MAKERERE UNIVERSITY

ASSESSING THE IMPACT OF RUST ON THE QUALITY OF CRUDE OIL FROM THE GEO-SAMPLES STORE, ENTEBBE UGANDA

BY

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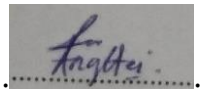
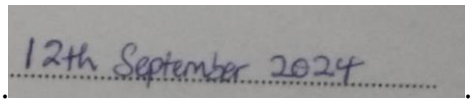
DECLARATION

I, ANGUMYA HEINZ ATEKYEREZA, declare that this report is based on my research conducted during my final year at Makerere University. The statements made and conclusions drawn herein are entirely my own, based on the findings of my research. I confirm that this report is my original work and has not been submitted for any academic award at any other institution.

SIGNATURE.....  .....DATE.....  .....

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APPROVAL

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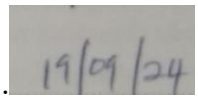
SIGNATURE: …..  …… DATE: …  ….

DR. JANE NAMUKOBE

SUPERVISOR

DEDICATION

This work is dedicated to my family, whose unwavering support and encouragement have been my source of strength throughout this journey. To my mentors and teachers, who have imparted invaluable knowledge and guidance, and to all my friends and colleagues, whose camaraderie and shared experiences have made this journey memorable.

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LIST OF ACRONYMS AND ABBREVIATIONS

PAU – Petroleum Authority of Uganda

EDP – Exploration, Development & Production

MEMD – Ministry of Energy and Mineral Development

API – American Petroleum Institute

NDP – National Development Plan

SDGs – Sustainable Development Goals

NAC – Naphthenic Acid Corrosion

ASTM – American Society for Testing and Materials

UV-VIS – Ultra violet-Visible

HDPE - High-density polyethylene

USTs – Underground Storage Tanks

ASTs – Above-Ground Storage Tanks

ABSTRACT

This study investigated the effects of rust contamination, primarily composed of Iron oxides, on the quality of crude oil samples stored in steel containers. It focused on viscosity and API gravity alterations. The objectives included identifying and quantifying rust in the crude oil samples, determining the API gravity, and measuring the viscosity of the crude oil samples. Crude oil samples A and B were each collected from the Petroleum Authority of Uganda (PAU). Inorganic residues of the crude oil samples were extracted and analyzed using UV-visible spectrophotometry. The results showed higher concentrations of Fe^{3+} in crude oil sample A (4.4 ppm), indicating significant rust contamination, which was linked to an exceptionally high API gravity of 62.2 °API and a low viscosity of 2.9802 cP. In contrast, crude oil sample B had lower Fe^{3+} levels (3.6ppm), an API gravity of 30 °API, and a viscosity of 7.2039 cP, aligning with typical Ugandan crude oil characteristics. The study concluded that rust contamination significantly alters crude oil properties, likely due to the catalytic cracking of heavier hydrocarbons, emphasizing the need for corrosion-resistant materials and regular maintenance in storage facilities to maintain oil quality.

CHAPTER ONE: INTRODUCTION

1.1. Background

The global energy landscape is in constant flux, with the demand for crude oil and its derivatives continuing to play a pivotal role in meeting the world's energy needs (McKinsey & Company, 2023). Uganda, a nation endowed with significant oil reserves, is poised to become a key player in this arena. However, the sustainable exploitation and processing of crude oil rely on a comprehensive understanding of the factors that can affect its quality, transportation, storage, and market value.

The Petroleum Authority of Uganda (PAU), a regulatory body was established under the Petroleum (Exploration, Development, and Production) Act, 2013 to monitor and regulate oil and gas activities in Uganda. The PAU also manages oil and gas, and related data from upstream and midstream petroleum activities on behalf of the State by the Petroleum Exploration, Development, and Production (EDP) Act 2013.

Crude oil at the geo-samples store was acquired mainly from exploration and appraisal drilling activities carried out in the Albertine Graben by oil companies over the years and submitted to the Ministry of Energy and Mineral Development (MEMD) by then. Since 2019, the PAU has been responsible for the maintenance of the old geo-samples store which is a shared facility with the MEMD. The PAU is in the process of setting up a modern geo-samples store that will have equipment for handling, storage, and long-term preservation of geological samples including physical cores, crude oil, rock samples, well cuttings and fluid samples.

Globally growing demand for crude oil has led to more exploration and development activities in previously unexplored areas around the world like the Albertine Graben. The petroleum sector generates a lot of geological data that includes physical cores, crude oil, rock samples, well cuttings and fluid samples that are strategic business assets that need to be readily available, accessed, stored, preserved, and used by various stakeholders. The crude oil samples need to be stored at temperatures above their pour point to prevent solidification. Ugandan crude oil has an average pour point of 40ºC (Boschee, 2022).

Steel, acknowledged for its strength, durability, and cost-effectiveness, stands as the material of choice for storage vessels in refineries worldwide (Keong, 2023). Steel drums have been

used for handling, storage, and long-term preservation of crude oil samples and are usually susceptible to corrosion due to their exposure to various environmental conditions. This causes alteration of the quality of the stored crude oil samples and may impact the essential characteristics of crude oil. Crude oil, in its various forms, possesses a multitude of vital characteristics, called bulk properties that influence its market value and processing requirements. These bulk properties encompass aspects such as viscosity, API gravity, sulphur content, pour point, cloud point, metal content (nickel and vanadium), and the distribution of saturates, aromatics, resins, and asphaltenes (S-A-R-A) (Harry Dembicki, 2017). Thus, the issue of corrosion in steel storage drums poses a significant challenge to maintaining the quality of the crude oil, as it can lead to degradation of key properties essential for processing and market valuation thereby prompting this study.

1.2. Problem Statement

Steel drums, used for handling and storage of crude oil at the geo-samples store, are susceptible to corrosion due to environmental conditions which causes alteration of quality of the stored crude oil. While this may be manageable in the geo-samples store where the oil is simply stored, in refineries, corrosion can contaminate crude oil with rust and metallic particles, alter its chemical properties, and pose serious safety hazards like leaks or fires. Additionally, such contamination can lead to operational inefficiencies, increased maintenance costs, and potential damage to refinery equipment.

1.3. General and Specific Objectives

1.3.1 General Objective

i. To evaluate the impact of rust on the quality of crude oil stored in the geo-samples store.

1.3.2 Specific Objectives

i. To identify and quantify rust in each crude oil sample.
ii. To determine the viscosity of each crude oil sample.
iii. To determine the API gravity of each crude oil sample.

1.4. Significance

The findings of this research provided a valuable understanding of the effects of rust in crude oil on the quality of the crude oil. This was done by investigating the effect on the API gravity and viscosity of the crude oil samples, properties that play a key role in the quality

and market value of oil. The findings also provided an understanding of quality measures to mitigate rust-induced effects on crude oil quality contributing to the oil and gas sector in Uganda.

This research is also aligned with broader development frameworks. By improving the quality and preservation of crude oil, the study supports Uganda's National Development Plan (NDP) goals of enhancing value addition in the oil and gas sector, promoting sustainable industrialisation, and ensuring environmental sustainability. Additionally, the research contributes to the United Nations Sustainable Development Goals (SDGs), particularly Goal 9 (Industry, Innovation, and Infrastructure) by fostering innovation in oil storage technologies, and Goal 12 (Responsible Consumption and Production) by ensuring that crude oil is stored and utilised in a manner that minimises waste and environmental impact.

CHAPTER TWO: LITERATURE REVIEW

2.1. Corrosion in the Oil and Gas Industry

Corrosion is a pervasive challenge in the petroleum industry, involving the gradual degradation of materials due to chemical reactions. The impact of corrosion extends beyond material wear, posing threats to infrastructure integrity, safety, and operational efficiency. To mitigate these risks, the industry employs protective coatings, inhibitors, and corrosion-resistant alloys, alongside regular inspection and maintenance practices.

Crude oil contains several components that contribute to its corrosiveness. These corrosive elements, present in oil and gas reservoirs, pipelines, and wellbores, contribute to the formation of acids, accelerating metal degradation. Key corrosive agents include naphthenic acids, sulphur compounds, organic acids and chlorides.

i. Naphthenic acids: These are a group of organic acids found in crude oil, known for their role in promoting naphthenic acid corrosion (NAC). NAC occurs predominantly in high-temperature environments, such as those found in distillation units. These acids are particularly corrosive at temperatures between 220-400°C leading to significant material degradation (Yuhchae, Kosacki, & Srinivasan, 2016).
ii. Sulphur compounds: Sulphur-containing compounds in crude oil such as Hydrogen sulphide (H_2S) and mercaptans, are highly corrosive. These compounds can lead to the formation of Iron sulphide scales on metal surfaces, which can be both protective and corrosive. In environments with high sulphur content, these scales may break down causing localised corrosion and pitting (Al-Moubaraki & Obot, 2021).
iii. Organic acids: In addition to Naphthenic acids, other organic acids present in crude oil can also contribute to corrosion, especially under specific refining conditions such as high temperatures.
iv. Chlorides: Chloride ions, often present in crude oil ass saltwater emulsions, contribute to corrosion through mechanisms such as under-deposit corrosion and chloride-induced stress corrosion cracking (Groysman, 2014).

Corrosion in the oil and gas industry occurs through various mechanisms, influenced by the nature of the crude oil and operational conditions such as temperature.

i. Electrochemical corrosion: This is the most common form of corrosion, where metal loss occurs due to electrochemical reactions between the metal and its environment. In the presence of water and dissolved gases like oxygen and carbon dioxide, electrochemical reactions lead to the formulation of oxides and hydroxides resulting in material degradation (Bhowmik, Hossain, & Shamim, 2012).
ii. Localized corrosion: Pitting and crevice corrosion are common in refineries. These localized forms of corrosion are often caused by the breakdown of the protective oxide layers on the metal surface, exposing the underlying metal to aggressive chemical species (Al-Moubaraki & Obot, 2021).
iii. High-temperature corrosion: At elevated temperatures, materials are susceptible to corrosion from naphthenic acids and sulphur compounds. NAC typically occurs in the temperature range of 220-400°C, leading to the thinning of equipment walls and potential failure (Bhowmik, Hossain, & Shamim, 2012).
iv. Sulphidation: This form of corrosion occurs when sulphur compounds react with metal surfaces at high temperatures forming metal sulphides. This type of corrosion is prevalent in refining units processing high-sulphur crude oils and can cause severe material degradation and operational hazards (Al-Moubaraki & Obot, 2021).

Corrosion poses significant challenges to the oil and gas industry, impacting infrastructure integrity, operational efficiency, and safety. Several studies have addressed these challenges, shedding light on the mechanisms, sources, mitigation strategies, and future outlook of corrosion in this sector.

Kermani and Harrop (1996) highlighted the pervasive impact of corrosion on oil and gas operations. They emphasised the need for robust corrosion management strategies to mitigate economic losses and ensure operational reliability. Perez (2013) echoed these concerns, noting that corrosion presents an increasing challenge for materials used in the industry due to evolving operational conditions and environmental factors.

Al-Moubaraki & Obot (2021) further explored corrosion challenges specifically within petroleum refinery operations. The study identified various sources and mechanisms of corrosion, emphasising the importance of understanding these factors for effective mitigation.

Additionally, they discussed future outlooks, indicating the need for continued research and development of corrosion-resistant materials and technologies.

Bharatiya (2019) focused on the effect of corrosion on crude oil and natural gas pipelines, with a particular emphasis on prevention using eco-friendly corrosion inhibitors. Their comprehensive review underscored the importance of proactive measures in protecting pipeline integrity and minimising environmental risks associated with corrosion.

While much attention has been given to the structural integrity of infrastructure and operational challenges, the alteration of crude oil properties due to corrosion also warrants consideration. Assessing the effects of corrosion on crude oil properties, such as viscosity and American Petroleum Institute (API) gravity, is crucial in understanding the impact of corrosion on the quality and marketability of oil products. Corrosion-induced changes in pipeline walls can lead to contamination of the transported crude oil, potentially altering its viscosity and API gravity. Increased viscosity and deviation from API gravity standards can impede oil flow through pipelines, affecting transportation efficiency and downstream processing. Moreover, altered properties may result in difficulties in refining processes, affecting product quality and market value. Understanding the relationship between corrosion and crude oil properties is essential for implementing effective corrosion management strategies and ensuring the integrity of oil products throughout the production and transportation chain.

2.2. Overview of Crude Oil Bulk Properties

Bulk properties are the large-scale physical and chemical properties of the crude oil, part of a larger set of analyses known as crude oil assay that help to assess the market value of the oil as well as its refining and transportation characteristics (Harry Dembicki, 2017). These include;

i. API Gravity: The American Petroleum Institute's (API) expression of the specific gravity of crude oils and condensates measured at 60°F (16°C). API gravity is a classification for crude oils. It is a measure of the oil's density, with heavy oils having lower API gravity than light oils. It affects crude oil separability and refining processes (Peters, 2012).

ii. Viscosity: This is the opposition to flow in fluids due to molecular cohesion, measured in centipoise (cP). It is influenced by crude oil composition, temperature, dissolved gas content, and pressure. Viscosity impacts crude oil's flowability and pumpability, as well as refinery processing and pipeline transport (Khan, 2017).

iii. Pour Point: This is the temperature at which crude oil becomes semisolid and will no longer flow. It is important for recovery and transportation. High pour points, usually in oils with significant paraffin content, can lead to wax deposition and flow issues. Ugandan crude oil has an average pour point of 40ºC (Boschee, 2022).

iv. Weight Percent Sulphur: This is a measure of both free and bound sulphur in crude oil, inversely proportional to API gravity. Indicates oil type, alteration processes, and sourness. High sulphur can reduce the market value and poison catalysts during refining.

v. Nickel (Ni) and Vanadium (V) Content: It reflects information about the proportions of nickel and vanadium in the source rock. High concentrations can reduce the market value by poisoning catalysts.

vi. S-A-R-A: Refers to saturates, aromatic, resin, and asphaltene fractions derived from separation analysis of crude oil. These are useful in classifying crude oils and deciphering alteration processes.

API gravity and Viscosity were selected for this study. This was because they are key indicators of crude oil quality and refining potential (Speight, 2014). The two parameters are directly affected by rust contamination, which can alter the physical properties of the crude oil (Al-Mutairi, 2018), and they are critical parameters in determining the suitability of crude oil for refinery processes, such as distillation and catalytic cracking (Gary, 2007).

The other parameters, while important for crude oil characterization, were excluded. Sulphur content is more relevant to environmental concerns and refining processes, but not directly affected by rust contamination (Speight, 2014). The pour point is more related to the crude oil's cold flow properties, and is not directly impacted by rust (Peters, 2012). Nickel and vanadium content are important for refining and catalyst performance, but their levels are not directly affected by rust contamination (Gary, 2007). S-A-R-A fractions are crucial for

understanding crude oil composition, but rust contamination does not directly impact these fractions (Speight, 2014).

2.3. Storage of crude oil in the Oil and Gas industry

Crude oil storage is a critical component of the oil and gas industry, as it enables the temporary holding of oil until it is refined or transported (Khan, 2017). The quality of crude oil can be impacted by various factors during storage, includiing contamination, oxidation, and corrosion (Jia, 2019).

Crude oil is typically stored in various types of tanks including

i. Fixed Roof Tanks; These tanks have a fixed roof and are used for storing crude oil with low volatility (API, 2020). They are often made of carbon steel or stainless steel.
ii. Floating Roof Tanks; These tanks have a floating roof that rises and falls with the oil level reducing vapor space and minimising contamination (Singh, 2020). They are typically made of carbon steel or aluminium.
iii. Underground Storage Tanks (USTs); These tanks are buried underground and used for storing crude oil and petroleum products (EPA, 2020). They are often made of steel or fiberglass.
iv. Above-Ground Storage Tanks (ASTs); these tanks are used for storing crude oil and petroleum products, and are often equipped with advanced monitoring systems (NFPA, 2020). They are typically made of carbon steel, stainless steel, or aluminium.

Steel is a common material used for tank construction due to its strength, durability, and relatively low cost. However, it can be susceptible to corrosion, particularly when exposed to moisture and oxygen. Rust from storage cans can contaminate crude oil affecting its quality and refining process (Al-Mutairi, 2018). Corrosion in storage tanks can lead to the formation of rust which can then mix with the crude oil (Singh, 2020).

2.4. Rust-induced Changes in Crude Oil

Rust is commonly composed of Iron oxides, particularly Fe_2O_3 and Fe_3O_4. It forms due to the corrosion of Iron and steel in the presence of moisture and oxygen. Rust primarily consists of:

i. Hematite (Fe_2O_3)**:** This is the main oxide responsible for the reddish-brown colour of rust. Hematite is a stable Iron oxide that forms when Iron reacts with oxygen over time (Morse, 2018).
ii. Magnetite (Fe_3O_4)**:** This Iron oxide appears as a black rust. It often forms during the initial stages of rust formation and can coexist with hematite (Schwertmann & Cornell, 2000).
iii. Goethite (FeO (OH))**:** This yellowish-brown Iron oxide-hydroxide is another common component of rust. It is formed in the presence of moisture and is less stable than hematite (Cornell & Schwertmann, 2003).
iv. Ferrihydrite ($Fe_4O_3(OH)_{12}\cdot xH_2O$)**:** This is an amorphous Iron oxide-hydroxide often found in rust and can transform into more stable forms over time (Jambor & Dutrizac, 2000).

Combustion method is recommended by the American Society for Testing and Materials (ASTM) according to ASTM D5863 for the determination of Nickel, Vanadium, Iron, and Sodium by Atomic Absorption Spectrometry (AAS) (ASTM D5863-00a, 2000). Trace metal contents such as Iron in crude oil can be determined by various techniques including AAS, Inductively Coupled Plasma-optical emission spectrometry (ICP-OES), Inductively Coupled Plasma-mass spectrometry (ICP-MS), X-ray Fluorescence (XRF) Spectrometry, High Performance liquid chromatography (HPLC). Some of these methods such as AAS mainly determine total Iron in the crude oil samples whereas other methods such as ICP are expensive. However Ultraviolet – Visible (UV-VIS) spectrophotometry is an accurate, inexpensive and reliable method for Iron determination in crude oil samples (Shehata, Mohamed, & Gab-Allah, 2017). UV-VIS Spectrophotometric method of determination Iron (III) was used in this study. This involved the determination of Iron (II) and total Iron content in the crude oil samples. The Iron (III) was then obtained by subtracting the concentration of the former from the latter. Iron (III) can be determined directly by using Ferric ammonium sulphate dodecahydrate (Jr, Smart, & Amis, 1955) to prepare the standard solution. This wasn't available for this study.

2.4.1. API gravity

Rust contamination can alter the API gravity of crude oil in two ways. It can decrease API gravity by introducing denser Iron particles. It can also increase the API gravity by removing or altering the crude oil's composition. The change in the API gravity depends on the concentration, size, and type of rust particles, as well as the crude oil's composition and storage conditions. Studies have found that API gravity decreased by 0.5-1.5 °API when crude oil was contaminated with 0.1- 1.0 wt.% rust and the API gravity increased by 0.2-0.5 °API when the crude oil was contaminated with 0.01-0.1 wt.% rust (Jia, 2019). The hydrometer method, ASTM D1298 (ASTM International, 2000), is a common method for determining the API gravity of crude oil and various petroleum products. Density of a substance can also be measured by a density bottle. The latter method was opted for in this study because the volumes of each of the crude oil samples provided weren't enough to be used in the hydrometer method.

2.4.2. Viscosity

Rust particles can alter the viscosity of crude oil in two ways. They can increase the viscosity by introducing particulate matter that hinders the flow and altering the crude oil's composition. They can also decrease the viscosity by breaking down the crude oil's molecular structure and reducing its molecular weight. The change in the viscosity depends on the concentration, size, and type of rust particles, as well as the crude oil's composition and storage conditions. Studies have found viscosity to be increased by 10-30% when the crude oil was contaminated with 0.1-1.0wt.% rust and be decreased by 5-15% when contaminated with 0.01-0.1wt.% rust (Jia, 2019). A common method for determining the viscosity of crude oil and petroleum products is the ASTM D445 (ASTM International, n.d.) that employs a viscometer.

Accurate and comprehensive oil quality testing is crucial for ensuring operational efficiency, regulatory compliance, and market competitiveness. An article from Petro Online titled "Why Does Oil Quality Testing Matter?" sheds light on the significance of oil quality testing in maintaining operational integrity and meeting stringent industry standards. The quality of oil not only helps to determine price and optimise feedstock choices, but it also safeguards expensive equipment. (Petro Online, 2021).

CHAPTER THREE: MATERIALS AND METHODS

1.1. Materials

- Crude oil samples A and B
- Crude oil sample Bottles
- Chemicals: Toluene, Ferrous Ammonium sulphate hexahydrate, Acetic acid, Sodium acetate, 1,10-phenanthroline, Sulphuric acid,
- Density bottle
- Viscometer
- Thermometer
- UV-VIS Spectrophotometer
- Personal protective equipment such as lab coat, gloves, masks, safety glasses etc.

1.2. Methods

1.2.1. Sample collection and preparation

Crude oil sample A and crude oil sample B were collected separately into glass jars from different storage containers at PAU. Crude oil sample A was obtained from a rusted container whereas crude oil sample B was obtained from a non-rusted container.

1.2.2. Identification and quantification of the Iron (III) in the crude oil samples.

To identify and quantify the amount of rust in the crude oil sample, Iron (III) concentration in the crude oil samples was determined. The identification and quantification of Iron (III) in the crude oil samples was done by UV-VIS spectrophotometry (Jr, Smart, & Amis, 1955) from the Spectrophotometry lab.

Crude oil samples A and B were each prepared by decomposition of the organic matrix by combustion (ASTM D5863-00a, 2000). The crude oil samples were each homogenised and then weighed into separate crucibles. Concentrated sulphuric (3ml/g oil) acid was added to each of the samples. The mixtures were each cocked on a hot plate while increasing the

temperature steadily to 300°C till no more smoke appeared. The remaining coke was burned off in a furnace at 600°C for 4 hours.

The inorganic residues obtained from crude oil samples, A and B, were each weighed and then dissolved in dilute sulphuric acid. The obtained solutions were each transferred to a 100ml volumetric flasks and diluted with distilled water to the mark making the sample solutions A1 and B1.

In order to get the wavelength at which the absorbance of Iron (II) is maximum and then obtain a calibration curve, a standard ferrous solution was prepared by weighing analytical grade ferrous ammonium sulphate hexahydrate (0.0705g) into a 1L volumetric flask and distilled water was added to dissolve it. Concentrated sulphuric acid ($2.5cm^3$) was added and the solution diluted with distilled water to the mark.

To prepare the complexing agent, 1,10 phenanthroline (0.1005g) was weighed into a 100ml volumetric flask and diluted with distilled water to the mark. Sodium acetate (0.8252g) was weighed into a 100ml volumetric flask and diluted with distilled water to the mark to prepare the 0.1M Sodium acetate solution. Acetic acid ($6cm^3$) was measured into a 100ml volumetric flask and diluted to the mark to prepare the 0.1M acetic acid. An acetic acid-sodium acetate buffer (pH 4.5) was prepared by mixing 0.1M acetic acid ($65cm^3$) and 0.1M Sodium acetate solution ($35cm^3$).

To a series of 100ml volumetric flasks, 5, 10, 15, 20 cm^3 of the standard Fe^{2+} solution were pipetted. Solution A1($20cm^3$) and solution B1($20cm^3$) were each pipetted into other 100ml volumetric flasks. 20 cm^3 of distilled water was pipetted into another similar volumetric flask to form the blank. $5cm^3$ of 1,10 phenanthroline solution was added to each of the flasks. Each solution was buffered by adding $8cm^3$ of acetic acid-sodium acetate buffer and allowed to stand for 15 minutes for full colour development. Each solution was diluted with distilled water to the $100cm^3$ mark and mixed well. The standard solutions obtained corresponded to concentrations of 0.5, 1.0, 1.5, and 2.0 ppm and the flasks were labelled respectively S.No 1, 2, 3, and 4.

The absorption spectrum of the 2.0ppm standard solution against the blank in the range of 370-670nm was recorded using the spectrophotometer. The absorbances obtained were

plotted against the wavelength. The wavelength that gave the maximum absorption was recorded, λ_{max}.

Where A is the absorbance of the solution at the wavelength of maximum absorption, c is the concentration the standard solution and b is the path length of the cuvette.

The absorbances for all the concentrations of the standard solution at the wavelength of maximum absorption, 510nm and at 396nm were measured and recorded. The absorbances of the solutions A1 and B1 were also measured in the same way. Absorbance of the standard solutions at 510nm and at 396nm were plotted against the concentrations of the standard solutions and the linear region of the curve used to estimate the concentrations of Iron (II) and total Iron in sample solutions A1 and B1.

Fe^{3+} and Fe^{2+} form a similar complex with the ligand 1,10-phenanthroline. The Fe^{3+} complex appears yellow and the Fe^{2+} complex appears orange. Both complexes have identical absorption at 396nm and are additive (Jr, Smart, & Amis, 1955). Therefore, measurement of absorption at 396nm would give the amount of total Iron present. The concentration of Fe^{3+} was obtained by subtracting the concentration of Fe^{2+} from the total Fe concentration and multiplying the difference by twenty. The factor twenty comes from the fact that 20 cm^3 of the sample solutions A1 and B1 were each taken and diluted to 100cm^3.

3.2.2. Determination of API Gravity

The density measurements were done using a density bottle, a more accurate method to determine the density of samples (Cox, 2008) in the Physical Chemistry laboratory.

The density bottle was cleaned and dried to ensure that no residues or moisture would affect the accuracy of the measurements. The volume of the density bottle was recorded. The cleaned density bottle was weighed using an analytical balance and the mass (M_0) was recorded. The temperature of distilled water was measured and the distilled water was added to the density bottle to the calibration mark. The density bottle with distilled water was weighed and the mass (M_{H2O}) was recorded. The density of the distilled water was determined by calculating the difference between the weight of the density bottle filled with the distilled water and the weight of the empty density bottle. This weight difference was then divided by the volume of the density bottle to obtain the density of the water at the reference

temperature. Each crude oil sample was homogenised and procedure was repeated for crude oil sample A and also crude oil sample B.

The specific gravity (relative density) of the crude oil samples was then calculated by comparing their density to the density of water at the same reference temperature. The following formula was used to convert the specific gravity to API gravity:

$$API\ Gravity\ = \frac{141.5}{specific\ gravity} + 131.5$$

The density measurement was corrected using the API tables (ASTM D1250 Table 5A) and the API gravity at 60°F was obtained.

3.2.3. Viscosity Measurement

The procedure is as follows, according to the standard ASTM D445. This was carried out in the Physical Chemistry laboratory:

The viscometer was prepared by cleaning, drying, and calibrating it and using distilled water. The time required for distilled water to flow through the capillary was recorded. Crude oil sample A was diluted using Toluene with a dilution factor of 0.2. crude oil sample B was diluted with the same solvent with a dilution factor of 0.083. The viscometer was filled with the crude oil-toluene mixture of each crude oil sample A. The timing device was started and the sample was allowed to flow through the capillary tube under gravity. The time required for the meniscus to pass between two marked points on the viscometer was recorded. The measurement was repeated thrice and the average flow time was calculated. The viscosity of the mixture was calculated from the equation:

$$\text{Viscosity}(\eta s) = \frac{\eta w * \rho s * ts}{\rho w * tw}$$

Where η_s – viscosity of the sample

η_w – viscosity of distilled water at a given temperature

ρ_s- density of the crude oil sample at a given temperature

t_s- time required by the sample to flow through the capillary tube of the viscometer

ρ_w- density of distilled water at a given temperature

t_w- time required for distilled water to flow through the capillary tube of the viscometer

The viscosity of each sample was obtained by multiplying the viscosity of the mixture by the dilution factor. The viscosity of water at 24°C used as the reference viscosity was 0.8903cP (Korson, Drost-Hansen, & Miller, 1968). The procedure was repeated for the crude oil-toluene mixture of crude oil sample B.

CHAPTER FOUR: RESULTS AND DISCUSSION

1.1. Combustion of the crude oil samples for UV-Vis spectrophotometric analysis

The inorganic residue from crude oil sample A appeared brown. The inorganic residue from crude oil sample B appeared green with traces of brown. The brown colour in the residues indicated the presence of Iron (III) oxide in each of the sample.

Table 1:Inorganic residue in the crude oil samples

Crude oil sample	A	B
Mass of crude oil sample(g)	10.4194	10.7983
Mass of inorganic residue of crude oil sample(g)	0.1461	0.0576
Percentage inorganic residue (%)	1.4022	0.5334

These values in Table 1 suggest that both crude oil samples A and B are each primarily composed of organic matter, with a small percentage of inorganic residues. The higher percentage of inorganic residue in crude oil sample A compared to crude oil sample B suggests that crude oil sample A may contain more inorganic impurities, potentially from rust contamination.

1.2. Identification and quantification of Iron (III) in the crude oil sample.

Identification of Iron (III)

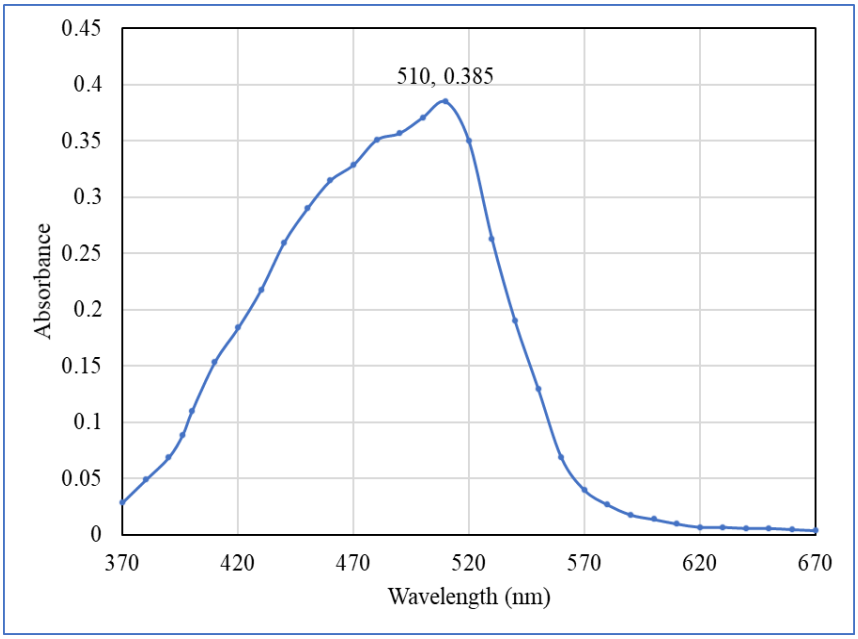

Figure 1:UV-Vis spectrum of the Iron (II)-phenanthroline complex

Wavelength at maximum absorbance of the Iron (II)-phenanthroline complex λ_{max} = 510nm as shown in Figure 1.

The addition of the complexing agent to the samples solutions A1 and B1 yielded faint yellow solution in sample solution A1 that indicated the presence of Iron (III). Sample solution B1 yielded a faint orange solution that indicate more Iron (II) in the solution.

Table 2: Absorbance values of the Iron-phenanthroline complexes of standard and sample solutions of ferrous ion and total Iron ions.

S. No.	**Concentration of Fe2+ ions (ppm)**	**Absorbance at 510nm**	**Concentration of Fe (ppm)**	**Absorbance at 396nm**
1	0.50	0.129	0.50	0.014
2	1.00	0.202	1.00	0.035
3	1.50	0.361	1.50	0.084
4	2.00	0.385	2.00	0.089
Solution A1	0.36	0.104	0.58	0.019
Solution B1	0.25	0.083	0.43	0.010

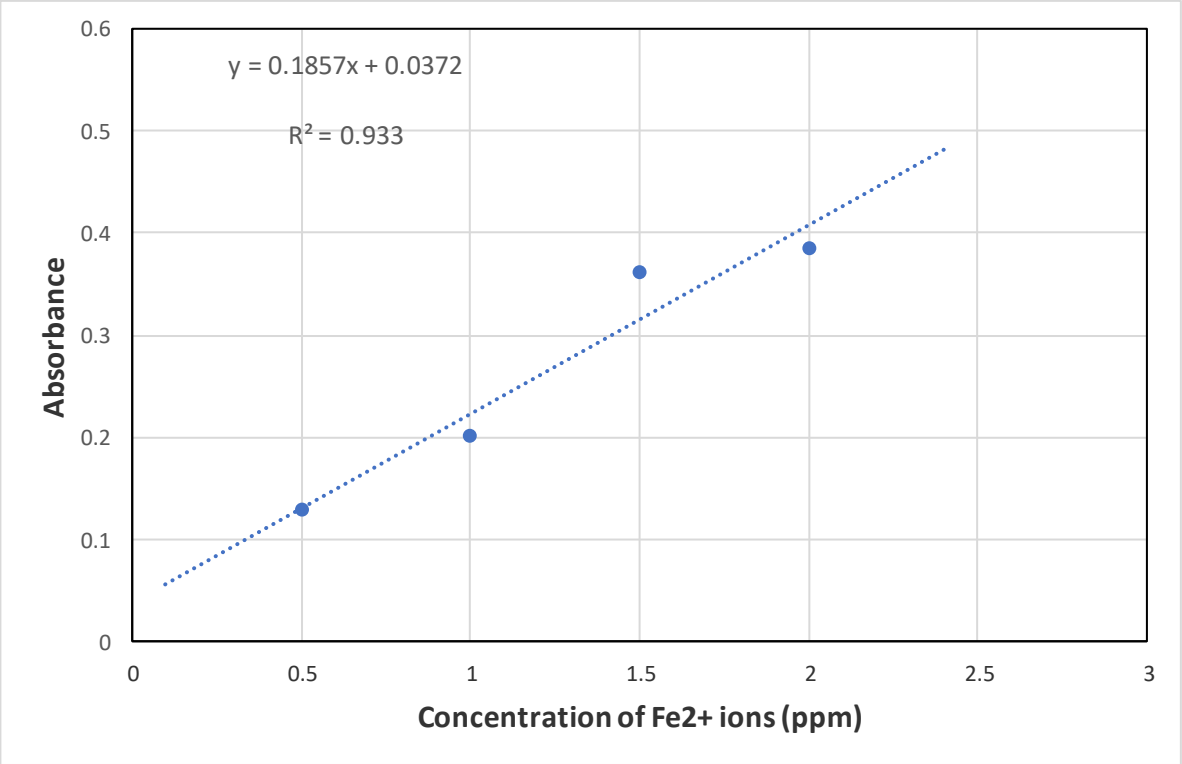

Figure 2:Graph of absorbance of the Iron (II)-phenanthroline complex against concentration of Iron (II)

The equation of the trendline was used to obtain the concentrations of Fe^{2+} in the solutions A1 and B1 in Table 2.

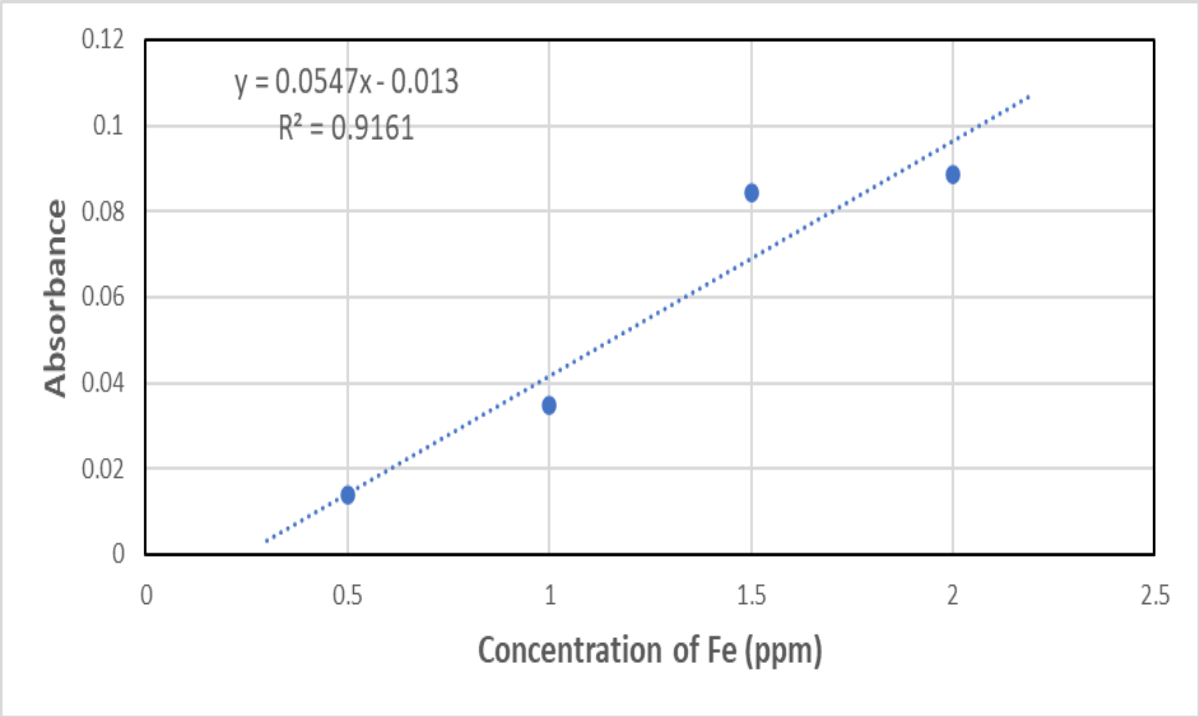

Figure 3: Graph of absorbance of Iron-phenanthroline complexes against the concentration of Fe at 396nm

The equation of the trendline was used to obtain the concentrations of Fe in the solutions A1 and B1 in Table 2.

Table 3: Concentration of Fe, Fe^{2+} and Fe^{3+} in the solution A1 and B1 from the curves.

	Solution A1	**Solution B1**
Concentration of Fe (ppm)	0.58	0.43
Concentration of Fe^{2+} (ppm)	0.36	0.25
[Fe]-[Fe^{2+}] (ppm)	0.22	0.18
Concentration of Fe^{3+} (ppm)	0.22x20=4.4	0.18x20=3.6

The factor twenty in Table 3 comes from the fact that 20 cm^3 of the sample solutions A1 and B1 were each taken and diluted to 100cm^3.

The concentration of the Fe^{3+} ions in crude oil sample A was 4.4ppm. The concentration of Fe^{3+} ions in crude oil sample B was 3.6ppm. This indicates that crude oil sample A was more affected by rust, as Fe^{3+} is a primary component of rust. These results indicate a higher

presence of Iron in crude oil sample A, which is consistent with the presence of rust as a contaminant. The presence of Iron, particularly Fe^{3+}, in crude oil can originate from corrosion processes, where steel storage containers oxidize and contribute to the metal content in the stored crude oil (Hilder, 2018). The calibration curve, in **Error! Reference source not found.**, obtained at 510 nm had a correlation coefficient (R^2) of 0.9335. The calibration curve, in Figure 3, obtained at 396 nm had a correlation coefficient (R^2) of 0.9161. The range $0.9 < R^2 < 1$ indicates a strong correlation i.e., small deviations from the calibration curve. The significant correlation coefficients (R^2 values) confirm the reliability of the spectrophotometric measurements, allowing for confident determination of Fe^{3+} concentration in the crude oil samples.

1.3. Determination of API gravity

Table 4: Determination of API Gravity

Water	
Density of water (g/cc)	0.9895
Crude oil sample A	
Density of A (g/cc)	0.7160
Specific Gravity of A	0.7236
API Gravity (°API)	64.1
API Gravity (°API) at 60°F	62.2
Crude oil sample B	
Density of B (g/cc)	0.863
Specific Gravity of B	0.8722
API Gravity (°API)	30.7
API Gravity (°API) at 60°F	30

The API gravity of Crude oil sample A (62.2 °API) as seen in Table 4 was exceptionally high, which suggested a very light crude oil, which is not typical for Ugandan Oil. The API gravity for Ugandan crude oil which ranges between 17-33 °API (Petroleum Authority ofUganda, 2024). In contrast, Crude oil sample B had an API gravity of 30 °API, which falls within the expected range for Ugandan crude oil. The catalytic cracking of heavier hydrocarbons into lighter ones can be accelerated by metal ions like Fe^{3+}, potentially explaining the abnormally high API gravity in Crude oil sample A. This catalytic effect can result from the presence of Iron (III) oxide, promoting the breakdown of complex

hydrocarbons into simpler, lighter molecules, thereby reducing the density and increasing the API gravity. (Fumoto, Sato, & Takanohashi, 2017).

1.4. Determination of viscosity

Table 5: Determination of viscosity of the samples A and B

Water	
Time required for water to flow (t)	
t_1(sec)	263
t_2(sec)	264
t_3(sec)	262
Average Time t_{H2O}(sec)	263
Viscosity of water at 25°C (cP)	0.8903
Crude oil sample A	
Time required for mixture to flow (t)	
t_1(sec)	243
t_2(sec)	245
t_3(sec)	242
Average Time t_A(sec)	243
Viscosity of mixture at 24°C (cP)	0.5960
Viscosity of A at 24°C (cP)	2.9802
Crude oil sample B	
Time required for mixture to flow (t)	
t_1(sec)	203
t_2(sec)	203
t_3(sec)	204
Average Time t_B(sec)	203
Viscosity of mixture at 24°C (cP)	0.6003
Viscosity of B at 24°C (cP)	7.2039

The viscosity of crude oil sample A at 24°C is 2.9802cP, while crude oil sample B has a viscosity of 7.2039cP as seen in Table 5. Crude oil sample A's viscosity is significantly lower than that of Crude oil sample B. The higher viscosity of Crude oil sample B indicates a thicker, heavier oil which is characteristic of Ugandan crude, while Crude oil sample A is much less viscous. This is consistent with Crude oil sample A's higher API gravity. Lighter crude oils generally exhibit lower viscosities due to a higher proportion of lighter hydrocarbon fractions (Santos, Oliveira, & C. R. E. Mansur, 2017). The lower viscosity in crude oil sample A might be due to the catalytic degradation of heavier hydrocarbons into

lighter ones by the Iron (III) oxide content. Given that rust contains Iron oxides, these act as catalysts in the crude oil, breaking down heavier molecules into lighter, less viscous ones. This aligns with the findings that crude oil sample A, which contains more Iron, has a much lower viscosity and higher API gravity, indicating a higher degree of cracking and formation of lighter hydrocarbons.

CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

The presence of rust was successfully identified in the crude oil samples through combustion of the crude oil samples. The yellow colour that appeared in the solutions A1 and B1 after the addition of the ligand 1,10-phananthroline confirmed the presence of rust derived from steel storage containers. The quantification of Iron ions, particularly Fe^{3+} was achieved by UV-Vis spectrophotometry. The UV-Vis analysis revealed higher concentrations of Fe^{3+} in crude oil sample A (4.4ppm) compared to crude oil sample B (3.6ppm), indicating a greater level of rust contamination in crude oil sample A. The API gravity of the samples provided further insights into their quality. Crude oil sample A had an exceptionally high API gravity (62.2 °API), suggesting a very light crude oil composition. This value is unusually high compared to typical Ugandan crude oil, which ranges between 17-33 °API. In contrast, crude oil sample B's API gravity (30 °API) fell within the expected range. The higher API gravity in crude oil sample A indicated a substantial alteration in its composition, likely due to the presence of Iron oxides from rust, which can act as catalysts in the cracking of heavier hydrocarbons. The viscosity measurements indicated a notable difference between the two samples. Crude oil sample A exhibited a significantly lower viscosity (2.9802 cP) compared to crude oil sample B (7.2039 cP). This reduction in viscosity in crude oil sample A can be attributed to the catalytic effects of Iron contaminants, particularly Fe^{3+}, which may have facilitated the breakdown of heavier hydrocarbons into lighter fractions, thus lowering the overall viscosity.

The findings demonstrate that these changes can affect the usability and market value of the crude oil, emphasizing the importance of proper storage conditions to prevent rust contamination.

In conclusion, the research successfully achieved its objectives by identifying rust in the samples, and determining their viscosity and API gravity. The study underscores the critical need for monitoring and mitigating rust contamination in crude oil storage to maintain the quality and integrity of the stored product.

5.2. Recommendations

Based on the findings of this study, the following recommendations are made to mitigate the impact of rust on crude oil quality and improve storage practices:

i. Further Studies on Catalytic Effects: Further research should be conducted to explore the catalytic effects of Iron contaminants on the chemical composition of crude oil. Understanding these mechanisms can help in developing more effective strategies for managing and preventing contamination.
ii. Use of Corrosion-Resistant Materials: It is recommended that storage tanks and containers for crude oil should be constructed from corrosion-resistant materials such as stainless steel or lined with anti-corrosive coatings. This would significantly reduce the formation of rust and contamination of the stored oil.
iii. Regular Maintenance and Inspection: Implementing a regular maintenance and inspection schedule for storage containers can help identify and address corrosion issues before they lead to significant contamination. This includes checking for signs of rust and repairing any compromised areas promptly.
iv. Periodic Testing for Contaminants: Regular sampling and testing of crude oil should be conducted to monitor the levels of contaminants, particularly Iron ions, to ensure the quality remains within acceptable limits. This should include both Fe^{2+} and Fe^{3+} ions, as their presence can indicate the onset of rust contamination.
v. Installation of Monitoring Systems: Deploying sensors and monitoring systems within storage facilities can provide real-time data on environmental conditions (e.g., humidity, temperature) that contribute to rust formation. This data can be used to adjust environmental controls to minimize corrosion risks.
vi. Use of Inhibitors in storage tanks: The application of corrosion inhibitors can be considered to prevent the oxidation of metal surfaces within storage tanks. These inhibitors form a protective layer that reduces the interaction between metal surfaces and corrosive elements in the environment.

By implementing these recommendations, the risk of rust contamination in crude oil storage can be minimized, thereby preserving the quality of the crude oil and maintaining its market value.

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