vapor and gaseous phase and corrosion in liquids (non-electrolytes are classified as chemical corrosion).

Examples of gaseous corrosion are corrosion of furnace structures, some parts of internal combustion engines, steam and gas turbine blades, oxidation of metals on heating, etc. The rate of gaseous corrosion is affected considerably by the composition of the corroding medium. An example of non-electrolytic corrosion is attack in liquids, which are non conductors of electric current (e.g. in various organic liquids, in alcohol, benzene, etc).

Refinery metals are not homogenous, but contain inclusions, precipitates and perhaps several different phases. The phenomenon of chemical corrosion is clearly explained as the loss of material due to chemical attack. It can also be described as the destructive attack of a metal by chemical reaction with its environment.

Generally, it occurs when a metal reacts with its environment and invariably followed by a loss of mass and weight by the metal. Corrosion may be classified into two types namely – the uniform and localized types of corrosion.

B. UNIFORM CORROSION

This is the most common type of corrosion. It is normally characterized by a chemical reaction, which proceeds uniformly over the entire exposed surface. The metal becomes thinner and eventually fails. Oxygen corrosion called rusting is a common type. Oxygen is more corrosive in salt water than in fresh water. The dissolved oxygen (DO) is the major cause of vessel corrosion.

Oxygen can cause severe corrosion at very low concentration, (less than 1ppm). If carbon (IV) oxide or hydrogen sulphide is dissolved in oxygen-contaminated crude, the corrosiveness is increased drastically. This type of corrosion can be prevented or reduced by the use of proper materials, coatings, inhibitors or cathodic protection.

C. LOCALIZED CORROSION

This is the type of corrosion that is being observed at the specific portions of the metal. It is the most difficult form of corrosion to be detected in the oil industry. Its attack takes several forms which include: galvanic, crevice, stress cracking, pitting, fatigue, selective leaching, fretting, electrolytic and erosion corrosion.

a. GALVANIC CORROSION

When two different metals are placed in contact in an electrolyte, the corrosion rate of the more reactive metal will usually increase and the corrosion rate of the less reactive metal will decrease. This principle is utilized in a beneficial way in cathodic protection. Steel is connected to a more reactive metal such as magnesium and is being protected from such corrosion. Accelerated corrosion due to galvanic effects is usually observed at the junction of the two metals. For instance, when new pipe is connected to old pipe, the new pipe acts as the anode and corrodes preferentially.

This type of localized corrosion can be prevented by proper welding practices, insulating metals from each other, keeping dissimilar metals apart and using metals that are relatively close together in the galvanic series.

b. CREVICE CORROSION

Crevices promote the formation of concentration cells. This is especially serious in oxygenated systems where the oxygen in the crevice may be consumed more rapidly than fresh oxygen can diffuse into the crevice. This causes the pH in the crevice to decrease, resulting in a more acidic environment, which accelerates corrosion.

c. STRESS CRACKING

This type of localized corrosion includes any combined effect of stress and corrosion on the behavior of the metal which leads to accelerated attack and cracking in some refinery metal, especially in the cyclic pipe networks that are difficult to avoid because of the complicated nature of Refinery systems.

Although, the mechanism of stress cracking is not completely understood, it is generally accepted that, the following conditions must be present before it can occur:

- ✓ Hydrogen sulphide (H_2S),
- ✓ Water: Even a trace amount of moisture is sufficient,
- ✓ High strength steel: The exact strength level varies with the composition and microstructure of the steel,
- ✓ The steel must be under tensile stress or load.

The materials for application in the environment containing hydrogen sulphide (H_2S), Sulphur (IV) (SO2) should be selected according to NACE standing MR 01-75 (latest revision).

d. PITTING CORROSION

This type of localized corrosion is characterized by the appearance of pit-like spot over the surface of the metal. It is caused by the presence of non-uniform conditions, such as low pH values of the immediate environment and its differential aeration. It is common with Aluminum and stainless steel in aqueous surroundings. Addition of sodium or potassium dichromate inhibits its effects.

e. FATIGUE CORROSION

This is the result of cyclic stress and corrosion. Most sucker breaks and transmission failures occur as a result of corrosion fatigue. It can also be the cause of pump failures. It is possible on any part that is subjected to a cyclic stress in a corrosive environment. It is a brittle type of failure which can occur at stress levels well below the yield strength.

f. FRETTING

This localized corrosion occurs when two metal surfaces are in contact with each other in a corrosive environment and are subjected to one vibration or the other relative to the motion. Accelerated attack results from the continuous removal of any protective films from the metal surfaces. It occurs mainly on machine parts such as ball and roller bearings, shafts and gears. This type of corrosive can be prevented by proper welding practices and insulating the metals.

g. EROSION CORROSION AND IMPINGEMENT

The formation of a layer of corrosion product on the surface of a corroding metal usually results in decreased corrosion rates. The corrosion product acts as an insulator and partially protects the surface.

The removal of the corrosion product by erosion due to high velocities, turbulence or the abrasive action of suspended solids can result in increased corrosion rates by continually exposing fresh metal to the electrolyte.

Other phenomenon similar to erosion is impingement. This occurs when a stream impinges upon a metal surface and breaks down protective films at very small areas resulting in pits.

h. INTERGRANULAR CORROSION

The components of alloys are not evenly distributed throughout the entire piece of the metal due to the effects of the heat-treating and other chemical processes that were involved during their productions.

This problem can be prevented by proper welding practices, addition of columbium or titanium and use of low carbon grades of stainless steel.

D. FACTORS AFFECTING CORROSION RATE

Various factors that can affect the rate of corrosion are: water, acid, gases, dissimilar metals, chloride content, high fluid velocity, air (oxygen), temperature and pressure.

a. WATER

This is the most common factor that affects corrosion in any environment. Its content in the untreated oil varies from 0.01% - 80%. It may be in the form of oil brine, water spray, vapor or condensate. Corrosiveness decreases with decreasing amount of free water. But in salt water (brine), it increases.

b. ACID GASES

Carbon (IV) oxide, hydrogen sulphide and Sulphur (IV) oxide are acid gases, which in solution decreases the pH of the solution and therefore promotes corrosion process. At a higher temperature, Carbon (IV) oxide helps in the formation of a protective carbonate film on steel. Hydrogen sulphide also forms a protective sulphide film that reduces carbon (IV) oxide corrosion at low temperature.

The partial pressure ratio of the gases CO_2/H_2S indicates the prevalent corrosion mechanism. Values greater than 200 indicate CO_2 corrosion, while those less than 200 indicate H_2S.

c. DISSIMILAR METALS

When metals that are far apart in the galvanic series are in contact, they allow the flow of current in between them and this promotes the corrosiveness of the metals.

d. CHLORIDE CONTENT

Chloride ions in crudes bearing water promotes the breakdown of normal protective films and encourages localized corrosion of the metal in contact. At high concentration, they affect the solubility of the inhibitors.

e. HIGH FLUID VELOCITY

High fluid velocity or turbulence is capable of producing shear stress in metals that can remove corrosion preventing films. Various flow regimes can either promote or hinder inhibitors.

f. AIR (OXYGEN)

The dissolved oxygen in the crude oil is the major cause of corrosion in process system. This gas at low concentration causes severe corrosion.

Oxygen is more soluble in fresh water than in salt water. It accelerates corrosion because it is a very effective oxidizing agent.

g. TEMPERATURE AND PRESSURE

Increased pressure normally results in increase in the solubility of dissolved gases. Increase in solubility thereby causes faster corrosion of metal. It can therefore be said that increases in pressure of a system subsequently results in increase in corrosiveness of the solution.

The corrosion rate is twice its original in every 10^0C rise in temperature. This happens especially in closed systems. For systems open to the atmosphere, corrosion rate may increase initially with rise in temperature but at higher temperature, dissolved gases begin to escape and so the corrosiveness of the solution decreases.

E. BASICS OF BLENDING OPERATION

Petroleum blending operation is the process of mixing and combining hydrocarbon fractions, additives and other components to produce finished products with specific performance properties. Mixed based crudes have varying amounts of each type of hydrocarbon. Refinery crude base stocks usually consist of mixtures of two or more different crude oils.

The Hendrix group inc. Refining Company, Texas defined crude oils in terms of API (American Petroleum Institute) gravity, the higher the API gravity, The lighter the crude. For example, light crude oils have high API gravity and low specific gravity. Crude oils with low carbon, high hydrogen, and high API gravity are usually rich in paraffin and tend to yield greater proportions of gasoline and light petroleum products; those with high carbon, low hydrogen, and low API gravity are usually rich in aromatics.

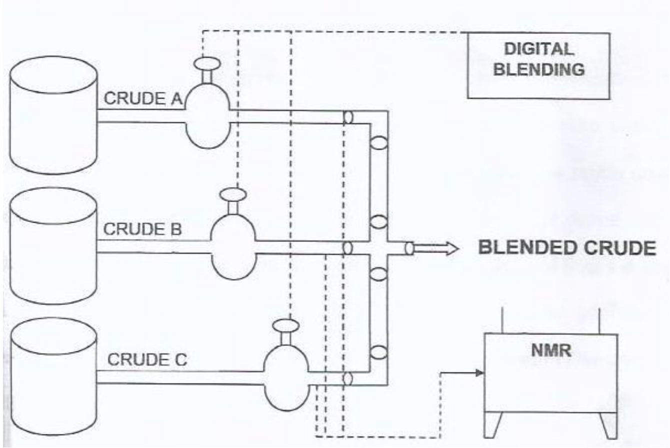

Figure 2.1: Crude Oil Blending

The crude blending application is an attractive solution for refiners with the ability to blend different crude types to provide a consistent and optimal feedstock to refinery operations.

Crude blending application is an intelligent blending operations control solution based upon Foxboro's extensive process knowledge and experience. This application solution includes the unique technology of our process NMR (Net Minimal Ratio) the combination of a unique analyzer, advance software and experienced engineering services for refinery customers to achieve business success.

Functions

Crude oil blending is based on the implementation of the Foxboro Company's I/A series NMR process analyzer and Foxboro's blend optimization and supervisory system (BOSS). BOSS calculates optimum blend ratio based on measurement of crude oil component quality and desired blended crude oil quality.

Optimal crude oil properties are provided by refinery models that define optimal utilization of downstream units for various crude oil types. Optimal flow set points are sent to a blend ratio controller similar to the type used for gasoline and diesel blending. Foxboro can supply a digital blending system (The I/A Series DBS), or an existing digital blender can be used.

Depending upon requirements, one or more NMR analyzers are applied to the blended crude oil stream and to the crude oil component streams. The NMR analyzer provides real-time analysis of essential qualities. Such as API gravity or density, true boiling point/ASTM distillation, initial and final boiling point, and water content.

CRUDE-OIL-SOURCE	**PARAFFINS (%VOL.)**	**AROMATICS (%VOL.)**	**NAPHTHENES (%VOL.)**	**SULPHUR (%VOL.)**	**API GRAVITY (%VOL.)**	**NAPH YIELD (%VOL.)**	**OCTANE NUMBER (%VOL.)**
Nigerian Light	37	9	54	0.2	36	28	60
Saudi Light	63	19	18	2	34	22	40
Saudi Heavy	60	15	25	2.1	28	23	35
Venezuela Heavy	35	12	53	2.3	30	2	60
Venezuela Light	52	14	35	1.5	24	18	50
USA Midcont Sweet	-	-	-	0.4	40	-	-
USA-W-Texas Sour	46	22	32	1.9	32	33	55
N. Sea Brent	50	16	34	0.4	37	31	50

Table 2.1: Typical Approximate Characteristics and Properties and Gasoline Potential of Various Crudes (Representative Average Group Inc. 2002)

F. COMMON REFINERY CHEMICALS

a. LEADED GASOLINE ADDITIVES

Tetraethyl Lead (TEL) and tetra-methyl lead (TML) are additives formally used to improve the gasoline octane ratings but are no longer in common use except in aviation gasoline.

b. OXYGENATES

Ethyl tertiary butyl ether (ETBE), methyl tertiary butyl ether (MTBE), tertiary amyl methyl ether (TAME), and other oxygenates improves gasoline octane ratings and reduces carbon (IV) oxide emission.

c. CAUSTICS

Caustics are added to desalting water to neutralize acids and reduce corrosion. They are also added to desalted crude oil in order to reduce the amount of corrosive chlorides in the tower overheads. They are used in some refinery treating processes to remove contaminants from hydrocarbon streams.

d. SULPHURIC AND HYDROFLURORIC ACIDS

Sulphuric acid and hydrofluoric acid are used primarily as catalyst in alkylation processes. Sulphuric acid is also used in some treatment process.

G. EFFECTS OF CRUDE OIL BLENDING ON REFINERY SYSTEM-CORROSION RATE

Moussa, M. (1983) measured the corrosion rate of X-52 mild steel coupon using a Sandia lab flow loop with a temperature range of 200-500^{0}F to be 253.42 mils per year. The corrosion rate was measured by weight loss technique under the rolling condition in which the fluid and the coupons are rotating.

Different formulations of the blend were tested at various temperatures increasing from 2000F to 500^{0}F with 100^{0}F increments. A flow loop rolling oven, which is thermally controlled with a temperature range from 0-500^{0}F, was used. It had only one rolling speed with indicating light.

The stainless steel rolling cells were designed to hold the coupon carrier rigidly. Also, there is no metal connection between the coupon and any metal surface during the run. The main purpose of measuring corrosion under refining conditions by rolling is to stimulate as conveniently as possible, the rotational motion of crude at operating condition. Based on the measured corrosion rates, he presented the following equations to calculate the uniform corrosion rates:

✓ The corrosion rate in mils per years as:

$$\text{MPY} = \frac{\text{Weight Loss,(mg)}}{\text{Specific gravity X 16.387 X area X time (year)}} \quad \ldots\ldots\ 2.5.1$$

The mild steel coupons used in the study have a specific gravity equal to 7.86g/cm^3; thus this formula may be reduced to:

$$\text{MPY} = \frac{\text{68.33 X Weight Loss,(mg)}}{\text{area (in2) X hours of exposure}} \quad \ldots\ldots\ldots\ 2.5.2$$

✓ The corrosion rate in Kilograms per square meter per year:

$$\text{Kg/m}^2\text{/yr} = \frac{\text{Wt.Loss,mg}}{1{,}000{,}000} \text{ x } \frac{10{,}000}{\text{area, cm2}} \text{ x } \frac{365}{\text{days of exposure}}$$

$$= \frac{\text{Wt.Loss,mg X 87.50}}{\text{area,cm}^2\text{ X hours exposed}} \quad \ldots\ldots\ldots\ldots\ldots\ 2.5.3$$

$$\text{Kg/m}^2\text{/yr} = \frac{\text{Wt.Loss,mg X 13.58}}{\text{area, in2 X hours exposed}} \quad \ldots\ldots\ 2.5.4$$

✓ The corrosion rate in pounds per square foot per year:

$$\text{Ib/ft}^2\text{/Yr} = \frac{\text{Wt Loss,mg}}{453{,}000} \text{ x } \frac{144}{\text{area,in}^2} \text{ x } \frac{365}{\text{days of exposure}}$$

$$= \frac{\text{Wt.Loss,mg X 2.781}}{\text{area,in}^2\text{ Xhours exposed}} \quad \ldots\ldots\ldots\ldots\ldots\ 2.5.5$$

H. CORROSION CONTROL

Corrosion control involves the scientific measures taken by the corrosion engineers in reducing the tremendous effects of corrosion in the oil and gas industries. The measures include:

a. *PLACING A BARRIER BETWEEN THE METAL AND ITS ENVIRONMENT*

This is done by coating, application of chemical inhibition and cathodic protection of the metal against the effects of corrosion. Coating can be organic, cementing, or metallic in nature. The most widely used industrial coatings are the coal tar epoxies (fused epoxy, modified epoxy, epoxy-polyamide etc.)

The principle of cathodic protection is to convert the whole metal surface into a cathode. It is accomplished by forcing sufficient current to flow to the structure which has to be protected, so that there will be no flow of current from any point on the metal surface. Chemical inhibition involves the introducing of anti corrosion chemicals such as Sodium Sulphide (Na_2SO_3), Sodium bi-sulphide ($NaHSO_3$) etc, to the surface of the metal in order to reduce the effect of corrosion.

b. *CHANGING THE USE OR WORN-OUT METAL*

This is done by changing or replacing the metal that has lost its metallic characteristics due to its long year installation. This is easily carried out through visual inspection of the metals.

c. *CHANGING THE ENVIRONMENT OF THE METAL*

This method is effected by reducing the temperature around the metal to an optimal range depending on the corrosion source. For CO_2 caused corrosion, temperature of 60^0C and above retard corrosion, whereas for H_2S caused corrosion, temperature of 60^0C promotes it.

Increasing the pH around the metal, removing dissolved gases, application of biocides, gas stripping and vacuum de-aeration are other means of controlling corrosiveness of metal in an environment.

The selection of the method or combination of methods to be used in controlling the corrosiveness in process plant is a dependent factor of cost effectiveness. This means that when applying any of the methods, you must consider the cost of the material, labor and present economic value of the firm, as it helps the firm to maintain its production efficiency.

I. HAZARDS OF CORROSION

The following are possible hazards caused by corrosion if not properly controlled:

a. *PLANT SHUT DOWN*

Most times, plants are shut down and the operation in some reactions of a process plant suspended because of unexpected operational failures due to corrosion.

Monitoring of a process plant therefore is helpful in preventing unexpected plant failure and eventual process shut down.

b. *LOSS OF VALUABLE PRODUCTS*

Corrosion also leads to the loss of valuable products such as pipeline leakage in and out of the industry. The leakage can lead to pollution of the environment especially the aquatic life and farmland.

c. *SAFETY AND RELIABILITY*

Corrosion can expose personnel's in the plant to risk of pollution by some dangerous pollutants that is released due to leakage of the vessels, as if this happens, safety and reliability is not guaranteed.

d. *CONTAMINATION OF PRODUCTS*

In most cases, the utility as well as market value of the product is directly related to its price and quality. For example, the caustics used as catalyst in refinery treating process can be contaminated by the corroded vessel.

e. *MAINTENANCE AND OPERATING COST*

Corrosion effect will create difficulties in the maintenance of metallic equipment used in various constructions. In the manufacturing and process industries, corrosion could lead to total failure of some unit leading generally to the collapse of the entire plant. For such to be maintained, then money that could have been used for valuable things has to sink into this area.

Based on the measured corrosion rates and its effects, the following equation can be used to predict "worse case" uniform corrosion rates.

$$\text{LogR} = 8.78 - \frac{2.32X103}{6+273} - 5.55X10^{-3}t + 0.67\text{LogPCO}_2 \ldots 2.71$$

Where:

R = Maximum uniform corrosion rate (mils/yr)

t = temperature (^{O}C)

PCO_2 = Partial pressure of CO_2 (psi)

Another corrosion rate that is widely used in the oil industry is stated below:

$$\text{Corrosion rate (R)} = 365000 \frac{W}{ADT} \ldots\ldots\ldots\ldots\ldots 2.7.2$$

Where:

R = Corrosion rate (mils/yr)
W = Weight loss, (g)
A = Coupon surface area, (in^2)
D = Metal density, (g/in^3)
T = Exposure time, (days)

J. REFINERY MATERIALS

a. *CHROMIUM AND CHROMIUM ALLOYS*

Chromium with atomic number 24 belongs to Group VI in the periodic table in the subgroup that contains molybdenum and tungsten, it is between Vanadium and Manganese horizontally, it shows a valence of 21, 3^+ and 6^+. Stable isotopes that have been found are 50, 52, 53 and 54. Chromium is a blue-white, very hard metal that crystallizes in the cubic system. Their only important source is the mineral chromites. Vauduelin in 1797 discovered Chromium, so-called from the Greek word "Chrome", meaning color, because its components are highly colored.

The first use of chromium ores (about 1800) was to make chemicals such as chromates for leather fanning and the production of pigments, and as refractory in 1879. It was not until 1910 that chromium ores became metallurgically important.

Two broad classes of chromium are available to industry: (1) ferrochromium and (2) chromium metal. Ferrochromium can be produced by the direct reduction of the ore. To produce chromium metal either electrochemically or by the reduction of chromium compounds, a chemical treatment is necessary to remove the iron and other impurities from the slanting material.

b. *PHYSICAL PROPERTIES*

The physical properties of chromium are summarized below; oxidation tests with a pressure of 760mmHg of oxygen on a specimen containing 0.04% carbon showed the formation of an oxide film 1500A thick in two (02) hour at 900^{0}C.

Chromium is resistant to the following acids, acetic, benzoic, butyric, carbonic, citric, fatty hydrobromic, hydroiodic, lactic, nitric, oleic, oxalic, palmitic, phosphoric, picric, sallcylic, stearic, and tartaric. It is not resistant to hydrochloric, hydrofluoric and sulphuric acids.

1.	Atomic Wight (^{12}Cr=12.0000)	51.996
2.	Isotopes	53(9.55%); 52(83.76%); 53(9.55%); 54(2.38%)
3.	Atomic number	24
4.	Crystal structure @ 20^{0}C, A	Body-centered cubic, a o=2.8844-2.8848
5.	Density at 20^{0}C, g/cm^3	7.19
6.	Melting point, ^{O}C	1875
7.	Boiling point, ^{O}C	2199
8.	Heat fusion, Kcal/mole	3.2-3.5
9.	Latent heat of vaporization at bp, Kcal/mol	76.635
10.	Specific heat at 25^{o}C, cal/mol	5.55 (0.11cal/(g)(^{o}C))
11.	Linear coefficient of expansion @ 20^{0}C	6.2 x 10^{-6}
12.	Thermal conductivity @ 20^{o}C, cgs	0.16
13.	Electrical resistivity, μΩ-cm @ 20^{0}C	12.9
14.	Magnetic susceptibility @ 20^{0}C, cmu	3.6 x 10^{-6}
15.	Total emissivity @ 100^{o}C, non-oxidizing atm.	0.08
16.	(a) λ, A (reflectivity), (b) R, % (reflectivity)	3000, 5000, 10000, 40000 67 70 63 88
17.	Refractive index (a) ∞ (b) Λ	1.64 –3.28 2570-6080
18.	Standard electrode potential, valence 0 to 3^+, V	0. 71

Table 2.2: Physical Properties of Chromium

c. *CHROMIUM ALLOYS*

The alloys most used for chromium additions steels are the different grades of ferrochromium. The percentage composition of various grades is given in Table 2.2 The remainder is iron in all cases.

The first eight grades of ferrochromium intention in table 2.8.2 are considered high-carbon ferrochromium or modification of it. Exothermic ferrochromium are proprietary alloys that give off heat by an exothermic reaction when added to a steel bath, thus causing less of temperature drop and increased solution rate by the addition.

High-carbon ferrochromiums (3-8%) is used to produce steels in which both chromium and carbon must be present or where blowing the bath with oxygen to produce low carbon steel is feasible. In producing this alloy, coke is used to reduce chromate ore. The change is fed into the top of an open-top submerged arc furnace and the molten alloy is collected at the bottom of the furnace from which it is cast into chills. After cooling, it is broken into lumps and graded.

Low-Carbon ferrochrome is used for producing chromium steels in which the presence of carbon is detrimental. It is made by silicon reduction of chromate in a two stage process. In the first stage, a high-silicon ferrochromium practically carbon free is produced in a submerged arc furnace. This product is then treated in an open arc type furnace with a synthetic slag containing Cr_2O_3.

However, low carbon ferrochromium can also be produced by oxygen top blowing on high carbon metal to reduce the carbon content; this process is said to be less costly than the two –stage silicon reduction process.

ALLOY TYPE	Cr,%	C,%	Si,%	S,%	Mn%
Blocking Chrome	55-63	4-6	8-12	0.03 max	
Charge Chrome	58-63	5-8	3-6	0.03 max	
Charge Chrome	50-56	6-8	4-7	0.03 max	
Refined Chrome	53-63	3-5	2.5 max	0.03 max	
Exothermic Ferrochrome	41-51	3.6-6.4	9-14	0.03 max	
Foundry Ferrochrome	55-63	4-6	8-12		
"SM" Ferrochrome	60-65	4-6	4-6		4-6
High-Carbon Ferrochrome	65-70	4-7	1-3		
Low-Carbon Ferrochrome	65-73	0.025-2	0.02-1		
"Simplex" Low-Carbon Ferrochrome	63-71	0.01 - 0.025	2-7		

Table 2.3: Compositions of Chromium Alloys

TYPE OF LOW-ALLOY STEEL AND AVERAGE CHEMICAL CONTENT, %	DESIGNATION
Nickel – chromium steels	
Ni 1.25; CrO 65	31xx
Ni 3.50; Cr 1.57	33xx
Chromium – Molybdenum steels	
Cr 0.50 and 0.95; Mo 0.25, and 0.12	41xx
Nickel – Chromium – Molybdenum Steels	
Ni 1082; Cr 0.50 and 0.80; Mo 0.25	43xx
Ni 1.05; Cr 0.45; Mo 0.20	47xx
Ni 0. 55; Cr 0.50 and 0.65; Mo 0.20	86xx
Ni 0.55; Cr 0.50; Mo 0.12	87xx
Ni 1.00; Cr 0.80; Mo 0.25	93xx
Chromium Steels	
Cr 0.27, 0.40 and 0.50	98xx
Cr 0.80, 0.87, 0.90, 0.95, 1.00 and 1.05	50xx
Cr 0. 50	51xx
Cr 1.02	501xx
Cr 1.45	511xx
Chromium-Vanadium Steels	
Cr 0.80 and 0.95; Vo. 10 and 0.15 (min)	61xx
Boron-treated Chromium Steels	Xx13xx

Table 2.4: Basic Numbering System for Chromium Steels

K. CORROSION INHIBITORS IN PETROLEUM REFINING

Corrosion agents in the refinery are similar to those causing trouble in production operations, but these are transferred to different equipment, and they are more often concentrated. Additional difficulties are caused by higher temperatures, pressures, and flow rates in refinery equipment and the prohibitively high costs of downtime caused by corrosion. Aqueous electrolytes containing acid gases such as CO_2 and H_2S, mineral acids such as hydrochloric or naphthenic acids are the principal causes of internal corrosion in refineries. Use of neutralizing inhibitors such as sodium hydroxide (NaOH), sodium Carbonate (Na_2CO_3), and Ammonia (NH_3), is much more widespread than in primary or secondary production of petroleum. Organic inhibitors are used extensively and often in conjunction with neutralizers. Thus, ammonia may be used to raise the pH of an acidic liquid to near 7.0, after which an organic inhibitor completes the job of protection. The use of the two materials in conjunction gives adequate protection more cheaply than does either material alone.

III. EXPERIMENTAL ESTIMATION OF CORROSION RATE

A. APPARATUS AND REAGENTS

The apparatus and reagents used are as follows:

- ✓ Beakers of 500ml volume (six)
- ✓ Strings and retort stand
- ✓ Electronic weighing balance
- ✓ Hydrometer and magcoban multi mixer
- ✓ Glass plates (air tight)
- ✓ Polish papers
- ✓ Sample thong
- ✓ Muffle oven of temperature range of 0-1650^{0}C
- ✓ Flat bottom flasks
- ✓ 40 x 40mm coupon of 5 Chromium. ½ molybdenum steel.

The reagents used are:

- ✓ Samples of crudes from various fields in Nigeria

Crude Oil Sample	Oil Field	API Gravity
A	Obigbo North	37.2
B	Agbada 1	33.4
C	Escravos	39.5
D	Omoku	30.9
E	Nembe Creek	38.8
F	Imo River	37.1
G	Kolo Creek	40.4

Table 3.1: Crude Oil Samples from Various Fields in Niger-Delta, Nigeria

- ✓ Arabian Light Crude
- ✓ Sets of corrosion inhibitors; (NaOH, $NaCO_3$, NH_3)
- ✓ Hydrochloric Acid
- ✓ Water

a. CORROSION MEDIA

The reagents for this experiment formed the basis for establishing the corrosion media, thus, there were three major media, namely A, B, C, which were blend of various crude oil samples, inhibited Nigeria crude blend, and Arabian light respectively.

B. METHODOLOGY

The analysis of possible effects of corrosion on refinery (Kaduna) material was investigated experimentally in three categories, through the weight loss method, under the process operating temperature and pressure.

a. PROCEDURES FOR API GRAVITY DETERMINATION

- ✓ Decant the crude oil sample by adding demulsifier, shake well and allow the water to settle out.
- ✓ Collect the upper content of the tube (oil) with the centrifuge tube and revolve.
- ✓ Fill the gravity settling tube up to the 100ml mark with the revolved portion.
- ✓ Place the thermo-hydrometer in the oil and allow it to come to rest.

- ✓ Read off the degree API and the corresponding temperature to the nearest ^{o}F.

This API value is later corrected to 60^{0}F using API correction.

CATEGORY I: CRUDE FORMULATION AND SAMPLE PREPARATION

This category covers the preparation of various media for this corrosion test. A trip was taken to various oil fields in Niger Delta region of Nigeria and NNPC to obtain samples of the materials and ratio of each component to meet specific desirable characteristics in the required Crude A (Nigerian Blended Crude Oil Sample).

A sample medium B (Inhibited Nigerian Blended Crude Oil Sample), was prepared by adding an inhibitor to the blend; and varying the concentration by 0.5g/mol and mixed very well by the magcoban multi mixer for a period of time long enough to ensure distribution of each component.

Some properties of the medium such as density, pH value, Degree API were measured and recorded. Medium C (Arabian Light Crude Oil Sample) was obtained from NNPC.

CATEGORY II: CORROSION TEST USING NIGERIA CRUDE OIL BLEND AND INHIBITED NIGERIA CRUDE OIL BLEND SAMPLES RESPECTIVELY

In this category, the analysis of possible effects of Nigerian crude oil blend sample on refinery material under operating temperature was investigated and recorded.

The coupons used were prepared by cutting out 40mm x 40mm sizes (six in number known as slots A-F) from a chromium steel, and a hole of 2mm was bored at one end for easier suspension in the medium. The coupon surfaces were polished using polish papers. The coupons were thoroughly rinsed with some distilled water. They were then dried, weighed and dipped into the medium.

The sample alongside the medium was inserted into the muffle oven and heated up to 230^{O}C – 400^{0}C; respectively at an interval of 30^{0}C. Corrosion rate data obtained from the test was as a result of exposing the coupons (slots) to the medium and varying the temperature periodically in steps of 230^{0}C - 400^{0}C. The time of exposure ranges from 24 – 48 hours, after which the coupons were re-weighed and difference in weight taken and recorded.

The experiment was evaluated for a period of six weeks. The difference in weight comes as a result of the coupon surface which is been cleaned with polish paper and corrosion seats removed before re-weighing.

Note that corrosion test on both media (A&B) were carried out simultaneously.

But since it was not possible to simulate a real industrial operation of temperature, pressure, rotation and shearing, fluid contamination etc. the weight loss technique was developed and under controlled system, and the reliability of the data obtained was dependent on the following:

- ✓ The length of exposure to these fluid under the test conditions,
- ✓ The test temperature and its control,
- ✓ The acidity or pH of the test fluid, and its control during exposure time,
- ✓ The composition and chemical reaction which includes the proper choice of inhibitors and catalyst and also their concentrations,
- ✓ The conditions of immersion of the specimens inside the crude oil media,
- ✓ The surface area exposed in the bulk,
- ✓ The heterogeneity of the media and the contents.

CATEGORY III: COMPARISON TEST USING THE ARABIAN LIGHT CRUDE OIL

The method described in this study is intended primarily to monitor the corrosion rate for the Arabian Light crude which served as a basis for comparison and economic evaluation. The same experimental procedure for category II followed.

IV. RESULTS, ANALYSIS AND DISCUSSION

The results obtained from testing medium A, B and C (Nigerian Crude oil blend, inhibited Nigerian crude oil blend and Arabian light respectively) for the various slots (coupon samples) are tabulated in tables 4.3, 4.4, 4.5, 4.6, 4.7 and 4.8 respectively.

Also, results obtained from the effects of temperature on the coupons are tabulated on table 4.2, while data generated from inhibitor evaluation are tabulated in table 4.9.

BLEND A

Crude Sample	Crude A	Crude B	Crude C
Blend Ratio	1	3	2
Final ^{0}API Gravity	39.3		

BLEND B

Crude Sample	Crude C	Crude E	Crude F
Blend Ratio	4	1	2
Final ^{0}API Gravity	35.9		

BLEND C

Crude Sample	Crude A	Crude C	Crude E
Blend Ratio	2	1	1
Final ^{0}API Gravity	33.7		

BLEND D

Crude Sample	Crude E	Crude D	Crude C
Blend Ratio	1	3	1
Final ^{0}API Gravity	30.2		

BLEND E

Crude Sample	Crude F	Crude D	Crude B
Blend Ratio	4	1	3
Final ^{0}API Gravity	38.9		

BLEND F

Crude Sample	Crude B	Crude A	Crude F
Blend Ratio	0	1	4
Final ^{0}API Gravity	33.6		

Table 4.1: Crude Oil Blend Ratios and Final API Gravity

COUPON A

Temperature	Weight of Coupon (g)	Weight Loss (g)
000	24.120	0.0000
230	23.921	0.1990

260	23.920	0.0010
290	23.903	0.0170
320	23.890	0.0130
350	23.739	0.1510
380	23.627	0.1120
400	23.571	0.0560

COUPON B

Temperature	Weight of Coupon (g)	Weight Loss (g)
000	25.399	0.000
230	25.363	0.036
260	25.349	0.014
290	25.339	0.010
320	25.302	0.037
350	25.290	0.012
380	22.242	0.048
400	22.215	0.027

COUPON C

Temperature	Weight of Coupon (g)	Weight Loss (g)
000	23.208	0.000
230	23.206	0.002
260	23.191	0.015
290	23.171	0.020
320	23.137	0.034
350	23.076	0.061
380	23.048	0.028
400	23.029	0.019

COUPON D

Temperature	Weight of Coupon (g)	Weight Loss (g)
000	23.566	0.000
230	23.140	0.426
260	22.791	0.349
290	22.577	0.214
320	22.261	0.316
350	21.824	0.437
380	21.696	0.128
400	21.265	0.431

COUPON E

Temperature	Weight of Coupon (g)	Weight Loss (g)
000	22.431	0.000
230	22.423	0.008
260	22.422	0.001
290	22.422	0.000
320	22.419	0.003
350	22.417	0.002
380	22.406	0.011
400	22.403	0.003

COUPON F

Temperature	Weight of Coupon (g)	Weight Loss (g)
000	23.238	0.000
230	23.223	0.065
260	23.208	0.015
290	23.220	0.004
320	23.207	0.013
350	23.180	0.027
380	23.134	0.046
400	23.116	0.018

Table 4.2: Effect of Temperature on the Coupons

MEDIUM A – CRUDE OIL BLEND

COUPON A

Duration (days)ΔT	Weight of Coupon (g)	Weight Loss (g)Δw	Rate Δw/Area/ΔT (g/mm^2/day)
01	23.9550	0.0000	0.000000000
03	23.9531	0.0019	0.000000593
05	23.9513	0.0018	0.000000562
07	23.9239	0.0274	0.000008562
09	23.9239	0.0140	0.000000000
11	23.9099	0.0140	0.000004375
13	23.8949	0.0150	0.000004687
15	23.8789	0.0160	0.000005000
17	23.8639	0.0150	0.000004687
19	23.8469	0.0170	0.000005312
21	23.8289	0.0180	0.000005625

COUPON B

Duration (days)ΔT	Weight of Coupon (g)	Weight Loss (g)Δw	Rate Δw/Area/ΔT (g/mm^2/day)	Mean Loss in Weight (g)
01	22.7940	0.0000	0.000000000	0.00000
03	22.7924	0.0016	0.000000500	0.00175
05	22.7803	0.0121	0.000003781	0.00695
07	22.7636	0.0167	0.000005218	0.01535
09	22.7458	0.0178	0.000005562	0.01560
11	22.7262	0.0196	0.000006125	0.01680
13	22.7056	0.0206	0.000006437	0.01780
15	22.6840	0.0216	0.000008343	0.01880
17	22.6573	0.0267	0.000008343	0.02085
19	22.6282	0.0291	0.000009093	0.02305
21	22.5959	0.0323	0.000010093	0.02515

Table 4.3: Corrosion Coupon: Low Alloy Steel (5cr. ½ Mo)

Concentration = 0.1M

Medium B-Inhibited Crude Oil Blend

SLOT A

Duration (days)ΔT	Weight of Coupon (g)	Weight Loss (g)Δw	Rate Δw/Area/ΔT (g/mm^2/day)
01	23.9530	0.0000	0.000000000
03	23.9390	0.0140	0.000004375
05	23.9250	0.0140	0.000004375
07	23.9080	0.0170	0.000005312
09	23.8899	0.0181	0.000005656
11	23.8706	0.0193	0.000006031
13	23.8512	0.0194	0.000006062
15	23.8313	0.0199	0.000006218
17	23.8106	0.0207	0.000006468
19	23.7895	0.0211	0.000006593
21	23.7677	0.0218	0.000006812

SLOT B

Duration (days)ΔT	Weight of Coupon (g)	Weight Loss (g)Δw	Rate Δw/Area/ΔT (g/mm^2/day)	Mean Loss in Weight (g)
01	22.4530	0.0000	0.000000000	0.00000
03	22.4390	0.0170	0.000005312	0.01125
05	22.4199	0.0191	0.000005968	0.01655

07	22.3943	0.0256	0.000008000	0.02130
09	22.3655	0.0288	0.000009000	0.02345
11	22.3343	0.0312	0.000009750	0.02525
13	22.2969	0.0374	0.000011687	0.02840
15	22.2566	0.0403	0.000012593	0.03010
17	22.2119	0.0447	0.000013968	0.03270
19	22.1630	0.0489	0.000015281	0.03500
21	22.1097	0.0533	0.000016656	0.03755

Table 4.4: Introduction of Corrosion Inhibitor (NaOH)
Concentration = 0.5M

SLOT A

Duration (days)ΔT	Weight of Coupon (g)	Weight Loss (g)Δw	Rate Δw/Area/ΔT (g/mm^2/day)
01	23.9290	0.0000	0.000000000
03	23.9220	0.0070	0.000002187
05	23.9143	0.0077	0.000002406
07	23.9064	0.0079	0.000002468
09	23.8979	0.0085	0.000002656
11	23.8888	0.0091	0.000002843
13	23.8793	0.0095	0.000002968
15	23.8696	0.0097	0.000003031
17	23.8590	0.0106	0.000003312
19	23.8475	0.0115	0.000003593
21	23.8351	0.0124	0.000003875

SLOT B

Duration (days)ΔT	Weight of Coupon (g)	Weight Loss (g)Δw	Rate Δw/Area/ΔT (g/mm^2/day)	Mean Loss in Weight (g)
01	25.3600	0.0000	0.000000000	0.00000
03	25.3530	0.0071	0.000002218	0.00705
05	25.3458	0.0072	0.000002250	0.00760
07	25.3383	0.0075	0.000002343	0.00770
09	25.3295	0.0088	0.000002750	0.00865
11	25.3502	0.0093	0.000002906	0.00920
13	25.3408	0.0094	0.000002937	0.00945
15	25.3310	0.0098	0.000003062	0.00975
17	25.3207	0.0103	0.000003218	0.01045
19	25.3093	0.0114	0.000003562	0.01145
21	25.2966	0.0127	0.000003968	0.01255

Table 4.5: Introduction of Corrosion Inhibitor (NaOH)
Concentration = 0.7M

SLOT A

Duration (days)ΔT	Weight of Coupon (g)	Weight Loss (g)Δw	Rate Δw/Area/ΔT (g/mm^2/day)
01	23.9430	0.0000	0.000000000
03	23.9369	0.0061	0.000001906
05	23.9304	0.0065	0.000002031
07	23.9235	0.0069	0.000002156
09	23.9164	0.0071	0.000002218
11	23.9090	0.0074	0.000002312
13	23.9009	0.0081	0.000002531
15	23.8922	0.0087	0.000002718
17	23.8827	0.0095	0.000002968
19	23.8728	0.0099	0.000003093
21	23.8616	0.0112	0.000003500

SLOT B

Duration (days)ΔT	Weight of Coupon (g)	Weight Loss (g)Δw	Rate Δw/Area/ΔT (g/mm^2/day)	Mean Loss in Weight (g)
01	25.3940	0.0000	0.000000000	0.00000
03	25.3875	0.0065	0.000002031	0.00630
05	25.3808	0.0067	0.000002093	0.00660
07	25.3739	0.0069	0.000002156	0.00690
09	25.3666	0.0073	0.000002281	0.00720
11	25.3589	0.0077	0.000002406	0.00755
13	25.3504	0.0085	0.000002656	0.00830
15	25.3419	0.0085	0.000002656	0.00860
17	25.3327	0.0092	0.000002875	0.00935
19	25.3233	0.0094	0.000002937	0.00965
21	25.3077	0.0156	0.000004875	0.0134

Table 4.6: Introduction of Corrosion Inhibitor (NaOH)
Concentration = 0.9M

SLOT A

Duration (days)ΔT	Weight of Coupon (g)	Weight Loss (g)Δw	Rate Δw/Area/ΔT (g/mm^2/day)
01	22.4600	0.0000	0.000000000
03	22.4550	0.0050	0.000001562
05	22.4596	0.0054	0.000001687
07	22.4439	0.0057	0.000001687
09	22.4380	0.0059	0.000001843
11	22.4312	0.0068	0.000002125
13	22.4244	0.0068	0.000002125
15	22.4169	0.0075	0.000002343
17	22.4090	0.0079	0.000002468
19	22.4008	0.0052	0.000001625
21	22.3922	0.0086	0.000002687

SLOT B

Duration (days)ΔT	Weight of Coupon (g)	Weight Loss (g)Δw	Rate Δw/Area/ΔT (g/mm^2/day)	Mean Loss in Weight (g)
01	22.7630	0.0000	0.000000000	0.00000
03	22.7579	0.0051	0.000001593	0.00505
05	22.7523	0.0056	0.00000175	0.00550
07	22.7464	0.0059	0.000001843	0.00580
09	22.7403	0.0061	0.000001906	0.00600
11	2.7339	0.0064	0.00000200	0.00660
13	22.7269	0.0070	0.000002187	0.00690
15	22.7196	0.0073	0.000002281	0.00740
17	22.7118	0.0078	0.000002437	0.00765
19	22.7037	0.0081	0.000002531	0.00815
21	22.6948	0.0089	0.000002781	0.00875

Table 4.7: Introduction of Corrosion Inhibitor (NaOH)
Medium C – Arabian Light Crude Oil

COUPON A

Duration (days)ΔT	Weight of Coupon (g)	Weight Loss (g)Δw	Rate Δw/Area/ΔT (g/mm^2/day)
01	23.9550	0.00000	0.000000000
03	23.9530	0.00020	0.000000062
05	23.9512	0.00180	0.000000562

07	23.9237	0.00275	0.000000859
09	23.9105	0.01320	0.000004125
11	23.9097	0.01180	0.000003687
13	23.8948	0.01490	0.000004656
15	23.8788	0.01610	0.000005031
17	23.8638	0.01650	0.000005156
19	23.8468	0.01730	0.000005406
21	23.8288	0.01540	0.000004812

COUPON B

Duration (days)ΔT	Weight of Coupon (g)	Weight Loss (g)Δw	Rate Δw/Area/ΔT (g/mm^2/day)	Mean Loss in Weight (g)
01	22.7939	0.0000	0.000000000	0.0000
03	22.7923	0.0016	0.000000005	0.0009
05	22.7802	0.0121	0.000003781	0.0070
07	22.7635	0.0167	0.000005218	0.0097
09	22.7457	0.0178	0.000005562	0.0155
11	22.7261	0.0119	0.000002718	0.0119
13	22.7055	0.0206	0.000006437	0.0178
15	22.6839	0.0216	0.000006750	0.0189
17	22.6572	0.0267	0.000008343	0.0216
19	22.6281	0.0291	0.000009093	0.0232
21	22.5958	0.0323	0.000010093	0.0239

Table 4.8: Corrosion Test with Arabian Light Crude Oil

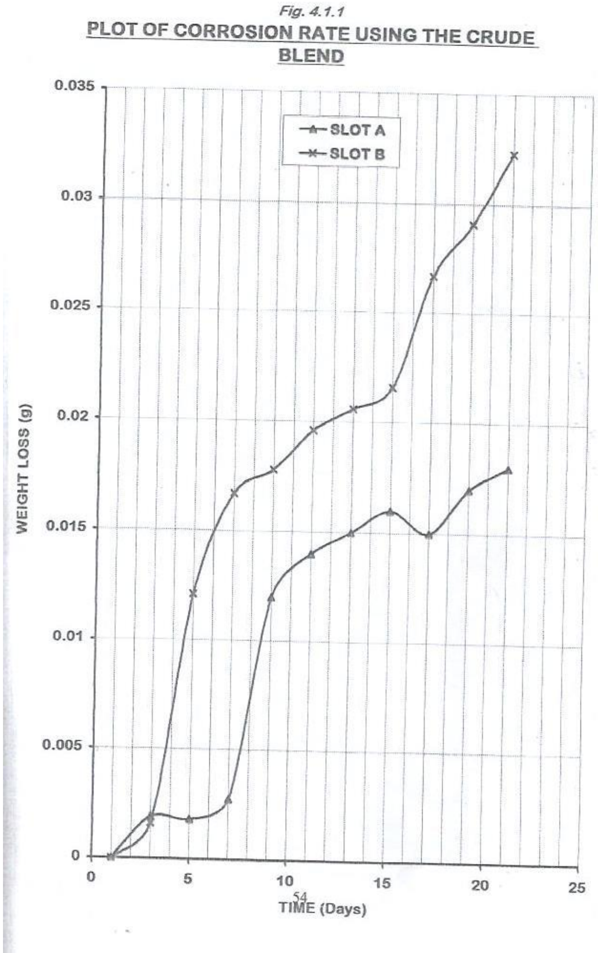

Figure 1

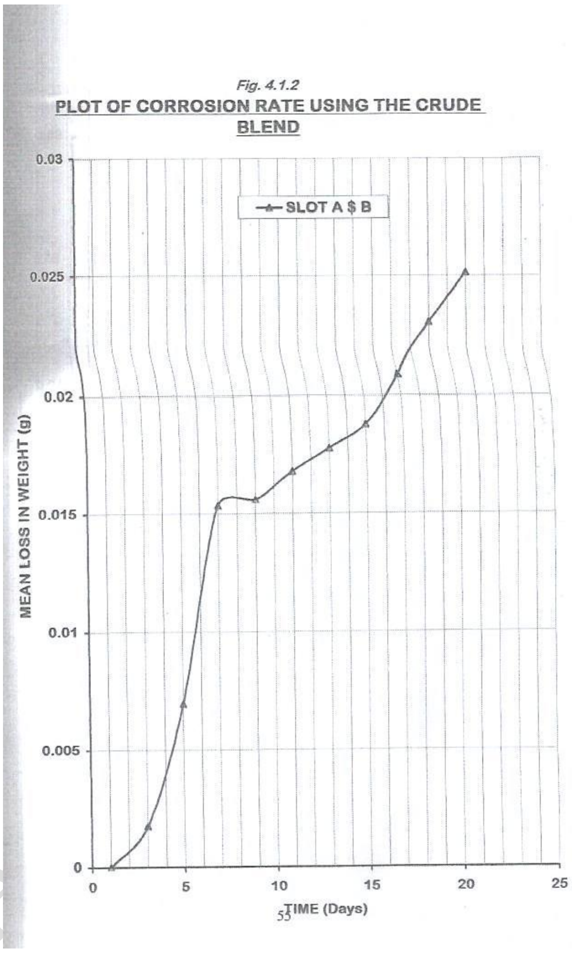

Figure 2

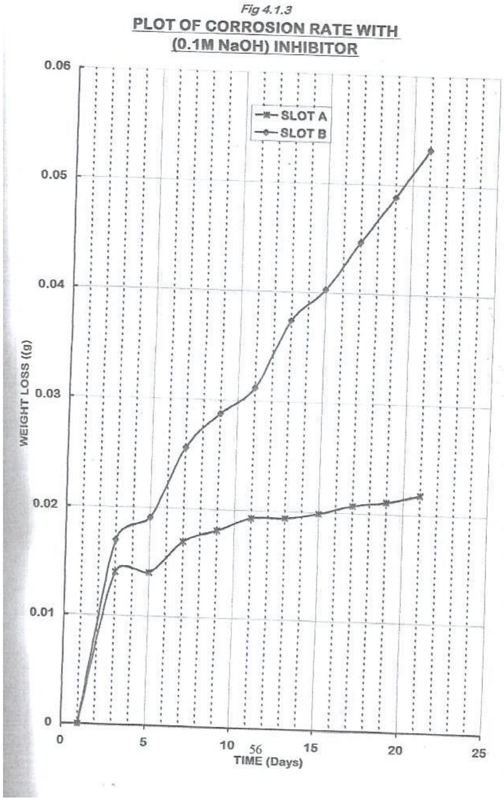

Figure 3

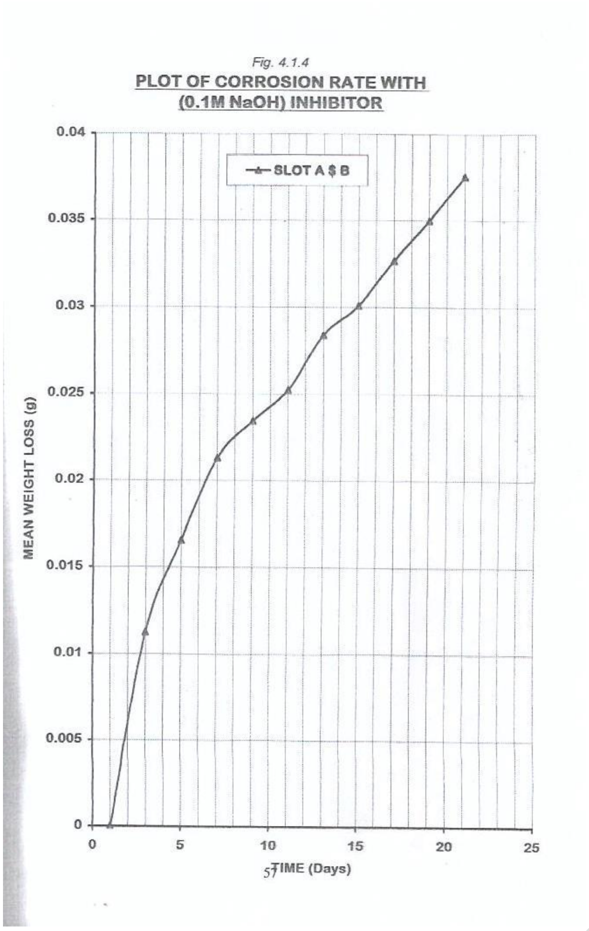

Figure 4

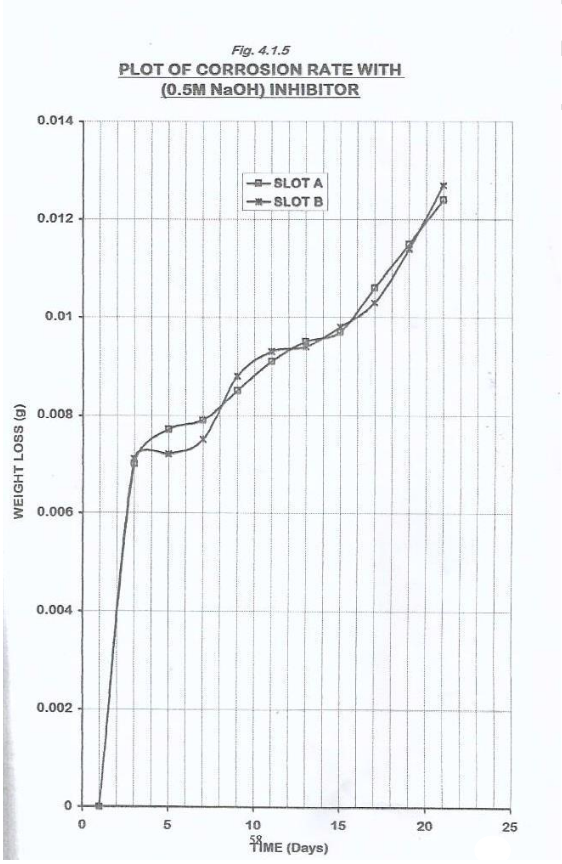

Figure 5

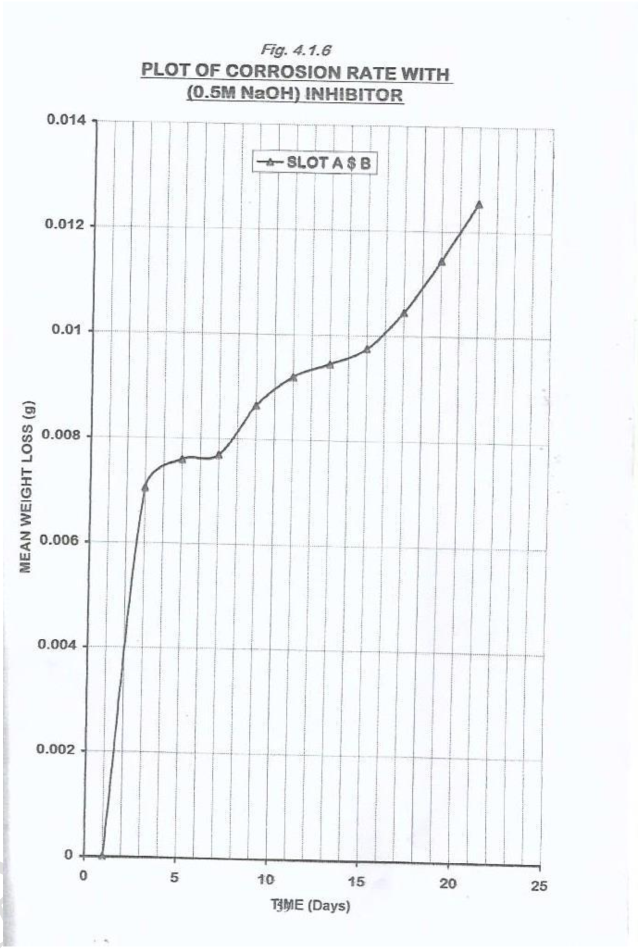

Figure 6

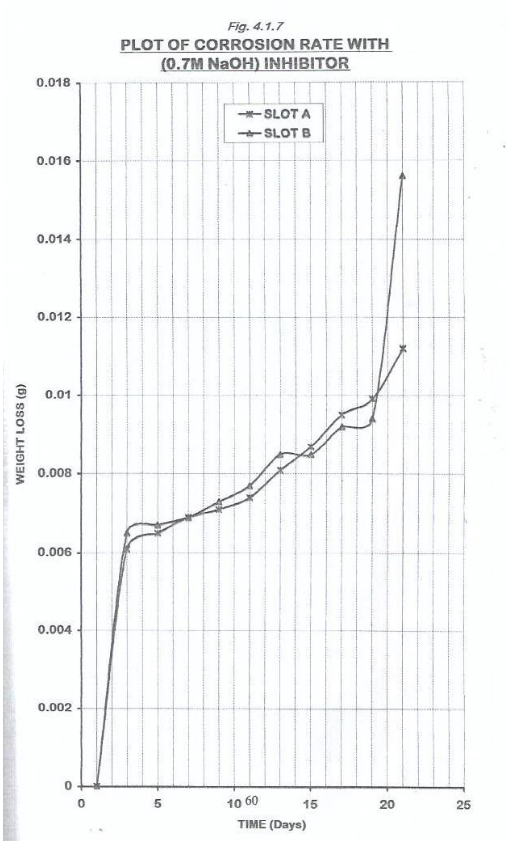

Figure 7

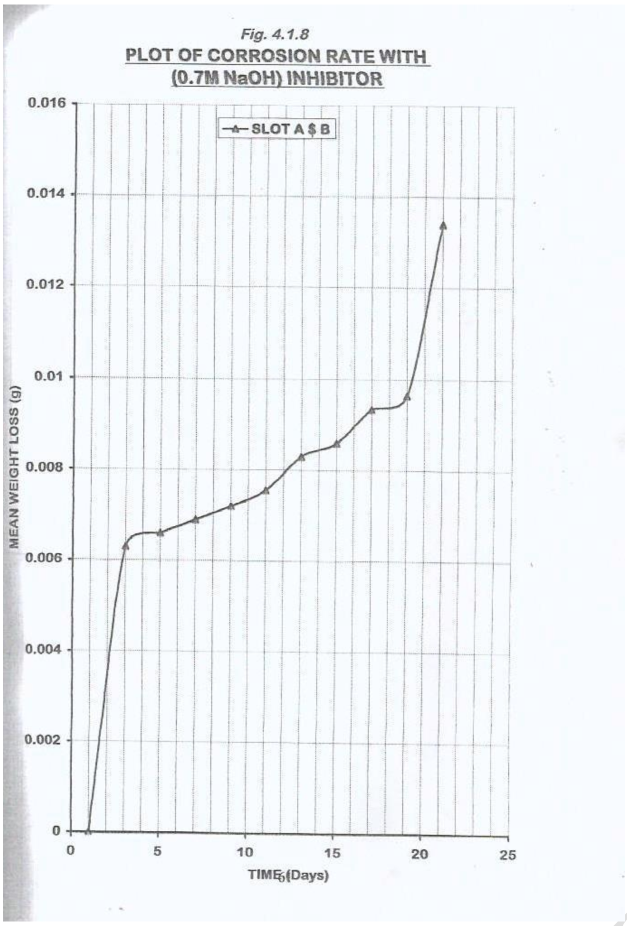

Figure 8

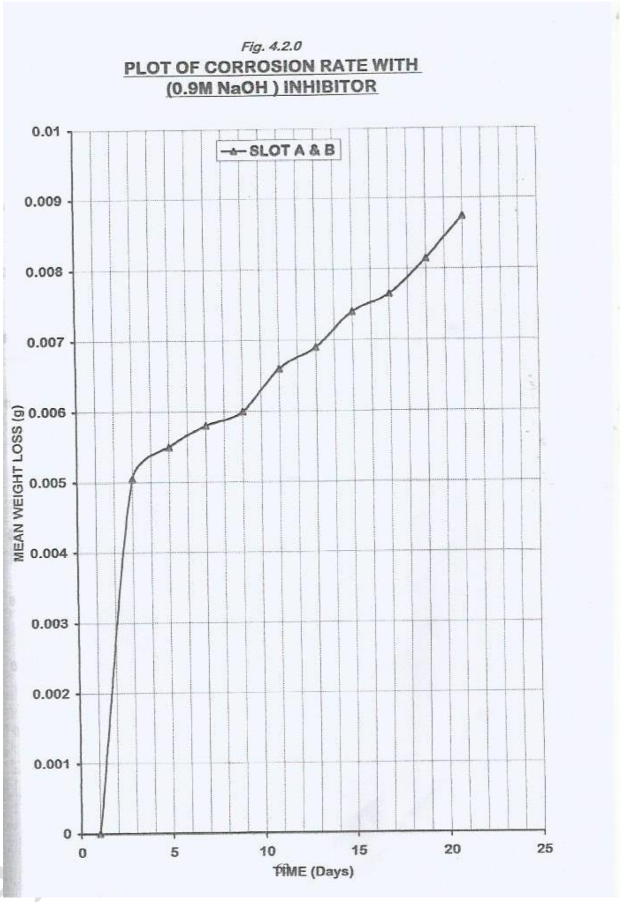

Figure 10

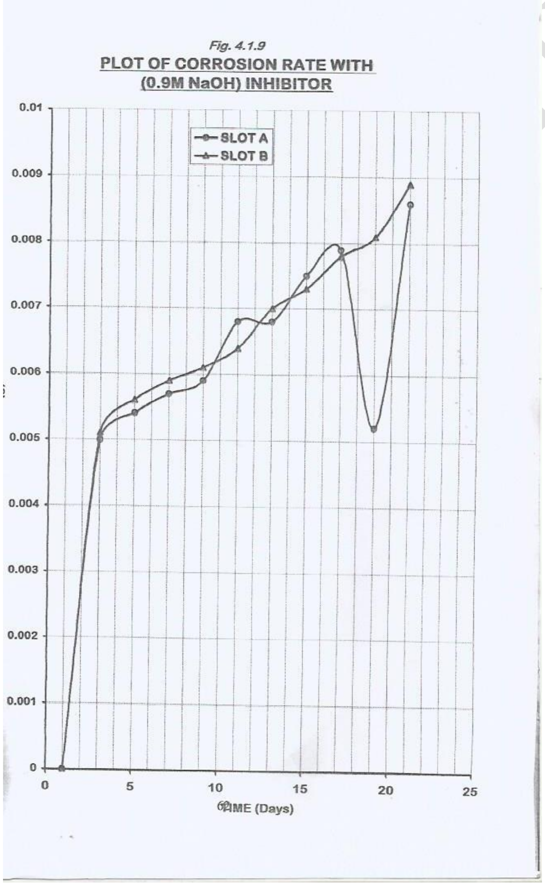

Figure 9

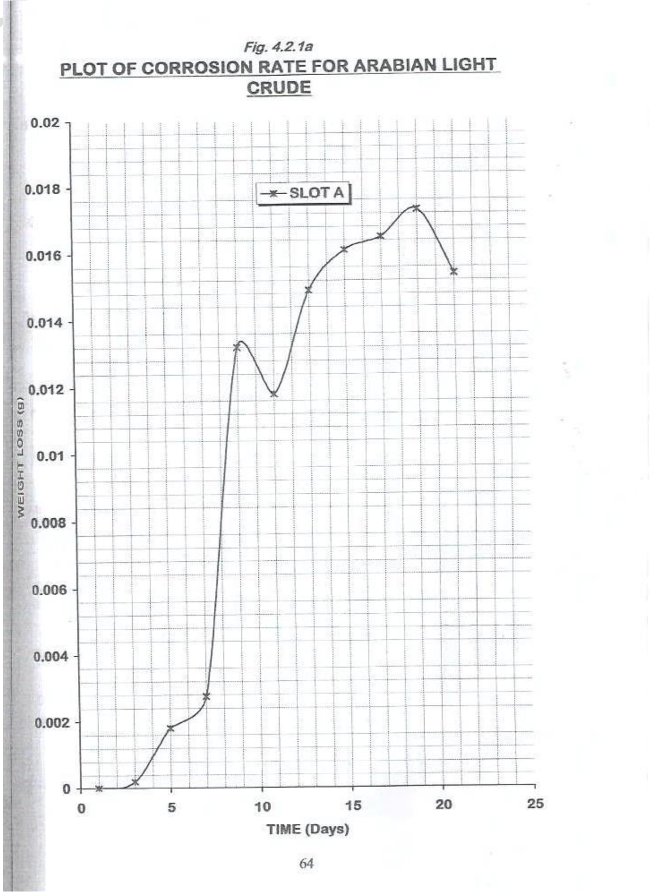

Figure 11

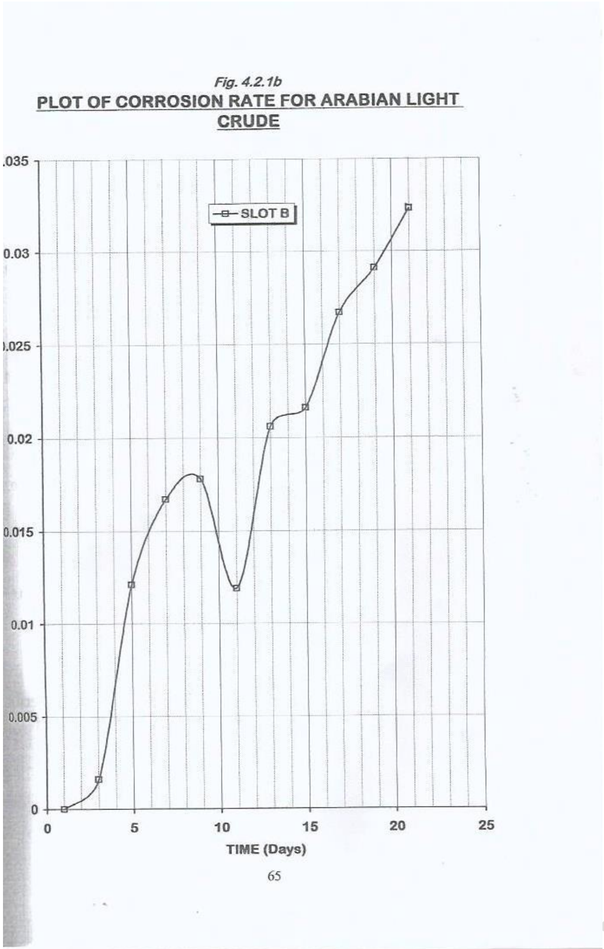

Figure 12

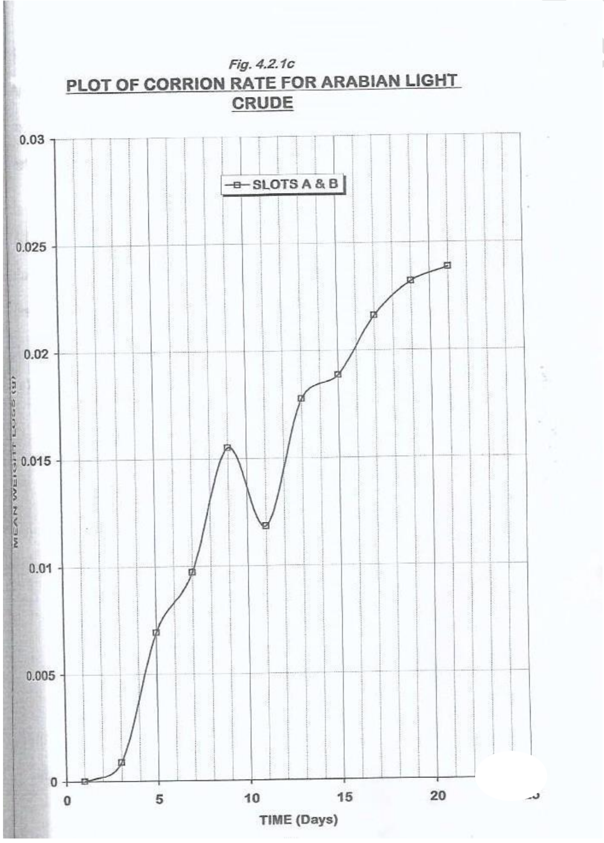

Figure 13

A. GENERATION OF DATA

Apart from the raw data collected in terms of the measured and weight loss recorded from the daily routine checks, other important parameters were estimated from the raw data.

B. PARAMETER ESTIMATION

Parameters generated from the raw data include metal loss in weight of grams, mean loss in weight of grams and corrosion rate.

- ✓ *METAL LOSS (G):* The weight loss in slots A – F of medium A, B and C were obtained by subtracting the final weight from the initial. i.e. $(W_2 - W_1) = \Delta W$ … 4.1
- ✓ *MEAN LOSS IN WEIGHT (G):* The mean loss in weight is obtained by adding two subsequent corresponding losses in weight and dividing by 2:
  i.e $\frac{w_1 + w_2}{2} = \Delta W$ …………………………………....4.2
- ✓ *RATE OF CORROSION ($G/MM^2/DAY$):* The rate of corrosion is obtained by dividing the loss in weight by the time interval.
  i.e $\frac{\textit{weight loss (g)x1}}{\textit{Area } (mm^2) \textit{ Time (day)}}$
  $= \frac{\Delta W}{A\,(\Delta T)}$ ……………………………… 4.3
- ✓ *PERCENTAGE INHIBITION (E).* This is a measure of effectiveness of the inhibitors for application and economic Evaluation.
  i.e $E = \frac{100(w_o - w_1)}{W_o}$ ………………......4.4

C. ANALYSIS OF RESULTS

The results obtained from testing the effects of temperature on sample A, B and C under varying temperatures and weekly evaluation were plotted in graphs shown in figures 4.1.1 – 4.2.8. The 4th blend was used for medium A and B, since it has characteristics API gravity close to that of the Arabian Light.

The test results and its graphical trend indicate the following:

Looking critically at table 4.2 (slot A). It will be observed that the weight loss is not in uniform trend, at a temperature of 230°C, a large amount of weight loss of 0.199g was observed, but getting to higher temperatures of 380°C – 400°C, the loss in weight was reduced to 0.056g, this could be as a result of its susceptibility to harden at higher temperatures and also the escape of trapped oxygen in the medium.

This is indicated by the trend of the graph in figure 4.2.3 of Appendix B, where a sharp curve at a temperature of 380°C was observed and subsequently, a total reduction in the trend at a temperature of 400°C emerged. The same phenomenon was observed in slots A – F of table 4.2.

Analyzing the corrosion test result of the uninhibited crude oil blend on table 4.2, for slots A and B, It could be observed that weight loss of 0.0018g was observed in the first two days, but a long time observation revealed that the corrosion effect was minimized as the weight loss on the 15th and 17th days were 0.0160g and 0.0150g respectively, hence, registering a corrosion rate of 0.000005g/mm^2/day and 0.0000048g/ mm^2/day respectively. A clearer illustration was made with the graph in figure 4.1.1, as a sharp curve was observed in the 15th day in slot A, but later increased with time.

Introducing inhibitors (Na_2OH, Na_2CO_3, NH_3) and varying molar concentrations (0.1 – 0.9) recorded quite a good number of changes. From table 4.4, it could be observed that introducing an inhibitor of 0.1 molar concentrations did not retard the corrosion rate with wide margin. Instead, the weight loss increased progressively with increasing temperature and time step. On the 19th and 21st days, the weight loss increased up to 0.0211g and 0.0218g respectively as against 0.0160g and 0.0150g of the uninhibited blend. The disparity in trend is clearly illustrated with graph in figure 4.1.3 as some inhibitors at some certain concentration and temperature are ineffective.

Further increment in the concentration of the inhibitors to 0.5 molar concentrations reduced the weight loss to 0.0106g in the 17th day as against 0.0150g in the uninhibited crude, hence recording a reduction of 0.00000138g/mm^2/day in corrosion rate. This is illustrated through a graph shown in figure 4.1.5, as the curves of slot A and B of Table 4.5 were intermingled, showing slight reduction in weight loss towards the 17th day.

At a concentration of 0.7M shown in table 4.6 at the 21st day revealed a weight loss of 0.0112g as against 0.0180g of the uninhibited blend, recording a reduction of 0.00068g and hence registered a 0.00000213g/mm^2/day reduction in corrosion rate. A graph illustrating the trend was exhibited on figure 4.1.7; this clearly shows the direct reduction in weight loss up to the 21st day.

At a concentration of 0.9M, shown in table 4.7, it could be seen clearly that there was reduction in weight loss as compared to the uninhibited crude oil. The weight loss reduced gradually from 0.0050g of the first two days up to 0.0086g at the 21st day. This could be as a result of the fact stated earlier about the effectiveness of varying concentrations over varying temperature. Based on this, a thorough evaluation and discussion of the various sets of inhibitors at varying concentrations and temperatures were carried out in the subsequent section.

The results obtained from testing medium C (Arabian Light) was tabulated in Table 4.8, the result indicates an average corrosion rate of 0.0000138g/mm^2/day on the 21st day. Also looking at the graphical illustration in figure 4.2.2, the trend does not represent a uniform curve, which could of course account for its sulphuric content. A comparative analysis between the corrosion rates in medium B and C (inhibited crude oil blend and Arabian light crude oil respectively), revealed a difference of 0.0000025g/mm^2/day in the corrosion rate in favor of the inhibited crude blend.

D. INHIBITOR EVALUATION

In any system utilizing corrosion inhibitors, the prime factor of consideration are effectiveness and cost. Because of the large number of materials commercially available, some method must be used to predict required dosage and effectiveness of the treatment, and to narrow the choice of materials to be considered. The best way to evaluate an inhibitor is to use it in the system to be treated under the conditions to which it is to the subjected. Dosage is varied throughout an economically acceptable range and the response of the system to the treatment is judged by reduction in equipment failure or by some other system variable assumed to be proportional to metal loss.

E. STATISTICAL CONCEPTS IN CORROSION INHIBITOR EVALUATION

Laboratory evaluation of inhibitors commonly involves weighting of test coupons before and after exposure to corrosive fluids in the presence and absence of inhibitors. Let W_0 be the weight loss of an uninhibited coupon, and W_1 be the weight loss of an inhibited coupon, then

$$\%\ \text{Inhibition} = E = \frac{100(w_0 - w_1)}{w_0} \text{----------------------4.5}$$

The performance of the inhibitors were determined by a series of tests employing various inhibitor concentration as shown in Table 4.3 – 4.7 and a plot of E (% Inhibition) as a function of concentration revealed the desired efficiency i.e. inhibition at 90%. Data obtained from computing the percentage inhibition of the various inhibitors used in the experiment and tabulated in tables 4.9a, 4.9b and 4.9c for NaOH (Sodium Hydroxide), Na_2CO_3, (Sodium Carbonate and NH_3 Ammonia) respectively as stated in the methodology.

$E(\%) = 100(W_0\text{-}W_1)/W_2$	**Concentration (M)**
-46.1	0.1
14.8	0.5
26.1	0.3
35.6	0.7
48.7	0.9

Table 4.9a: NaOH (Sodium Hydroxide)

$E(\%) = 100(W_0\text{-}W_1)/W_2$	**Concentration (M)**
-52.000	0.1
10.900	0.5
26.128	0.3
35.629	0.7
48.733	0.9

Table 4.9b: Na_2CO_2 (Sodium Carbonate)

$E(\%) = 100(W_0\text{-}W_1)W_2$	**Concentration (M)**
-55.00	0.1
10.90	0.5
28.30	0.3
29.40	0.7
33.60	0.9

Table 4.9c: NH_3 (Ammonia)

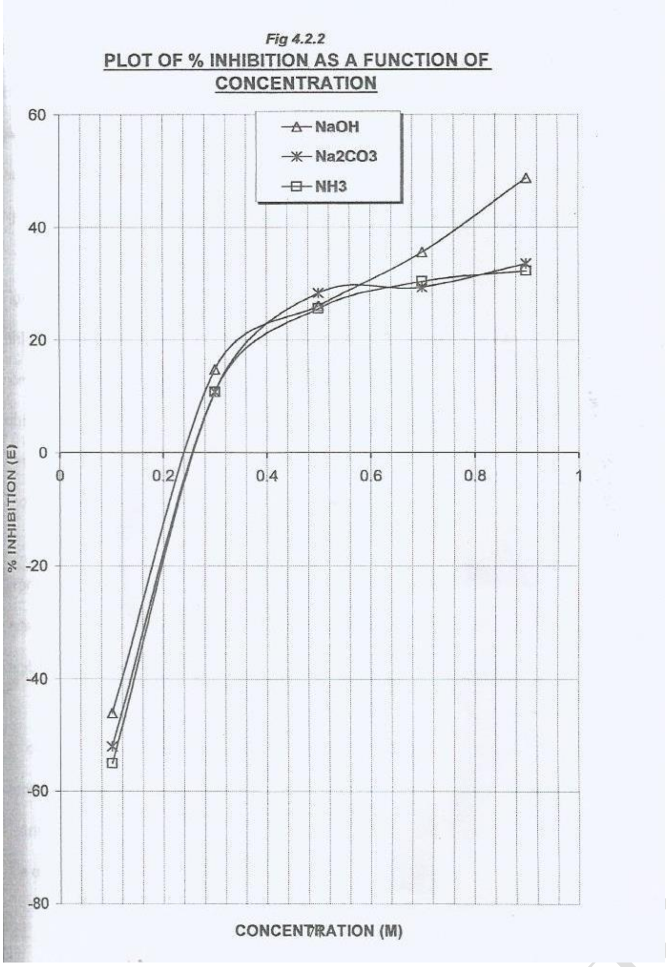

Figure 14

F. DISCUSSION OF RESULTS

It has been commonly asserted that corrosion tests in inhibited systems often give poorly reproducible weight loss data. Despite the curve taken, it was found that the inhibitor merit ranks, as judged by weight loss data, gave no agreement at intermediate inhibitor concentrations of economic interest.

Figure 4.2.2, which is a graphical illustration of the efficiency of various inhibitors indicates that weight loss at a given inhibitor concentration followed a normal distribution curve. Plot of all the data on one Cartesian plane revealed inhibition efficiency of 48.7% for Sodium Hydroxide (NaOH), 33.6% for Sodium Carbonate and 32.3% for Ammonia at the same molar concentration of 0.9M and temperature of 360^{o}C.

From tables 4.9a, 4.9b and 4.9c, it could be seen that the scatter of replicate determination is evidence, as is the increased weight loss, as shown in the low-inhibitor concentration runs, which is indicated by a negative value.

A comparative test between the three inhibitors revealed that at equal concentration and temperature, NaOH exhibited the maximum efficiency. An Extrapolation from the existing data indicates that the amount of inhibitor for the desired efficiency of 90% is 1.66M.

Thus ammonia may be used to raise the pH value of the acidic crude oil to near 7.0, after which NaOH inhibitor completes the job of protection. The use of the two materials in conjunction gave adequate protection more cheaply than does either material alone.

G. INHIBITOR APPLICATION

Inhibitors should be added to process installation either intermittently or continuously. The principal difficulties in the use of inhibitors in crude oil refineries are related to operating problems of getting the desired quantity of inhibitor to the proper place in process plant at the proper time.

Accordingly, intermittent inhibitors treatments can be as effective as continuous inhibitor addition, and much more convenient and economical. Going by the scope of this research work, it was revealed that the inhibitor squeeze technique suits the application technique in all ramification to reduce the frequency of treatment to as low as once in 6-12 months. In this treatment, a large quantity of inhibitor having a concentration that suits the volume of the inhibitor should be pumped into the fractionating columns, once the plant is turned into production, the inhibitor circulates.

H. SUMMARY OF DISCUSSION

From the analysis and discussion made in the previous sections, it could be summarized that the alloy in question (5Cr. ½Mo) can withstand an extreme operational, temperature of about 380^{o}C – 560^{o}C as the test result of temperature effect on coupon gave poorly reproducible weight loss data.

A maximum corrosion rate of 0.00000563 g/mm^{2}/day was recorded from testing the Nigerian crude oil blend at a temperature limit of 400^{o}c through a six (6) weeks evaluation period. A comparative analysis between results obtained from the inhibited and uninhibited test registered a reduction of 0.00000295 g/mm^{2}/day in corrosion rate at a maximum inhibition efficiency of 0.9 molar concentrations.

The inhibitor evaluation carried out indicated a maximum percentage of 48.7% for NaoH, 33.6% for Na_2CO_3 and 32.3% for NH3 for 0.9 molar concentrations. Also a concentration of 1.66m was established from the available test result for the desired 90% maximum inhibition efficiency. The negative values recorded for the various inhibitors at 0.1 molar concentrations indicate an increment in the corrosion rate despite the introduction of an inhibitor of 0.1M.

V. CONCLUSION AND RECOMMENDATION

From the analysis made so far, it is evident that the metal under consideration (5Cr.½Mo) was subjected to severe test using various crude oil samples, after which several deductions were made, and this gave a guide to the recommendations made for the use of Nigerian crude oil blend in Kaduna refinery.

A. THIS STUDY CONCLUDED THE FOLLOWING

✓ The coupon in question (5Cr.½Mo) can withstand higher operating temperature of about 480^{o}c – 630^{o}c, as indicated by the temperature effect test, since weight loss at varying operating temperatures recorded insignificant loss of weight.

- ✓ Blend work carried out in the research work justified the reliability and efficiency of blending operation as an alternative to Arabian light (crude) as it gave the same characteristic property of the latter crude.
- ✓ The corrosion rate of the crude blend was maximum at 0.00000563g/mm^2/day for a maximum test temperature of 400°C at the peak of six (6) weeks.
- ✓ Corrosion rate varied considerably with the medium in context in other words, the corrosion rate measured by medium B is always lower than that measured by medium A, at the same temperature limit.
- ✓ Corrosion tests in the inhibited systems gave poorly reproducible weight-loss data. A maximum inhibition of 48.7% was recorded at a maximum concentration of 0.9 for NaOH, 36.6% for Na2C03 and 32.33% for Ammonia. Hence, recommending NaOH, the most effective at an operating temperature of 400°C. Thus a concentration of 1.66M is required for 90% effective inhibition.
- ✓ A comparative analysis between the corrosion rate measured by the crude oil blend and the Arabian light at the same temperature limit indicates a reduction of 0.0000025 g/mm^2/day in corrosion rate in favor of the Nigerian crude oil blend and hence proves the effectiveness of Sodium Hydroxide inhibitor and the feasibility of the operational reliability and economic evaluation.

A. RECOMMENDATIONS

From the analysis, discussions and conclusions made so far, the following recommendations are necessary:

- ✓ As has been previously mentioned, corrosion rate is generally not uniform, so that safety factors must be added to take account of accelerated corrosion in pitted areas, because inhibitors generally are of decreasing effectiveness at elevated temperatures above 300°F. The top temperature for their use appears to be about 450°C, which is far below the temperature of Kaduna refinery streams, special alloys and coatings should be used in such applications.
- ✓ Since the sets of inhibitors evaluated are of neutralizing type, they should be added continuously to every batch of stream (crude oil) to be refined, by the “inhibitor squeeze” technique at a molar concentration of 1.66M, since this gives the maximum required percentage inhibition of 90%.
- ✓ If in any case, the concentration of naphthenic acid in the system should increase as to pose operational problem in equipment malfunction, Ammonia should be used to raise the pH of the acidic liquid to near 7.0, at the same concentration of 1.66M.
- ✓ In the absence of the above stated inhibitors, any other inhibitors to be used should be tested and compared at concentrations which would give inhibition efficiencies of 90-100%.
- ✓ However, should a film forming inhibitor be used, then the application have to be intermittently, to reduce the frequency of treatment to as low as once in 6-12months.
- ✓ In concordance with the inhibitor evaluation carried out in this research work, it should be recommended strongly that NaOH inhibitor be applied as the most economical and effective inhibitor.

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