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CONTRIBUTIONS OF PETROLEUM DRILLING MUD TO ENVIRONMENTAL POLLUTION: ASSESSMENT OF HEAVY METALS AND POLY AROMATIC HYDROCARBONS IN OIL BASED PETROLEUM DRILLING MUD

BY

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BEING A RESEARCH PROJECT SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE AWARD OF MASTER OF SCIENCE (M.SC) IN FOSILL FUEL CHEMISTRY

TO THE DEPARTMENT OF PURE AND INDUSTRIAL CHEMISTRY
UNIVERSITY OF NIGERIA, NSUKKA

JANUARY, 2014
This work has been approved by the Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka.

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EXTERNAL EXAMINER                                               Date________________________

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DEDICATION

This research work is dedicated to God Almighty for His kindness to me and to my parents for their support and encouragement.
ACKNOWLEDGEMENTS

I wish to express my profound gratitude to God Almighty for His grace throughout the period of this programme.

My unreserved appreciation goes to my amiable supervisor, Prof. C. A. Nwadinigwe, for his expert guidance and patience which contributed to the successful completion of this research work. May God continue to strengthen and protect you. Worthy of mention are other members of staff in the Department of Pure and Industrial Chemistry, University of Nigeria Nsukka for their contributions towards the successful completion of this M.Sc programme. They include Prof. P. O. Ukoha, Head of the Department, Prof. J. A. Ibemesi, Prof. C.O.B. Okoye, Dr. P.M. Ejikeme, Dr. O. T. Ujam, Dr. R.N. Ekere, Dr. L. N. Obasi, Dr. J. N. Asegbofoyin, Dr. C. N. Ibeto, Mrs. N. N. Ukwueze and others.

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List of Abbreviations

AAS = Atomic Absorption Spectrophotometer
API = American Petroleum Institute
ATSDR = Agency for Toxic Substances and Disease Registry
BTEX = Benzene, Toluene, Ethyl benzene and Xylene
DNA = Deoxyribonucleic Acid
FID = Flame Ionization Detector
GC = Gas Chromatography
GrFAAS = Graphite Furnace Atomic Absorption Spectroscopy
IQ = Intelligent Quotient
IARC = International Agency for Research on Cancer
OBM = Oil Based Petroleum Drilling Mud
PAHs = Polycyclic Aromatic Hydrocarbons
SVOCs = Semi Volatile Organic Compounds
USEPA = United State Environmental Protection Agency
WBM = Water Based Petroleum Drilling Mud
WHO = World Health Organization
ABSTRACT

Untreated and treated samples of oil based petroleum drilling mud formulated by ANA Industries used at Nembe Creek off-shore well in the Niger-Delta area of Nigeria, were studied to evaluate the possible environmental impacts that may result from their indiscriminate disposal. Aggregate samples of the oil based drilling muds were collected and analyzed for six heavy metals: iron, nickel, chromium, cadmium, manganese and vanadium, using Buck Scientific Atomic Absorption Spectrophotometer of Model 210/211 VGP with 220GF Graphite furnace and 220AS Auto sampler. The polynuclear aromatic hydrocarbons (PAHs) content of the oil based mud samples were also determined using Buck scientific gas chromatography of Model 910 with 30meter, Restek column. The results revealed that both untreated and treated muds contain the heavy metals: Fe, Ni, Cr, Cd, Mn and V. It was observed that the treatment reduced the mean concentration of Fe from 89.020 to 65.000 ppb, Ni from 85.030 to 69.330 ppb, Cr from 10.050 to < 0.001 ppb, Cd from 10.030 to < 0.001 ppb, Mn from 77.000 to 39.840 ppb and V from 96.503 to 58.000 ppb. The untreated mud contains more polynuclear aromatic hydrocarbons (µg/µl) than the treated mud, i.e., more in numerical spread and concentration: naphthalene 21.47 vs 0.48, 2–methylnaphthalene 32.60 vs nil, acenaphthalene 10.05 vs 0.51, fluorene 2.59 vs 0.31 and anthracene 2.58 vs nil. These data novel will be quite useful to policy makers on environmental pollution and to stakeholders using drilling mud with respect to their usefulness and hazards. The results obtained from the analyses generally have values lower than W.H.O and USEPA standards for waste disposal, thereby implying that the treated mud has no immediate deleterious impact on the environment.
CHAPTER ONE

1.0 INTRODUCTION

All the activities involved in the hydrocarbon exploration and production normally have one impact or the other on the environment. However, the greatest impact arises from the release of wastes into the environment in concentration that is not naturally found in such environment\(^1\). The wastes generated during petroleum production can be broadly classified into liquid (produced water and drilling mud) and solid (cuttings). Many of the additives used for the drilling mud are believed to be toxic and should be regulated. Drilling muds and cuttings may be oil-based or water-based in nature and are associated with varying concentrations of hydrocarbons and heavy metals\(^1\).

Drilling mud is very important to both rotary and directional drilling processes. Although most oil and gas wells drilled nowadays use rotary drilling technique. Without drilling muds and their additives, corporations would find it difficult if not impossible to drill for oil and gas and we would hardly have any of the fuels and lubricants considered essential for modern industrial civilization\(^2\). Basically, drilling mud is a mixture of water, clays, special minerals and chemicals called additives\(^3\). Drilling mud can also be in non aqueous form usually called oil-based mud (OBM) and in gaseous phase called gaseous drilling fluid, in which a wide range of gases can be used. A successful drilling operation requires enhanced quality of drilling mud with well formulated properties that will enable them to perform creditably during drilling operations\(^4\).

1.1 Effects of Drilling a Well Without and with Drilling Mud

a) Hydrocarbons blow out due to insufficient pressure.

b) A lot of heat is generated during drilling which can cause bit balling.
c) Drilling strings get stuck due to cutting and formation caving.

d) Formation instabilities; swelling. (That can lead to falling of the formation into the well).

e) Inability to carry cuttings to the surface.

Therefore, well formulated drilling mud do the following essential jobs in oil and gas wells:

I. Lubricate the drill bit, string, bearings, mud pump and drill pipe, particularly as it wears against the sides of the well when drilling deviated wells around corners\textsuperscript{5, 6}.

II. Clean and cool the drill bit as it cuts into the rock.

III. Lift rock cuttings to the surface and allow cuttings to drop out in the mud pit or shakers to prevent them re-circulating.

IV. Provide information to the drillers about what is happening down hole by monitoring the behavior, flow rate, pressure and composition of the drilling fluid.

V. Prevent well blow-out by including very heavy minerals such as barites (weighing agent) to counteract the pressure in the hole (reservoir pressure).

VI. Drilling mud helps in suspension of drilling assemble and casing, delivery of hydraulic energy, being a suitable medium for logging and to being environmentally acceptable.

The above highlights of the various functions of drilling mud justify the need for a very careful formulation and selection of the right mud used for different drilling operations\textsuperscript{7, 8, 9}.

1.12. Properties of well program

The properties of well program which are monitored during drilling include the following:

1. Rheology,

2. Density

3. Filtration rate

4. Solid content.
**Rheology**: The success of the overall drilling operation is determined by the rheological properties of the drilling mud. The rheology of the mud indicates the flow behavior of the mud and is characterized by viscosity (which affects the ability to carry cuttings), plastic viscosity, gel strength and yield value\textsuperscript{10}.

**Density**: The weight of mud affects the ability of formation fluid blow out. Additives increase the density of drilling fluid. Therefore, additives to add depend on the reservoir pressure. The hydrostatic pressure should be higher than the reservoir pressure to avoid blow out of hydrocarbon deposits.

**Filtration Rate**: This affects the ability of the mud to build an effective wall cake to prevent fluid loss.

**Solid Content**: This affects the rate of penetration of the drill bit\textsuperscript{11}.

For any type of drilling fluid, these properties may be manipulated using various additives. A type of mud additive used for lowering rotary and axial friction in the well bore as well as lubricate bit bearings in oil well drilling is referred to as drilling mud lubricants.

Amidst these successes, the drilling mud has certain side effects viz:

1. Open hole formation damage.
2. Casing and drill string corrosion.
3. Reduction in rate of penetration.
5. Differential sticking.
6. Settling in the pit.
7. Environmental contamination.

For each of these side effects the mud engineers have a solution.
Drilling mud gets contaminated on its journey from the mud pit to the sub-surface and back to the pit through the circulating system equipment. The contaminants of the drilling mud are: heavy metals, cement, anhydrite and gypsum, carbonates, hydrogen sulphide and hydrocarbons. These contaminants affect the properties of the mud which in turn brings about hole problems (if not monitored and corrected by the use of chemicals and materials suited to the problems).

1.13 Heavy Metals in Drilling Mud

Heavy metals are parameters to be considered among other parameters such as pH, salt, hydrocarbons and cuttings when muds are to be disposed. Heavy metals are metallic elements having density greater than 5g/cm$^3$.[13,14] They are commonly referred to as trace metals because they are present at much lower concentrations in water compared to major ions $\text{SO}_4^{2-}$, $\text{Cl}^-$, $\text{NO}_3^-$, $\text{Mg}^{2+}$, $\text{Ca}^{2+}$.[15] In small concentrations, some of the heavy metals such as iron, manganese, cobalt, molybdenum and copper are useful for animal and plant growth. If they are not present and available in the soil at a minimum level, deficiency will occur, but excessive amounts may be toxic. Other heavy metals such as lead, cadmium, nickel, chromium and mercury are non-essential ones.[14,16] When present in an accessible form they can be taken up by living organisms without playing any vital role. Due to their potential toxicity, it is of interest to make an analytical estimation of their presence in drilling mud and cuttings, when these materials are to be disposed off to the environment.[17]

When water based mud are to be disposed, there are several parameters to be considered such as hydrocarbon, heavy metals, salts and pH. In most cases reducing or eliminating heavy metals from the additives will reduce the problems associated with disposal. Even if all heavy metals are eliminated from the additives placed in a mud system, this contaminant can still
become incorporated into the mud from the formation that is being drilled. Heavy metals from both the additives and formation tend to react with drill solid and clays to spread its potential toxicity which has detrimental effect on the environment. They will not biodegrade but could cause problems for many years. Heavy metals can bioaccumulate and pass up the food chain causing health problems, such as birth defect.

The heavy metals analyzed in this work are limited to iron, nickel, chromium, cadmium, manganese and vanadium. Other heavy metals could also be present in the mud. These metals were analyzed using Buck Scientific Atomic Absorption Spectrophotometer of model 210/211 VGP with 220GF Graphite furnace and 220AS Auto sampler.

1.14 Polycyclic Aromatic Hydrocarbons in Drilling Mud

Polycyclic aromatic hydrocarbons (PAHs) are particularly relevant in the analysis of environmental pollution because of their ubiquity, toxicity and persistence. Poly aromatic hydrocarbons are potent atmospheric pollutants that consist of fused aromatic rings and do not contain heteroatoms or other substituents. PAHs can be incorporated into the mud from the base fluid used especially for oil based mud. In the 1980’s, the American Environmental Protection Agency (US EPA) compiled a list of the 16 most relevant PAHs in terms of environmental pollution which include: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo[k]fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene. Consequently these PAHs have become the most intensively studied pollutants in environmental analysis. Standard and official methods for their analysis are available in Guidelines for Fluids, Solid Waste and Food analysis. These methods include: Gas
Chromatography, usually with flame ionization detector (FID) and High Pressure Liquid Chromatography, usually with UV and fluorescence detection, with run times in excess of 30 mins. To attain a better selectivity, stationary phases specifically designed for PAH analyses are required.

But for the purpose of this work, Buck Scientific Gas Chromatography of Model 910 was used and therefore enabled the use of 30meter, Restek column.

1.2 Aims/Objectives

The aim of this research work was to carry out laboratory analysis on the untreated and treated samples of oil based petroleum drilling muds :

I. To ascertain the heavy metals present in the oil based muds.

II. To compare the concentrations of those heavy metals in the drilling muds with the guide lines from the standard regulatory bodies like USEPA and WHO

III. To find out and quantify the polycyclic aromatic hydrocarbons (PAHs) present in the oil based muds.

IV. To compare the concentrations of those PAHs in the drilling muds with the guide lines from the standard regulatory bodies.

1.3 Scope/Limitation

This research work was restricted to the analysis of six heavy metals (Fe, Ni, Cr, Cd, V and Mn) and poly aromatic hydrocarbons in untreated and treated samples of oil based petroleum drilling muds formulated by ANA Industries Limited which was used at Nembe Creek 74, offshore well in Bayelsa State, Nigeria.
1.4. Statement of Problems

Heavy metals and polycyclic aromatic hydrocarbons as contaminants in drilling mud result to problems which by way of summary may include one or all of the following:

I. Being hazardous to operators.

II. Being damaging or offensive to the environment.

III. High cost of mud program due to expensive treatment.
CHAPTER TWO

2.0. LITERATURE REVIEW

2.1 A Brief History of Petroleum Drilling Mud

The process of drilling a hole in the ground using mud is a primordial technique; it was used to soften the formation and aid cuttings removal. Drilling fluids have been in existence far before the emergence of the petroleum industry\textsuperscript{22}. There is very little information on the early history of drilling muds, as the first wells drilled by the rotary method apparently used only whatever mud the formations made. Evidently during these early days the mud, while necessary, did not warrant special attention. The physical properties of the fluid apparently were not of sufficient interest to merit recording as there are no discussions available regarding them\textsuperscript{23}.

In 1844, the first Patent covering rotary drilling methods were issued Robert Beart a British pioneer of modern oil drilling technology in England\textsuperscript{24}. In 1845, a French engineer Fauverlle, was the first to drill a well using the technique of water flush tools where water was circulated in an effort to remove the drill cuttings (particles of crushed rocks generated by the grinding action of the drill bit). Also, water as a drilling fluid had been used in China, Persia, Egypt and Europe to drill wells; thus water must be considered to be the first drilling fluid. The use of only water was with the understanding that fine cuttings will mix with water to produce a mud that will perform the function required of drilling mud then. This technique was however found to have many shortcomings.

In 1889, oil was introduced as a drilling fluid in place of the conventional ‘‘mud’’ made up of water and native clay. In 1916, Lewis and Murrah came out with the idea that to be able to suspend clayey materials in water for a considerable time, a good mud-laden fluid should be introduced which would be free from sand, lime cuttings or similar materials and should have
specific gravity within the range 1.05 – 1.15. They also point out some of the dangers associated with using only water as a drilling fluid. Some of these dangers stem from the possibility of formation damage due to excessive water loss to the formation\textsuperscript{23}. A good mud was considered to be thick enough to clog the pores of sand and rock and not pass into them. A thick mud was considered as having the advantages of plugging the sand, preventing caving of formations and holding back high gas pressures. This as of 1916 is undoubtedly the status of rotary drilling fluids\textsuperscript{23}.

In 1921, the modern history of drilling fluids began with the first attempt to control mud properties through the use of additives. Stroud in 1921 was engaged in finding a means of weighting drilling fluids to prevent wells from blowing out from high gas pressures. Several bad blow outs and fires had resulted during the drilling of gas fields with lightweight gas-cut muds, and means of weighting the mud were sought\textsuperscript{23}.

The term “Drilling fluid” mostly used is to emphasize that the properties of the mud are designed to optimize the drilling operation and are not those arrived at just by mixing native clay and water in given proportion. Mud implies simple fluids, but presently drilling fluids are sophisticated with complex rheological, filtration and chemical properties. Initially, the primary purpose of the mud was to remove cuttings continuously. With progress, more sophistication was added and more was expected from the drilling mud.

The idea of improving the weight of the mud using additives came from Stroud in 1921. He used ground iron oxide for this purpose, but later discarded it due to its low specific gravity. Further work in this respect led to the advancing of barium sulphate (\(\text{BaSO}_4\)), commonly known as barite, for mud weighting. This is as a result of the fact that it has a high specific gravity, low abrasive properties and is non toxic\textsuperscript{23}. Bentonite and bentonitic clays were also introduced to the
drilling mud act in 1929 as viscosifiers. In the search for better mud making, many other additives for almost every conceivable purpose were introduced and what had started out as a simple fluid became a sophisticated mixture of liquids, solids and chemicals. Instruments and methods for testing muds required special development as the industry recognized those physical and chemical properties of interest.

The greatest development in instrumentation has been for viscosity and fluid loss measurements. Viscosity was first measured with Marsh funnel adopted by the American Petroleum Institute (API) in 1930 as a standard instrument but later viscometer came into play\textsuperscript{23}. As many people ventured into studying the effect of drilling muds on formations being drilled, it became clear that the chemistry of drilling mud is very important and drilling muds are responsible for problems such as well bore narrowing, invasion, reduction in formation permeability and overall decrease in well productivity which were then evident in most of the producing wells. Drilling mud chemistry is quite complicated and unfortunately, is incompletely understood. This is true of the entire field surface chemistry and should not be considered as a failing unique to this industry. This led to the realization that no matter what mud type is used there existed a reduction in the permeability of the rock around the well bore, this in fact confirms the existence of formation damage\textsuperscript{25}.

\subsection*{2.2 Definition of Mud}
Mud is a common on-the-job name for the most popular circulating fluid associated with rotary drilling, and is used to perform any or all of the various functions required in the drilling operation\textsuperscript{26, 27}.

\subsection*{2.3 The Circulating System}
The circulating system is needed to get drilling mud down the hole through special steel pipes called drill pipes and drill collar out of the bits that is attached to the bottom most drill collar and to the surface. Large heavy duty pumps called mud pumps are the heart of the circulating system. Usually two pumps are installed even though only one at a time is normally in use during drilling operations. The second serves as a backup if the first requires repairs. However, both pumps can be used simultaneously for very deep hole to achieve the needed increased pump capacity.

However, one pump or the other usually picks up mud from steel tanks or pits in which the mud is stored and sends it through a stand pipe and rotary hose. Exiting the rotary hose, mud goes into the swivel to which the drill string is attached. The mud then goes down a special length of pipe called the KELLY down through the drill pipes and the drill collars and out of the bit nozzles, and up to surface through annular space “annulus’’ carrying cuttings. Meaning that the mud carries the crushed or cut rock “cuttings’’ up the annular space “annulus” between the drill string and the sides of the hole being drilled, up through the surface casing, where it emerges back at the surface.

The mud and cuttings leave the well through a mud return line. The cuttings fall onto a vibrating screen called the shaker and are disposed off, but mud falls through the screen and back into the pits. This would be picked by the pumps and sent back again down the hole. Normally, mud circulation continues as long as the bit is on bottom and drilling.

The cuttings that fall onto the shale shaker move down a shale slide into the reserve pit. The pit serves mainly as disposal area but at times may be circulated through the reserve pit if the mud contains an unusually large amount of drill solid which can be allowed to settle out in the reserve pit before the mud is re-circulated back into the hole. The mud pits let the drilled
“fines” settle; the pits are also where the fluid is treated by addition of chemicals and other substances. The returning mud can contain natural gas or other flammable materials which will collect in and around the shale shaker/conveyor area or in other work areas. Because of the risk of a fire or an explosion if they ignite, special monitoring sensors and explosion-proof certified equipment is commonly installed and workers are advised to take safety precautions. Agitators are installed on the mud pit to help maintain uniform mixture of liquids and solids in the mud. The mud is then pumped back down the hole and further re-circulated. Maintaining desirable characteristics of the mud may require additional equipment. For example a desander and de-silter may be installed to remove very small solids that cannot settle out in the pits, and a degasser may be inserted to remove entrained gas from the mud.

More so, treatment can be done on the mud if contaminants are detected in the mud tests carried out by site engineer to ensure properties which optimize and improve drilling efficiency, bore hole stability and other requirements.
2.4. Drilling Fluid Compositions, Additives and their Functions

2.4.1 Composition

The composition of drilling fluids will depend upon the requirements of a particular drilling operation. Holes must be drilled through different types of formation requiring different types of drilling fluid. The most common drilling mud is a liquid-based mud typically composed of a base fluid (such as water, diesel oil, mineral oil or a synthetic compound), with optional additives such as weighting agents (most commonly barium sulphate), bentonite clay helps to remove cuttings and to form a filter cake on the well bore walls \(^{37}\), and lignosulphates and lignites (to
keep the mud in a fluid state). Also drilling fluid may compose of air. Example; one may decide to use air for drilling a hard rock on mountain side.

**Muds have the following Compositions:**

I. Water phase or oil continuous phase of the mud, depending on location and/or available water, this may be fresh water, sea water, hard water for water base, mineral oil, diesel oil and vegetable oil for oil based.

II. Reactive solids phase (colloidal phase): This is composed of commercial clay (bentonite and attapulgite) and incorporated hydrated clays and shales from drilled formations, and held in suspension in the fluid phase. These solids are subject to chemical treatment to control the properties of the mud. The clays serve a dual purpose. First, to give viscosity to the drilling fluid and second, to seal the walls of the hole so that the fluid being circulated will not be lost to permeable formations being drilled.

III. Inert solids phase: here in we refer to these solids in suspension which are chemically inactive. These may be inert drilled solids such as limestone, dolomites, or sand. Barium sulfate (barite) is added to the drilling fluid to increase the fluids density, and is also an inert solid.

IV. Various chemical additives necessary to control properties within desired limits.

The additives include various thickeners used to influence the viscosity of the fluid, example, xanthan gum, guar gum, glycol, carboxymethylcellulose, polyanionic cellulose (PAC), or starch. In turn, deflocculants are used to reduce viscosity of clay-based muds; anionic polyelectrolyte (example acrylates, polyphosphates, lignosulphonates or tannic acid derivatives such as quebracho) are frequently used.
2.4.2 Drilling Mud Additives

Over the years individual drilling companies and their expert drillers have devised proprietary and secret formulations to deal with specific types of drilling operations. These mud “recipes” are based on long experience knowledge and special skills. One of the problems in studying the effects of drilling waste discharges is that the drilling fluids are made from a range of over one thousand ingredients (additives), many of them known, others confusingly by different trade names, generic descriptions, chemical formulae and regional or industry slang words. Most people had little idea of the composition of additives. It was even hard for a mud engineer from one company to really know what another company was calling the same product.38

Usually, the controls of drilling fluids always present two problems namely:

I. The determination of what is needed in the way of properties (density, viscosity, gel strength and filtration) for the drilling mud to satisfactorily handle a drilling operation.

II. The selection of the type of the mud and the materials and chemicals (additives) that will produce the desired mud properties.12

The properties of drilling muds can be adjusted to meet any reasonable set of conditions, thereby overcoming most drilling problems such as abnormal pressures, lost circulation and sloughing shale. The selection of the proper mud additives for certain conditions is sometimes confusing, however because of the large number of mud dealers and the wide variety of trade names. To simplify this problem, it is convenient to think of mud additives according to their application or specific performance requirements.

Therefore a wide range of chemical additives are used in the formulation of drilling mud and these additives include: Weighting agents, viscosifiers, thinners, filter-loss control agents, pH
adjusters, surfactants/emulsifiers, loss circulation materials, defoamers, lubricants and corrosion inhibitors. The product classifications for each additive are those generally accepted by the sub-committee on drilling fluids ‘International Association of Drilling Contractors’ (IADC). Some additives have multiple uses, and for those a primary and two secondary function categories are listed.

1. Weighting Agents
These are materials added to increase the overall density of the drilling fluid so that sufficient bottom hole pressure can be maintained thereby preventing an unwanted (and often dangerous) influx of formation fluids. Examples are barium sulphate (barite), calcium carbonate, galena, lead sulphide, hematite, kaolin ($\text{Al}_2\text{O}_3.2\text{SiO}_2.2\text{H}_2\text{O}$)

2. Viscosifiers/Filtrate Reducers
Filtrate (or fluid loss reducers), such as bentonite, xanthan gum, guar gum, glycol, carboxymethyl cellulose (CMC), polyanionic cellulose (PAC), Pregelatinized starch and some various other polymers, serve to cut filter loss, a measure of the tendency of the liquid phase of the drilling fluid to pass into the formation. Akaranta and Osuji (1997) studied decarboxylation of orange mesocarp cellulose and its use in drilling fluid formulation. It was observe that drilling fluid formulated with orange mesocarp based sodium carboxymethyl cellulose had physical properties comparable to those of drilling fluids formulated with commercial sodium carboxymethyl cellulose.

3. Thinners/Deflocculants
Thinners are primarily used to reduce viscosity of clay-based muds, gel strength control and secondarily used as emulsifiers. They include: acrylates, polyphosphate, lignosulfates, sodium pyro phosphate acid, tannins, lignin, tannic acid derivates such as quebracho.

4. Surfactants

These materials are used for creating a heterogeneous mixture of two liquids. Examples are modified lignosulphonates, certain surface active agents (soap and detergents), anionic and non-ionic (negatively charged and non-charged) products.

5. Lost Circulation Materials

The primary function of lost circulation additives is to plug the zone of loss back in the formation away from the face of the bore hole so that subsequent operations will not result in a loss of drilling fluids. These materials include: hay, saw dust, bark, cotton seed hulls, laminated (flat) materials such as mica, cellophane, granular bridging materials such as nut shell, berlite, and ground plastic.

6. Flocculants

These are sometimes used to raise the gel strength of muds used during drilling. Salt (or brine), hydrated lime, gypsum and sodium tetra phosphates may be used to cause colloidal particles in suspension to group into bunches, or ‘flocs’, causing solids to settle out.

7. Lubricants

Drilling mud lubricants are major constituents of drilling muds used for drilling troublesome directional oil wells. Drilling mud lubricants are substances designed to reduce torque and increase horse power at the bit by reducing the coefficient of friction and ensuring easier movement between contact surfaces. Drilling mud lubricants may be solids such as plastic beads,
glass beads, nut hulls and graphite. It could also be liquid such as oils, synthetic fluids, glycols, modified vegetable oils, fatty acids, soaps and detergents. Other materials used as mud additives to improve lubricity are bentonite, asphalt, diesel, crude oil and fine mica. Solid drilling mud lubricants reduce friction by acting like a ball bearing or like sliders. This is due to the fact that these materials interfere with the contact surface of the well bore and the drill strings without bonding to them. Consequent upon the non-bonding of these materials on contact surfaces, their performance is usually independent of the mud type.

Fanta et al (2002) studied the effect of a semisolid high molecular weight lubricant in starch water–based mud system, and discovered that these materials impacted lubricity on the drilling fluid and also inhibited fluid loss in the geological formations by enhancing the filtrate control properties of the fluid. Liquid drilling mud lubricants on the other hand reduce friction by forming thick films that mask surface roughness and are strong enough to withstand high compressional forces. Their lubricity performance depends on their concentration and is usually determined by their reduction of coefficient of friction (COF) on contact surface. Lubricity coefficients of friction which are routinely run on formulated drilling fluids reflect how effective such drilling fluids reduce friction between contact surfaces of well bore and drill string.

8. Defoamers

These are products designed to reduce foaming action particularly in brackish and saturated salt water muds. Altristreate is the defoamer used to defoam saturated salt water muds.

9. Corrosion inhibitors

Hydrated lime, aluminum bisulphate, zinc chromate and amine salts are often added to muds to check corrosion. A good fluid containing an adequate percentage of colloids, certain emulsion muds and oil muds should exhibit excellent corrosion inhibiting properties.
10. Preservatives

Various bactericides and biocides, example, formaldehydes are added to preserve the mud.12

11. pH adjusters

These are products designed to control the degree of acidity or alkalinity of a drilling mud to meet standard results for drilling operations. These can include: lime, caustic soda, caustic potash, hydrated lime, soda ash and bicarbonate of ash. High hydroxyl ion content limits the solubility of calcium, which is a mud contaminant. Therefore, pH is important in mud treatment and one of the effects is to increase the effectiveness of chemical, thinners (organic agents such as tannins, lignins and lignosulphonates).

2.5.0 Functions of Drilling Mud

During the early days of rotary drilling, the primary use of this fluid was to transport cuttings to the surface, but these days the functions have been greatly expanded and made quite complex, and the success of the drilling program depends on the proper understanding and application of them. Drilling fluids which are special chemical substances play important roles in the drilling of oil wells and also fulfill a wide variety of other functions which include:

2.5.1 Cooling and Lubrication of the Bit

During drilling of wells, considerable heat and friction is built up due to bit contacts with the formation. The heat built up by the continual friction is transmitted to the drilling fluid and circulated to the surface where it is dissipated. The drilling fluid also lubricates the bit by reducing the friction factor of the formation on the bit and drill string. Since most drilling fluids contain additives (example bentonite, polymers) which help reduce the down hole friction, further lubricants need not be used unless warranted by difficult and unusual conditions such as
severe doglegs or high torque. More so, certain components of drilling fluids called lubricants form a film between contact surfaces that are strong enough to withstand compressional forces, thereby reducing friction between these contact surfaces \(^{41}\).

2.5.2. Cleaning the Bottom of the Hole

This function of the drilling fluid is essential to achieve the optimum penetration rate with a given bit, weight, rotary speed, and hydraulics program. A properly designed hydraulic program should provide an adequate flow rate to create a sufficient cross-flow across the bottom of the bit to instantaneously lift the cuttings being drilled up, otherwise, penetration will be retarded due to re-grinding of the cuttings by the bit\(^{12}\).

2.5.3 Removal of Drill Cuttings

One of the most important functions of drilling mud is to transport the drilled cuttings to the surface during a drilling session. The circulating mud comes from the bottom of the drill string and carries the cuttings to the surface. Due to the gravitational force on the cuttings, they will tend to sink through the upward moving mud. But by circulating a reasonably sufficient volume, and quickly enough, one can overcome these difficulties and the cuttings will be transported to the surface.

2.5.4 Keeping Cuttings in Suspension

When the mud circulation is temporarily stopped (example, during round trip operation to change the bit), the cuttings which have not readily been transported to the surface must be kept floating in the mud. If this is not done, the cutting will fall to the bottom of the well and create serious problems when drilling is to be resumed. A colloidal drilling mud with good gel
properties greatly reduces the slip velocity of a particle and prevents them from falling to the bottom.

Magcobar (1997) reported bentonite as a suitable drilling fluid that has the ability to suspend drill cuttings and enhance fluid properties with moderate filtrate loss. The report showed that in addition to suspension of drill cuttings, bentonite also has the ability to provide the necessary gel strength required to move solids out of the drill hole. A measure which can give a certain control of this property of the mud is the 10-minute gel strength test. Too high 10-minute gel strength is not wishful since it will require high pump pressure to keep the fluid in circulation once again. This high pump pressure may create a lot of problems, example lost circulation.

2.5.8. Ensuring Adequate Information from the Hole and Prevent Damage to the Pay Zone

The main purpose of drilling is to strike oil or gas in commercial quantity. The drilling mud should therefore enable the drillers to obtain all the information which are necessary to determine the productive potentialities of a formation. The mud characteristics must be such that good cuttings, core samples and electrical logging can be obtained. The mud should give maximum protection too and not damage productive formation.

2.5.5. Formation of Filter Cake

A good mud will deposit a good filter cake on the wall of the hole to prevent the formation from caving into the well-bore and to prevent the invasion of the well formation by the mud filtrate and minimize the thickness of the filter cake that builds upon the bore hole wall, thereby reducing formation damage and the chances of differential sticking. This is termed well bore stabilization. The cause of formation instability can be numerous and different in each drilling area. This property of the fluid is regulated by increasing the colloidal fraction of the mud. The
colloidal fraction of the mud is increased by the addition of bentonite and other chemical treatments to the drilling fluid to prevent pulverization and spreading of the particles \(^{45,12}\).

### 2.5.6. Transmission of Hydraulic Horse-power to the Bit

A good drilling mud should serve as a medium through which optimum hydraulic horse power can be transmitted to the bit. A viscoelastic drilling fluid, that is a drilling fluid whose viscosity at the bit approaches the viscosity of water, will minimize the friction losses and maximize the available hydraulic horse power at the bit.

### 2.6. Types of Drilling Mud

Many types of drilling fluids are used on a day-to-day basis. Some wells require that different types be used at different parts in the hole, or that some types be used in combination with others. In the drilling processes numerous types of muds are utilized but all have been grouped by engineers to be Water Base, Oil Base and Air/Gas muds \(^{12,23,46,47}\).

#### 2.6.1 Water Based Mud

The Water Based Mud (WBM) family is the type in which fresh, salt or sea water is the continuous phase. Basically, water base mud system begins with water, then clays and other chemicals are incorporated into the aqueous solution to create a homogenous blend resembling something between chocolate milk and a malt (depending on viscosity). The clay (called ‘‘shale’’ in its rock form) is usually a combination of native clays that are suspended in the fluid while drilling, or specific types of clay that are processed and sold as additives for the WBM system. The most common of these is BENTONITE, frequently referred to in the oilfield as ‘‘gel’’. Gel likely makes reference to the fact that while the fluid is being pumped, it can be very thin and free-flowing (like chocolate milk), though when pumping is stopped, the static fluid builds a
“gel” structure that resists flow. When an adequate pumping force is applied to “break the gel”, flow resumes and the fluid returns to its previously free-flowing state. Many other chemicals (additives) as have mentioned before are added to a WBM system to achieve various effect, including: viscosity control, shale stability, enhance drilling rate of penetration, cooling and lubricating of equipment\textsuperscript{12}.

**Water Based Mud Comprises of the Following Categories of Muds:**

1. **Spud Mud**

Spud muds are used to drill the hole for conductor pipe. This usually consists of viscous slurry of bentonite or attapulgite to provide enough carrying capacity to large diameter surface hole. They are discarded after drilling of the conductor pipe\textsuperscript{12}.

2. **Bentonite Treated Mud**

These are simply drilling fluids that can be utilized for drilling shallow wells in trouble-free areas. Bentonite will provide improved carrying capacity and prevent minor sloughing problems that may be encountered with clear water drilling. But when contaminating formations such as salts (NaCl), gypsum (CaSO\textsubscript{4}.2H\textsubscript{2}O) and anhydrites (CaSO\textsubscript{4}) are encountered, bentonite treated muds are unsatisfactory. These contaminants are sources of calcium ions which cause flocculation of the clay particles. This flocculation of the clay particles causes increased water loss, viscosity and gel strengths, and chemical additives must be added to restore the desired properties. Where the source of calcium contamination is small and of predictable magnitude,
such as cement plug, it may be treated out of the system directly by using sodium bicarbonate, or Barium carbonate. These remove the soluble calcium as precipitated CaCO$_3$\textsuperscript{12}.

### 3. Calcium Treated Mud

If considerable calcium ion contamination is anticipated, it is a common and an economical practice to pre-treated the system with calcium ions, Ca$^{++}$. Calcium muds are applicable in drilling thick and anhydrite section and also were sloughing shales and salt are common. These muds differ from other water base muds, in that sodium clay (bentonite) are converted to calcium base clay through the additions of lime or gypsum. Such muds have been called low lime, lime base, lime treater, gypsum and calcium treated muds, depending on the calcium ion salts and the manner and degree of treatment. Therefore the difference between calcium ion contaminated and calcium ion treated mud is that in the latter, the calcium is not treated out, but is allowed to remain in the mud for special benefits. Those muds, in general, have the ability to tolerate other flocculating salts up to 50000ppm NaCl. They contain high solid percentages at low viscosity, and have low and relatively easily maintained filter-loss and gel strengths. These properties have made their use exceedingly widespread, particularly in deep drilling areas\textsuperscript{12}.

#### 2.6.2 Oil Based Mud

Oil based muds (OBM) are commercially available from several sources. Oil based muds are the oil muds containing less than 5% water. Oil based drilling muds have been developed for situations where water-based muds (WBM) were found inadequate. Oil-based mud can be a mud where the base fluid is petroleum or a petroleum product such as diesel oil and mineral oil, vegetable oil can also be used. Generally, they are invert emulsion of brine into an oil major continuous phase stabilized by surfactants. Also, other additives are often added to the organic
phase to impart the necessary physical properties and to make a controllable drilling fluid \textsuperscript{12, 23}. Applications of oil based mud vary. Some of the common uses of oil muds are:

1. Drilling deep, hot holes.
2. Protecting producing formations.
3. Drilling water soluble formations.
4. Preventing differential pressure sticking.

These uses result from unique performance characteristics that can be obtained with muds having oil as the continuous phase. The desired characteristics are not provided by oil muds that are formulated without sufficient knowledge of oil-mud technology and from inadequate products \textsuperscript{12, 23}. Oil mud is ideally suited as a drilling fluid where high mud densities are required and high temperature are expected. In holes where high-density water-based muds undergo degradation from high temperatures, oil muds have been successfully used and have presented no problems even at temperatures in excess of 400 °F.

However, although OBM often gives better performances, they have major drawbacks such as being generally expensive and less ecologically/environmentally friendly than water based mud. The initial cost of oil mud is relatively high, but this can be materially controlled by proper handling, storage and provision of facilities for moving the mud from well to well \textsuperscript{12}. Consequently, although OBM gives greater shale stability than WBM; this latter system has also been developed by many researchers in order to respond to environmental regulations \textsuperscript{48}.

Oil based mud can be grouped as:

1. Invert-emulsion muds
2. Synthetic based mud
The water-in-oil emulsion (W/O), substituted into the hole, is oil-base mud with 90% of oil which is very expensive considering the pipe state. But oil-in-water (O/W) emulsion is a water-base mud.

1. Invert-Emulsion Muds

The water-in-oil emulsions contain water as the dispersed phase and oil (usually diesel oil) as the continuous phase. Up to 40% water can be dispersed and emulsified in the oil. Invert-emulsion muds utilize emulsified water to lessen the concentration of soaps and/or asphalitic materials required for cuttings-carrying capacity and suspension of weighting material. The dispersed water phase does not increase the viscosity of the continuous liquid phase, but it does increase the plastic viscosity of the mud. Having little effect on the viscosity of the oil, the emulsified water would not be expected to lower filtration rates in the same way as the viscosifiers. Invert emulsion have the characteristic of oil base muds, since oil is the continuous phase and the filtrate is only oil. These are highly stable temperature stable-fluids that are inert to chemical contamination and can be weighted to any mud weight after adjusting the oil/water ratio. The use of oil mud and invert emulsion mud requires safe guards for environmental protection.

2. Synthetic-Based Muds

Synthetic based mud (SBM) (otherwise known as Low Toxicity Oil Based Mud or LTOBM): synthetic-based fluid is a mud where the base fluid is synthetic oil. This is most often used on offshore rigs because it has the properties of an oil-based mud, but the toxicity of the fluid fumes are much less than oil based fluid. This is important when men work with the fluid in an enclosed space such as an offshore drilling rig.
The third family of drilling fluids comprises gas, aerated muds (classical muds with Nitrogen) or aqueous foams. These drilling fluids are used when their pressure is lower than that exerted by the petroleum located in the pores of the rock formation. These fluids are called ‘‘under balanced fluids’’. This under balanced drilling technology is generally adopted for poorly consolidated and/or fractured formations\(^\text{12}\).

Controlled drilling rate tests in various rocks have confirmed that air or gas is a faster drilling fluid than water or oil. Although, it does not build up a filter cake and stabilize the walls of the well bore, neither can it control formation fluids. In addition, natural gas flowing into the well can form a flammable mixture with the injected air. Air mud is typically used in low permeability and porosity reservoir intervals where oil or water is not expected to be encountered during drilling. If (or when) natural gas is encountered during drilling, the gas may be safely combusted at the drill site using a flaring device over a waste containment pit\(^\text{5,12}\).

**Air/Gas Mud are Categorized into:**

1. **Air**

   Compressed air is pumped either down the bore holes annular space or down the drill string itself.

2. **Air/Water**

   This is same as using ordinary air, as mentioned, with water added to increase viscosity, flush the hole, provide more cooling, and/or to control dust.

3. **Air/Polymer**
A specially formulated chemical, most often referred to as a type of polymer, is added to the water and air mixture to create specific conditions. A foaming agent is a good example of a polymer.

2.7.0. Drilling Mud Properties

In order to gain better control over the mud system, a more meaningful monitoring strategy of the mud properties is important. The mud program is not the same for every well. In fact, in the course of drilling a well, the composition of the mud can be changed in order to deal with variations in formation properties and mechanical factors that affect the drilling rate\textsuperscript{11}.

The basic mud properties usually defined by the well program and also monitored during drilling include:

- Rheology
- Density
- Fluid Loss
- Solids Contents
- Chemical Properties

2.7.1. Rheology

This is the study of the deformation or flow behavior exhibited by fluid material. It is primarily concerned with the use of shear stress and shear rate relationship of drilling fluids. Rheological properties are used to design and evaluate the rig circulating systems (annular hydraulics) and to assess the functionality of the mud system\textsuperscript{10,49}. The rheology of the mud indicates the behavior of the mud and is characterized by: viscosity, plastic viscosity, yield value and gel strength\textsuperscript{39}.
2.7.1.1. Viscosity

This is the internal resistance offered by a fluid to flow. This phenomenon is attributable to attraction between molecules of a liquid and is a measure of the combined effects of adhesion and cohesion to the effects of suspended particles, and to the liquid environment. The greater this resistance, the greater the viscosity. Highly viscose or thick muds are more likely to hold formation chip on bottom than low viscosity mud reducing the penetration rate.

Only Newtonian fluids, such as water, which exhibit linear follow characteristics, have a true viscosity that can be defined by a single term. All non-Newtonian fluids, including drilling muds, exhibit non linear flow characteristics and require more than a single viscosity term to define their visions behavior. Viscosity of a drilling fluid is a function of the following:

1. Size, shape and number of solid particles per unit volume.
2. Viscosity and the base liquid.
3. Inter particle forces and.
4. Degree of emulsification of oil in water or water in oil and stability of emulsion.

The drilling fluid viscosity can be expressed as either relative or absolute measurements. The relative measurements are the funnel viscosity and the apparent viscosity. The absolute measurements are the quantitative values of the non-Newtonian characteristics namely: the Plastic viscosity (PV), the Yield value (YV) and Gel strength. The funnel viscosity is simply the time it takes for one quart of mud to flow out of the Marsh funnel into the viscosity cup. The apparent viscosity of a fluid is the viscosity the fluid appears to have on a given instrument at a stated rate of shear.

2.7.1.2. Plastic Viscosity
The plastic viscosity (PV) is a measure of the internal resistance to fluid flow attributable to the amount, type and size of solids present in a given fluid. Accumulation of drilled solids, additions of barite, and presence of chemical contaminants will increase the plastic viscosity while dilution with water, effective use of solids control equipment and flow line flocculation to remove fine-size solids will lower the PV

2.7.1.3 Yield Value

The yield value (YV) is the resistance to initial flow, or it represents the stress required to start fluid movement. This resistance is due to electrical charges located on or near the surface of the particles. Effective control of the YV at an optimum level will directly depend on the effective control of the drilled solids.

2.7.1.4 Gel Strength

This is the ability or the measure of the ability of a colloid to form gels. Gel strength is a pressure unit usually reported in 1b/100sq ft. it is a measure of the same inters particle forces of a fluid as determined by the yield value except that gel strength is measured under static condition. As with other properties the ability to maintain the gel strength within a specified range depends on effective solids control. The gel strength is needed in order to suspend the drilled cuttings and weighting materials during connections or trips when circulation of mud is stopped.

2.7.2. Density

Fluid density is the first parameter to consider. Its definition according to America Petroleum Institute (API) is matter measured per unit volume expressed in pounds per gallon (ppg), pounds per square inch per 1000feet, and pounds per cubic feet. For desired densities greater or lower than 1, WBM or OBM can be used, respectively. The latter are recommended especially for clay
formations where this density should be sufficient for drilling. The density of formulated drilling fluid is controlled to balance formation pressure in order to prevent well blow out. The mud density must be accurately measured to provide sufficient hydrostatic pressure required to prevent oil well bore hole from caving in, and also to keep formation fluid from entering the well bore.

Ideally, a mud weight as low as the weight of water is desired for achieving optimum penetration rate. In practice however, because of the primary function of suppressing subsurface pressure, mud weight as high as two and one-half times the weight of water may be needed. The implication of this is that certain materials need to be added to water or oil phase to achieve this weight. These materials are called weighting materials. In the same vein, removal of solids, dilution with water, and/or addition of oil may be used to reduce mud weight. Other undesirable solids issued from geological drilled formations are not easily removed but will be reduced to finer particles, which could have some adverse effects on mud properties. The way to avoid such undesirable phenomena is to use high-speed shale shakers. In additional stages, to remove finer solids down to the 1 µm range, these devices are equipped with 50- to 100-mesh screens, using desanders, desilters, mud cleaners, and centrifuges. Undesirable solids that are less than 1 µm can only be removed chemically using medium- to high-molecular-weight flocculants. In addition, some recommendations specify the effects of size on rheology and fluid performances. Solids less than 1 µm have 12 times more effect on drilling rate than larger particles. For these solids less than 1 µm, the shearing stress required to start the fluid motion will be greater than for larger particles. The control of drilling fluid weight is critical, because an unnecessarily heavy drilling mud can cause breakdown of formations leading to loss of circulation or even a complete
loss of a well, and reduction in drilling rate. On the other hand, if the mud weight becomes too small to suppress subsurface pressures, well kick and/or blow-out may occur\textsuperscript{12, 23}.

### 2.7.3 Fluid-loss

The loss of drilling fluid is generally defined as the volume of the drilling mud that passes into the formation through the filter cake formed during drilling. It is often minimized or prevented by blending the mud with additives. A number of factors affect the fluid-loss properties of a drilling fluid, including time, temperature, cake compressibility; but also the nature, amount and size of solids present in the drilling fluid\textsuperscript{51}. In high-pressure and high-temperature environments, optimization of the above mentioned three parameters is essential to lighten instability problems when drilling through shale sections. Under these conditions, selection of suitable mud parameters can benefit from analyses that consider significant thermal and chemo–mechanical processes involved in shale–drilling fluid interactions. Nevertheless, some other factors are not taken into consideration in these mathematical models. For instance, it has been widely experienced that random factors related to soil layers, drill bits, and surface equipment, greatly affect drilling performance\textsuperscript{22}.

Optimization involves the post-appraisal of offset well records to determine the cost effectiveness of elected variables, which include mud and bit types, weight on bit, and rotary speed. Stochastic models are introduced to describe such random effects. This more practical model provided a better characterization for real oilfield situations as compared with other deterministic models, and has been demonstrated to be more efficient in solving real design problems\textsuperscript{22}.

### 2.7.4 Solid Contents
Materials such as barite and other weighting agents like clays, polymers and bridging substances that are deliberately added in the mud in order to enhance density and viscosity of mud systems, in addition to drill solids from cuttings and ground rock constitute the solids content of a drilling mud. The amount and type of solids in the mud affect a number of mud properties.

Low solids muds are usually used in drilling situations in which mud weight are no greater than 10ppg and circulation rate are high enough to lift cuttings out of the hole. Small particles of weighting materials in the mud can have detrimental effect on rate of penetration. Solid content can be kept low by a number of different means: circulating through the reserve pit allows fine solids to settle out of the mud. Also devices like desilters and centrifuges maintain low solids content mechanically. Centrifuges are normally used on weighted mud, although they may be used with mud cleaners to maintain mud weights. Chemicals that cause the fine particles to aggregate and settle out as larger particles are also used.

On the hand, high solids content will increase plastic viscosity and gel strength of the mud, because high solids mud systems have thicker filter cakes and posses slower drilling rates. Large particles of sand in the mud can cause abrasion on the pump parts, tubular and measurement equipment and down hole motors. Measurement and control of solids content of a mud are necessary and are traditionally carried out using a retort, which distills off the liquid allowing it to be measured, leaving the residual solids.

2.7.5. Chemical properties

The chemical properties of drilling fluids are central to their performance and the stability of well bore. Thus, well properties that must be anticipated include the dispersion of formation clays and dissolution of salt formations. This is because certain mud additives like polymers are affected by pH, Ca$^{2+}$ and corrosion, which might be caused by dissolution of salty clay
formations. Therefore, rig side measurements should rely on simple chemical analysis to determine pH, Ca\(^{2+}\), total hardness, concentration of Cl\(^{-}\) and sometimes K\(^{+}\).

Hale and Mody (1993) investigated the dispersion of clay in a water based system, and observed that specific cations such as K\(^{+}\) and Ca\(^{2+}\) inhibited water sensitive formation from dispersing as a result of the exchange of cations with the clay in the shale, thereby creating a more stable rock that is able to resist hydration.

Sherwood and Bailey (1994) while studying the movement of water based mud filtrate from the well bore into the surrounding shale discovered that such movement is controlled by the difference between chemical potentials of the various species with the formation. They also reported that chemical potentials depend on the mud hydrostatic pressure in the well bore and on its chemical composition.

2.8. Mud Contamination

One of the contributing factors to unstable mud properties is contamination. Mud contaminants are materials that enter the drilling fluid and adversely alter its physical and or chemical properties and can also be detrimental to the environment. If not minimized or treated out they could result in hole problems. What constitutes a contaminant in one mud system could not necessarily be a contaminant to another. The common mud contaminants are: Anhydrite and gypsum, salt, acid gases, hydrocarbons and heavy metals.

2.8.1 Anhydrite and Gypsum Contaminant

Anhydrite (CaSO\(_4\)) and Gypsum (CaSO\(_4\).2H\(_2\)O) have nearly the same chemical composition; but gypsum has an attached water of crystallization which made it more soluble than anhydrite. The calcium which is gotten from gypsum or anhydrite is a contaminant in some water base mud.
Calcium contamination from the anhydrite formation severally limits the hydration of bentonite and will flocculate hydrated bentonite, causing sharp increases in the fluid loss and the viscous properties of the drilling fluid\textsuperscript{12}. Their initial effect on a polymer type mud system is high viscosity, high gel strength, increase fluid loss and decrease pH. The extent of these effects is dependent on the concentration of chemical deflocculant in the drilling fluid and the amount of anhydrite or gypsum drilled. The first sign of anhydrite or gypsum contamination which is increased viscosity and progressive gel strength is also common to other types of contamination. It will be better to perform quantitative and qualitative test for a correct identification\textsuperscript{12}.

\textbf{2.8.2. Salt Contamination}

In the course of drilling, some rock types can be encountered, this produce a severe effect on the bentonite type of mud system. The effects are increase in the chloride content of the mud, increase in mud pit level due to formation water influx, high water loss with thick spongy cake and reduction in bentonite concentration. The effect is not pronounced in some polymer most especially the KCl polymer. Three naturally occurring types of rock salts are: NaCl (common salt), potassium chloride and carllites (KMgCl$_3$.6H$_2$O).

Salt water flow can be far more destructive on flow properties than drilling into rock salt since the salt are already solubilized and react with the clay more rapidly. At these times also the mud density must be increased to kill the flow before it can be taken to consider mud properties. The mechanism of contamination in the case of salt is based on action by the predominant cation and sometimes pH. Salt contamination is also associated with decrease in pH\textsuperscript{12}.

\textbf{2.8.3 Hydrogen Sulphide Contamination}

Hydrogen sulphide (H$_2$S) can result in severe pitting of the various elements in the drill string, bit bearings and mud pump expendables. Large influxes from the formation can result in sudden
drill string failure as well as present a hazard to rig personnel. Hydrogen sulphide can be identified by the reduction of mud pH, discoloration of mud to dark color due to the formation of fes from barite, rotten egg odor, and viscosity and fluid loss increase due to pH reduction. H$_2$S is an acid gas and reduce the pH of the mud very fast by neutralizing the OH radical. In order to offset the harmful aspect of the H$_2$S, the pH must be increased to at least 11 or a safer level of 12 by adding caustic soda soda or lime$^{12}$.

**2.8.4 Hydrocarbon and temperature contamination**

Oil and condensate can cause the viscosity to rise undesirably in water base muds. Insufficient quantities of oil and condensate can thin an oil base mud and cause the weighting materials to fall out of the mud. Many water base muds suffer from thermal degradation. In general, the operating temperature range of specific muds should not be exceeded unless temperature extending chemicals are added to these systems $^{23}$. Effects of high temperature will be to reduce the effectiveness of chemical additives, increase the fluid loss, and to create gelatin of muds laden with drilled solids. In general, the lower the drilled solids content, the easier it is to maintain the desired properties at higher temperatures $^{12}$. One of the benefits of the oil muds is their ability to drill in areas of high down hole temperature with little degradation.

**2.8.5 Heavy Metals Contamination and Possible Sources**

Metal fatigue is a common cause of drill-stem failures. Corrosion can take many forms and may combine with other destructive processes like erosion, abrasive wear and notch failures to cause severe damage. It is well known that metal is weaker under working loading than under static condition $^{23, 27}$. Metals can be incorporated into the mud as a result of sever pitting of various elements in the drill string, bit bearings and other metallic components of the drill rig $^{23, 27, 30}$. These metallic components of the drill rig are made of Stainless steel, Steel and Nichrome.
Stainless steel is composed of iron with up to 35% chromium, nickel may also be present. Stainless steel is used to manufacture steel with great resistance to corrosion example: industrial pipes, knives, sinks and jet engines. Steel is composed of iron with small amount of carbon and manganese. Steel can be used in the construction of materials where strength but greater ductility and malleability than iron are needed. Nichrome is composed of Nickel 60%, Iron 20% and Chromium 20%. It can be used to manufacture wires for electrical equipments and other purposes.

Also, the site of the petroleum deposit can contribute to heavy metals contamination of the mud. If the deposits occur in a mineralized area possibly while drilling, those mineral ores can be incorporated into the drilling mud. Since all crude oil contain reasonable amount of heavy metal like (nickel, vanadium, iron, cobalt, manganese, cadmium), nickel and vanadium however are the most important. They are present in all crudes, usually at concentration far higher than any other metal. Some quantities of crude are drilled out with the mud and in the course of performing this operation; heavy metals can be introduced into the mud. Drilling mud metals could cause environmental harm if they are present in water column or sediments in soluble, bioavailable forms.

2.9.0 Heavy Metals

Heavy metals are the stable metals or metalloids whose density is greater than 5g/cm³ namely: lead, nickel, zinc, chromium, cobalt. Heavy metals are natural components of the earth’s crust. They are stable and cannot be degraded or destroyed and therefore they accumulate in soils and sediments. Due to the toxicity of these metals, when disposed on land or river would create infertility and cause a lot of harm to the living organisms. The extent to which organisms respond to metal toxicity varies and widely depends on species of plants and animals. There
are wider range of effects caused by heavy metals in plants and animals when absorbed above their respective threshold level. In animal’s biochemical system, many metals like Fe, Cu, Mn and Zn have been found to be indispensable for normal metabolism while the presence of other metals such as Cr, Sn, and Pb may only be accidental due to abundance of all metals in earth crust. Also, in plant, Fe, Cu, Mn and Zn, are regarded as micronutrients as they are useful in plant biochemical system. However, over supply of these, lead to bio-accumulative toxicity effects in plants and animals and thus their toxicity potential, as an environmental hazard deserves more attentions. It was observed that the uncontrolled inputs of heavy metals are undesirable, because once accumulated in the soil, the metals are generally very difficult to remove and potentially harmful effects that may arise in the future should not be ignored.

2.9.1. Some Heavy Metals and their Environmental Effects

1. Iron

Iron is a lustrous, ductile, malleable, silver-gray metal in group VIII of the periodic table. It is known to exist in four distinct crystalline forms. Iron rusts in damp air, but not in dry air. It dissolves readily in dilute acids. Iron is chemically active and forms two major series of chemical compounds, the bivalent iron (II), or ferrous, compounds and the trivalent iron (III), or ferric, compounds.

Applications

Iron is the most used of all the metals. It can be used in the manufacturing of food containers, cars and ships. Steel is the best known alloy of iron, and some of the forms that iron takes include: pig iron, cast iron, carbon steel, and wrought iron, alloy steels and iron oxides.

Health Effects of Iron
Iron can be found in meat, whole meal products, potatoes and vegetables. The human body absorbs iron in animal products faster than iron in plant products. Mc Donald et al.(1995) reported that farm animals fed on herbage with high level of iron, may be affected by its toxicity which results in alimentary disturbances, reduced growth and phosphorus deficiency. Iron is an essential part of hemoglobin; the red coloring agent of the blood that transports oxygen through our bodies. Iron may cause conjunctivitis, choroiditis, and retinitis if it contacts and remains in the tissues. Chronic inhalation of excessive concentrations of iron oxide fumes or dusts may result in development of a benign pneumoconiosis, called siderosis, which is observable as an x-ray change. Inhalation of excessive concentrations of iron oxide may enhance the risk of lung cancer development in workers exposed to pulmonary carcinogens. A more common problem for humans is iron deficiency, which leads to anaemia.

**Environmental Effects of Iron**

Iron (III)-O-arsenite, pentahydrate may be hazardous to the environment. It is strongly advised not to let the chemical enter into the environment because it persists in the environment.

**2. Chromium**

Chromium, discovered by Vaughlin in 1797 is a lustrous, brittle, hard metal. Its colour is silver-gray and it can be highly polished. It does not tarnish in air, when heated it burns and forms the green chromic oxide. Chromium is unstable in oxygen, it immediately produces a thin oxide layer that is impermeable to oxygen and protects the metal below.

**Applications**

Chromium main uses are in alloys such as stainless steel, in chrome plating and in metal ceramics. Chromium plating was once widely used to give steel a polished silvery mirror coating. Chromium is used in metallurgy to impart corrosion resistance and a shiny finish; as
dyes and paints, its salts colour glass an emerald green and it is used to produce synthetic rubber; as a catalyst in dyeing and in the tanning of leather; to make molds for the firing of bricks. Chromium (IV) oxide (CrO$_2$) is used to manufacture magnetic tape$^{62}$.

**Health Effects of Chromium**

People can be exposed to chromium through breathing, eating or drinking and through skin contact with chromium or chromium compounds. The level of chromium in air and water is generally low$^{14}$. In drinking water the level of chromium is usually low as well, but contaminated well water may contain the dangerous chromium(IV); hexavalent chromium$^{62}$. Various ways of food preparation and storage may alter the chromium contents of food. When food is stored in steel tanks or cans chromium concentrations may rise$^{62}$. Chromium (III) is an essential nutrient for humans and shortages may cause heart conditions, disruptions of metabolisms and diabetes. But the uptake of too much chromium (III) can cause health effects like skin rashes$^{16}$. Chromium (VI) is dangerous to human health. When it is a compound in leather products, it can cause allergic reactions, such as skin rash. Inhalation of hexavalent chromium compounds, chromium (VI), can cause nose irritations and nosebleeds$^{66}$. Other health problems that are caused by chromium (VI) are: Upset stomachs and ulcers, respiratory problems, weakened immune systems, kidney and liver damage, alteration of genetic material, lung cancer and death$^{62}$. International Agency for Research on Cancer (IARC) has listed chromium metal and its trivalent compounds within Group III$^{62}$. $^{67}$.

**Environmental Effects of Chromium**

There are several different kinds of chromium that differ in their effects upon organisms.
Chromium enters the air, water and soil in the chromium (III) and chromium (VI) form through natural processes and human activities\textsuperscript{62}. The main human activities that increase the concentrations of chromium (III) are steal, leather and textile manufacturing. The main human activities that increase chromium (VI) concentrations are chemical, leather and textile manufacturing, electro painting and other chromium (VI) applications in the industry\textsuperscript{68}. These applications will mainly increase concentrations of chromium in water. Through coal combustion chromium will also end up in air and through waste disposal chromium will end up in soils. Chromium is not known to accumulate in the bodies of fish, but high concentrations of chromium, due to the disposal of metal products in surface waters, can damage the gills of fish that swim near the point of disposal\textsuperscript{69}.

3. Cadmium

Cadmium, discovered by Fredrich Stromeyer in 1817 is a lustrous, silver-white, ductile, very malleable metal. Its surface has a bluish tinge and the metal is soft enough to be cut with a knife, but it tarnishes in air. It is soluble in acids but not in alkalis\textsuperscript{16,62}.

Applications

Cadmium is used in Ni-Cd batteries, pigments, coatings and plating, and as stabilizers for plastics. Cadmium has been used particularly to electroplate steel. Cadmium has the ability to absorb neutrons, so it is used as a barrier to control nuclear fission\textsuperscript{62}.

Health Effects of Cadmium

Foodstuffs that are rich in cadmium can greatly increase the cadmium concentration in human bodies. Examples are liver, mushrooms, shellfish, mussels, cocoa powder and dried seaweed. Cadmium is first transported to the liver through the blood\textsuperscript{62}. Blood will transport it through the
rest of the body where it can increase effects by potentiating cadmium that is already present from cadmium-rich food. High exposures can occur with people who live near hazardous waste sites or factories that release cadmium into the air and people that work in the metal refinery industry.

Other health effects that can be caused by cadmium are: diarrhea, stomach pains, damage to the central nervous system, reproductive failure and possibly even infertility, damage to the immune system, Psychological disorder and cancer\footnote{\textsuperscript{62}}.

**Environmental effects of Cadmium**

Cadmium waste streams from the industries mainly end up in soils. The causes of these waste streams are zinc production, phosphate ore implication and bio industrial manure. Cadmium waste streams may also enter the air through (household) waste combustion and burning of fossil fuels. Another important source of cadmium emission is the production of artificial phosphate fertilizers\footnote{\textsuperscript{62}}. Part of the cadmium ends up in the soil after the fertilizer is applied on farmland and the rest of the cadmium ends up in surface waters when waste from fertilizer productions is dumped by production companies. When cadmium is present in soils it can be extremely dangerous, as the uptake through food will increase. Soils that are acidified enhance the cadmium uptake by plants. This is a potential danger to the animals that are dependent upon the plants for survival. Cadmium can accumulate in their bodies, especially when they eat multiple plants\footnote{\textsuperscript{62}}.

4. **Nickel**

Nickel, discovered by Alex Constedt 1751 is silvery-white, hard, malleable and ductile metal. It is of the iron group and it takes on a high polish. It is a fairly good conductor of heat and
electricity. Nickel dissolves slowly in dilute acids but like iron, becomes passive when treated with nitric acid. Finely divided nickel adsorbs hydrogen\textsuperscript{62}.

**Applications**

The major use of nickel is in the preparation of alloys. Nickel is used in making stainless steel, alloy steel, rechargeable batteries, catalysts and other chemicals, coinage, foundry products and plating\textsuperscript{62}. Nickel is easy to work and can be drawn into wire. It resists corrosion even at high temperatures and for this reason it is used in gas turbines and rocket engines. Monel is an alloy of nickel and copper (e.g. 70\% nickel, 30\% copper with traces of iron, manganese and silicon), which is not only hard but can resist corrosion by sea water, so that it is ideal for propeller shaft in boats and desalination plants\textsuperscript{62}.

**Health effects of Nickel**

In small quantities nickel is not harmful, but when the uptake is too high it can be a danger to human health\textsuperscript{14}. An uptake of too large quantities of nickel has the following consequences: higher chances of development of lung cancer, nose cancer, larynx cancer and prostate cancer, sickness and dizziness after exposure to nickel gas, lung embolism, respiratory failure, birth defects, asthma and chronic bronchitis, allergic reactions such as skin rashes, mainly from jewelry and heart disorders\textsuperscript{14}.

**Effects of Nickel on the Environment**

Nickel is released into the air by power plants and trash incinerators. It will then settle to the ground or fall down after reactions with raindrops. It usually takes a long time for nickel to be removed from air. Nickel can also end up in surface water when it is a part of wastewater streams. The larger part of all nickel compounds that are released to the environment will adsorb to sediment or soil particles and become immobile as a result\textsuperscript{62}. High nickel
concentrations on soils can clearly damage plants and high nickel concentrations in surface waters can diminish the growth rates of algae\(^6\).

5. Manganese

Manganese, discovered by Johann Gahn in 1774 is a pinkish-gray, chemically active element. It is a hard metal and is very brittle. It is hard to melt, but easily oxidized. Manganese is reactive when pure, and as a powder it will burn in oxygen, it reacts with water and dissolves in dilute acids\(^6\).

Applications

Manganese is essential to iron and steel production. Manganese is a key component of low-cost stainless steel formulations and certain widely used aluminum alloys. Manganese dioxide is also used as a catalyst. Manganese is used to decolorize glass and make violet coloured glass. Potassium permanganate is a potent oxidizer and used as a disinfectant. Other compound that find applications are Manganese oxide (MnO) and manganese carbonate (MnCO\(_3\)): the first goes into fertilizers and ceramics the second is the starting material for making other manganese compounds\(^6\).

Health Effects of Manganese

Manganese is one of the three toxic essential trace elements, which means that it is not only necessary for humans to survive, but it is also toxic when too high concentrations are present in a human body \(^6\). The uptake of manganese by humans mainly takes place through food, such as spinach, tea and herbs. The foodstuffs that contain the highest concentrations are grains and rice, soya beans, eggs, nuts, olive oil, green beans and oysters. After absorption in
the human body manganese will be transported through the blood to the liver, the kidneys, the pancreas and the endocrine glands. Manganese effects occur mainly in the respiratory tract and in the brains\textsuperscript{62}. Because manganese is an essential element for human health, shortages of manganese can also cause health effects\textsuperscript{62}.

**Environmental Effects of Manganese**

Manganese compounds exist naturally in the environment as solids in the soils and small particles in the water. Manganese particles in air are present in dust particles. Humans enhance manganese concentrations in the air by industrial activities and through burning fossil fuels. Manganese that derives from human sources can also enter surface water, groundwater and sewage water. Through the application of manganese pesticides, manganese will enter soils \textsuperscript{62}. In plants manganese ions are transported to the leaves after uptake from soils. Manganese can cause both toxicity and deficiency symptoms in plants \textsuperscript{62}.

**6. Vanadium**

Vanadium is a rare, soft, ductile gray-white element found combined in certain minerals and used mainly to produce certain alloys. Vanadium resists corrosion due to a protective film of oxide on the surface\textsuperscript{62}. Common oxidation states of vanadium include +2, +3, +4 and +5.

**Applications**

Vanadium is used as ferrovanadium or as a steel additive. Mixed with aluminum in titanium alloys is used in jet engines and high speed air-frames, and steel alloys are used in axles,
crankshafts, gears and other critical components. Vanadium alloys are also used in nuclear reactors because vanadium has low neutron-adsorption abilities and it does not deform in creeping under high temperatures\(^6\).

Vanadium oxide (V\(_2\)O\(_5\)) is used as a catalyst in manufacturing sulfuric acid and maleic anhydride and in making ceramics. It is added to glass to produce green or blue tint. Glass coated with vanadium dioxide (VO\(_2\)) can block infrared radiation at some specific temperature\(^6\).

**Health Effects of Vanadium**

The health hazards associated with exposure to vanadium are dependent on its oxidation state. Vanadium compounds are not regarded as serious hazard, however, workers exposed to vanadium peroxide dust were found to suffer severe eye, nose and throat irritation. The uptake of vanadium by humans mainly takes place through foodstuffs, such as buckwheat, soya beans, olive oil, sunflower oil, apples and eggs. Vanadium has serious effects on human health, when the uptake is too high\(^6\).

**Effects of Vanadium on the Environment**

Vanadium can be found in the environment in algae, plants, invertebrates, fishes and many other species. In mussels and crabs vanadium strongly bio-accumulates, which can lead to concentrations of about \(10^5\) to \(10^6\) times greater than the concentrations that are found in seawater. Vanadium causes the inhibition of certain enzymes with animals, which has several neurological effects\(^6\). Laboratory tests with test animals have shown that vanadium can cause harm to the reproductive system of male animals, and that it accumulates in the female placenta. Vanadium can cause deoxyribonucleic acid (DNA) alteration in some cases, but it cannot cause
cancer with animals.  

2.10. Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are potent atmospheric pollutants that consist of fused aromatic rings and do not contain heteroatom or other substituents. PAHs are group of semi-volatile organic compounds (SVOCs) that are present in crude oil that has spent time in the ocean and eventually reaches shore and can be formed when oil is burned. PAHs come from other sources as well. They are formed during the incomplete burning of gas, coal, garbage, or other organic substances and from motor vehicle exhaust. As pollutants, they are of concern because some compounds have been identified as carcinogenic, mutagenic and teratogenic. PAHs are also found in cooked foods. Studies have shown that high levels of PAHs are found, for example, in meat cooked at high temperatures such as grilling or barbecuing, and in smoked fish. They are also found in the interstellar medium, in comets, and in meteorites and are candidate molecule to act as a basis for the earliest forms of life.

2.10.1 Occurrence and Pollution

Polycyclic aromatic hydrocarbons are lipophilic, meaning they mix more easily with oil than water. The larger compounds are less water-soluble and less volatile. Because of these properties, PAHs in the environment are found primarily in soil, sediment and oily substances, as opposed to in water or air. However, they are also a component of concern in particulate matter suspended in air. Natural crude oil and coal deposits contain significant amounts of PAHs, arising from chemical conversion of natural product molecules, such as steroids, to aromatic hydrocarbons. They are also found in processed fossil fuels, tar and various edible oils. In a study evaluating the genotoxic and carcinogenic risks associated with the consumption of repeatedly heated coconut oil (RCO), one of the commonly consumed cooking and frying
medium, it was concluded that dietary consumption of RCO can cause a genotoxic and preneoplastic change in the liver\textsuperscript{77}. Coal burning produces a different mixture than motor-fuel combustion or a forest fire, making the compounds potentially useful as indicators of the burning history. Hydrocarbon emissions from fossil fuel-burning engines are regulated in developed countries\textsuperscript{78}.

2.10.2 List of PAHs

The United States Environmental Protection Agency (EPA) has designated the following PAH compounds as priority pollutants\textsuperscript{78}. They include: naphthalene, acenaphthene, acenaphthyene, anthracene, benz[a]anthracene, benzo[a]pyrene, benzo[e]pyrene, benzo[b]fluoranthene, benzo[ghi]perylene, benzo[j]fluoranthene, benzo[k]fluoranthene, chrysene, coronene, dibenz(a,h)anthracene, fluoranthene, fluorine, indeno(1,2,3-cd)pyrene and pyrene. These list of PAHs are often targeted for measurement in environmental samples\textsuperscript{78}.

2.10.3 Health Effects of Poly Aromatic Hydrocarbons

PAHs that are known for their carcinogenic, mutagenic and teratogenic properties are benz[a]anthracene and chrysene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene, coronene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene and ovalene\textsuperscript{78}. High prenatal exposure to PAHs is associated with lower intelligent quotient (IQ) and childhood asthma. The Center for Children's Environmental Health reports studies that demonstrate that exposure to PAH pollution during pregnancy is related to adverse birth outcomes including low birth weight, premature delivery, and heart malformations. Cord blood of exposed babies shows DNA damage that has been linked to cancer. Follow-up studies show a higher level of developmental delays at age three, lower scores on IQ tests and increased behavioral problems at ages six and eight\textsuperscript{78}. Animal studies showed that mice exposed
to 308 parts per million (ppm) of PAHs specifically benzo (a) pyrene in food for 10 days (short term exposure) had offspring with birth defects. Mice exposed to 923 ppm of benzo(a)pyrene in food for months developed problems in the liver and blood\textsuperscript{79}.

### 2.10.4 Some PAHs Compounds

![Naphthalene](image)

**Naphthalene**

![Anthracene](image)

**Anthracene**

![Benzo[a]pyrene](image)

**Benzo[a]pyrene**

![Chrysene](image)

**Chrysene**

![Coronene](image)

**Coronene**

![Pyrene](image)

**Pyrene**
2.10.5 Detection

Detection of PAHs in materials is often done using gas chromatography- FID or mass spectrometry or liquid chromatography with ultraviolet-visible or fluorescence spectroscopic methods or by using rapid test PAH indicator strips.\(^{78}\)

2.11.0. Environmental impact of Drilling Mud

The major challenge in formulating drilling fluids would be to meet the increasing demanding conditions of high temperature and pressures found in deep, extended and horizontal wells without harming the environment.\(^{4, 80}\) Therefore, the selection of drilling fluid and their components should be based on their minimum environmental impact, so that any discharge of drilling waste would have little or no adverse effects on the environment.\(^{80, 81}\)

To determine the effects of drilling fluid on the environment, the fluids are subjected to various test such as toxicity, biodegradation and bio concentration tests. Toxicity test often referred to as ecotoxicity test, which is usually performed on the various drilling fluid chemicals and materials is used to predict the impact of these materials on the receiving environment.\(^{82}\) The results of
Ecotoxicity test experiments are used to estimate the minimum amount of test materials that can be discharged without having a direct toxic effect on the environment. Ecotoxicity results also provide information on the possible effect of drilling fluids on the biota, and therefore is a basis on which to assess their environmental acceptability. Current ecotoxicity testing is predominantly based on acute toxicity effects, where various toxicity indices such as Lethal Concentration (LC50) or Effective Concentration (EC50) may be used as means of measuring relative toxicities. LC50 refers to the lethal concentration required for 50% of a group of test organisms to die over a period of time.

Similarly, EC50 refers to a concentration of drilling fluid that causes 50% algal growth inhibition. Acute toxicity tests should be performed on representative base fluids and all additives used in mud formulations. Biodegradation test is usually performed to predict the extent to which the drilling fluids can be separated into individual parts by bacterial activities. Water based mud are generally the least damaging compared to oil based or synthetic based muds. A study carried out in Igbokoda onshore oil wells, Southwestern Nigeria on the environmental impact of exploratory wastes (drilling muds & cuttings) generated during the drilling of Igbokoda X and Igbokoda Y onshore oil wells, was studied by analyzing its total hydrocarbon (TPH), aliphatic hydrocarbon (AH), polycyclic aromatic hydrocarbon (PAH) using gas chromatography-mass spectrophotometry (GC-MS) method and metal contents using atomic absorption spectrophotometry (AAS). The result showed that these drilled wastes generated from the drilling of the onshore well sites indicated an exceedingly very high values of AH compared with the values of PAHs in both the oil based and water based muds and cuttings respectively. Both the oil based drilled mud and cuttings have higher values of PAHs when compared with water based drilled mud and cuttings. Most of the analyzed parameters generally have values
higher than that of the United States Environmental Protection Agency\(^1\).

Fang (1990), studied petroleum drilling and production operations in the Gulf of Mexico and observed that the ocean platform and dump sites contains emulsified mixtures of silt, hydrocarbons and water. He suggested that hydrocarbons were from crude oil and chemical additives for various operational necessities, including additions of biocides, corrosion inhibitors, anti-freezers and coagulants which are harmful to the environment\(^32\).

Drilling muds and cuttings derived from Ewan and Dibi off-shore wells in the Niger-Delta petroleum province of Nigeria was studied in order to evaluate their toxicity and possible environmental impacts that may result from their indiscriminate disposal. Oil based drilling wastes samples collected were analyzed for aliphatic hydrocarbon (AH) and polynuclear aromatic hydrocarbon (PAH) using Gas Chromatography Mass Spectrophotometry (GCMS) method. Also, some metals were analyzed using Atomic Absorption Spectrophotometry (AAS) method. It was observed that the concentration ratio of the polynuclear aromatic hydrocarbon to the aliphatic hydrocarbon in the total petroleum hydrocarbon (TPH) is in the ratio of 1:1000 for both the cuttings and drilling muds in both wells. Most of the total petroleum hydrocarbon (TPH), polynuclear aromatic hydrocarbon (PAH) has been found to be relatively lower than the World Health Organization standards. They concluded that the drill muds and cuttings wastes would increase pollution problems in the aquatic environment, thereby causing stress for the fish and other aquatic organisms\(^88\).

Curtis et al. (2001) investigated the environmental impact of base fluids used in oil based mud formulation on the environment and found that the biodegradation of diesel and branched paraffin are considered more resistant to rapid biodegradation than isomerized olefins which are intermediate in biodegradability, while esters exhibit the highest rate of biodegradability. They
further studied the toxicity of these based fluids and reported that diesel and ester based fluids are more toxic than the branched paraffins. Lee et al., (2002) studied the bio remediation and ecotoxicity of drilling fluids used in onshore drilling, and reported that bioremediation of isomerized olefin, alpha olefins and isomerized tetradecenene forest subsoil resulted in almost complete degradation of these fluids. They also stated that not only were these fluids highly biodegradable, they were also found to be non-toxic after remediation based on short-term plant, earth worm and micro toxicity bio assays. They further demonstrated that degradation of isomerized paraffins and mineral oil in the subsoil is attributed primarily to the abiotic loss of the large volatile components in this fluid. Alexander (1994) reported the biodegradation of base fluid used in drilling fluid formulation and opined that unbranched hydrocarbon base fluids degrade more readily than hydrocarbon characterized by extensive branching or complex aromatic ring structures.

Kozak and Shparkovski (1991) investigated the effect of drilling fluids and their components with the use of fish from Barents sea, and found that water based clay fluids effected changes in the respiratory rates and heart beats in Salmon fry exposed to concentration of drilling fluids between 2 and 15 milligrams per liter for a couple of minutes. They also discovered reduced survival of cod and flounder exposed to concentrations of drilling fluids of 5mg/l for 10 to 30 days.

Borisov et al, (1994) studied the impact of WBM on bioresources of Barents sea and found 50% mortality in salmon fry and amphipods exposed for between 48 and 96 hours to 5-22 mg/l concentrations of water based lignosulphate and ammonium drilling fluids. They further discovered that chronic test of copepods, amphipods bivalves and cod fry exposed to water based systems at 10 to 103 mg/l produced no observed effect.
2.12. Health Effects Associated with Drilling Fluids Contact

The risk of adverse health effects from drilling fluids is determined by the hazardous components of the fluid, additives and by human exposure to those components.

Some of the health effects of drilling muds and their causative components are as follows:

- Dermatitis (hydrocarbons)
- Dizziness (hydrocarbons)
- Headaches (hydrocarbons)
- Drowsiness (hydrocarbons)
- Nausea (hydrocarbons)
- Irritation and inflammation of the respiratory system (oil mist)
- Cancer (PAHs, benzene and mildly refined oil mist)
- Skin sensitization (hydrocarbons)

Other Hazardous Substances include:

- Hydrogen sulphide (H\textsubscript{2}S)
- Carbon monoxide (CO)
- Sulphur dioxide (SO\textsubscript{2})
- Heavy metals.

The effects are caused by the physico-chemical properties of the drilling fluid as well as the inherent properties of drilling fluid additives, and are dependent on the route of exposure such as dermal, inhalation and oral.

2.12.1 Inhalation Exposure

Gardner (2003) reported that the potential chemical changes in drilling during use and recycling can result in more toxic substance being released. Since drilling fluids are subjected to elevated
temperatures and increased pressures, there has been a concern that organic components might break down, or chemical reactions might occur, to form more toxic substances\textsuperscript{29}. There was a particular concern that base oil high in aromatics might contain, or form Polycyclic Aromatics Hydrocarbons (PAHs), while drilling muds based on alkyl benzenes might break down to yield free benzene.

It was also reported that drilling fluids are often circulated in an open system at elevated temperature with agitation that can result in a combination of vapors, aerosol and/or dust above the mud pit. Non aqueous drilling fluids, the vapours can consist of the low boiling-point fraction of hydrocarbons (paraffins, olefins and naphthenes), and the mist contains droplets of hydrocarbon fraction used. It should be noted that although the hydro carbon fraction may contain negligible amounts of known hazardous constituents such as benzene, toluene, ethyl benzene and xylenes (BTEX) at low boiling point, these will evaporate at relatively higher rates potentially resulting in higher concentrations in the vapor phase than anticipated\textsuperscript{95}. Mc Dougal \textit{et al.} (2000), also reported that petroleum distillates such as crude oil, diesel oil (used in non aqueous muds) have been associated with renal, hepatic, neurologic, immunologic and pulmonary toxicity when they are inhaled or ingested\textsuperscript{96}.

ATSDR (1999), reported some health effects associated with inhalation exposure as: Neurological effects, Carcinogenicity, Haematological effect, Immunological effect, Lymphoreticular effects and Pulmonary effects\textsuperscript{97}.

\textbf{2.12.2. Dermatitis and Irritation}

Skin is a more significant route of exposure than the lung\textsuperscript{98}. Skin contact with drilling fluid can also cause inflammation of the skin, referred to as dermatitis. Signs and symptoms of dermatitis include: itching, redness, swelling, blisters, scaling and other changes in the normal condition of
the skin. On the drill floor, in particular, skin contamination can be broad, but occasionally dermatitis also occur in divers who make contact with discarded cuttings on the sea bed.

Petroleum hydrocarbons will remove natural fat from the skin, which results in drying and cracking. These conditions allow compounds to permeate through the skin leading to skin irritation and dermatitis. Skin irritants can be petroleum hydrocarbons, specifically with aromatics and C8-C14 paraffins. Petroleum streams containing these compounds, such as kerosene and diesel (gas oil), are clearly irritating to skin. This is suggested to become Malignant caused by the paraffins, which do not readily penetrate the skin but are absorbed into the skin, thereby causing irritation. Linear alpha olefins and esters commonly used in drilling fluids are only slightly irritating to skin; whereas linear internal olefins are not irritating to skin. In addition to the irritancy of the drilling fluid hydrocarbon constituents, several drilling fluid additives may have irritants, corrosive or sensitizing properties. For example calcium chloride has irritant properties and zinc bromide is corrosive whereas a poly amine emulsifier has been associated with sensitizing properties.

Although water based fluids are not usually based on hydrocarbons, the additives in the fluid may still cause irritation or dermatitis. Excessive exposure under conditions of poor personal hygiene may lead to oil acne and folliculitis. ATSDR (1997), concluded that it is reasonable to expect that adverse haematological and immunological effects might occur following dermal exposure to benzene.

2.12.3. Oral Exposure

Oral exposure is negligible as compared to the other exposure routes such as dermal, inhalation and others. Oral exposure may occur when hands are not well washed before they are used to handle things like cigarette. Data for the oral route of exposure are less extensive. The BTEXs
cause neurological effects, generally central nervous system depression, by the oral route. Renal and hepatic effects are also seen with oral exposure to these compounds. Renal effects are the basis for the intermediate. The hepatic effects tend to be mild, including increased liver weight and cytochromes. Benzene causes haematological effects by the oral route that is similar to those seen from inhalation exposure\textsuperscript{102}.

1.13. Mud Treatment

Oil and gas production generally produce drilling wastes that contain mud, rock fragments and cuttings from the wellbore and chemicals added to improve the properties and performance of drilling muds. Certain methods have been adopted to reuse or reduce drilling waste as well as to diminish the toxicity of various drilling waste\textsuperscript{103}.

Two basic reasons for OBM treatment are:

1. Outright burning of the base oil from the cutting (Incinerating system) and the cuttings used for refilling of mud pits and other purposes. This incineration method involves burning the oil off through direct heating of oil based mud in an incinerator at a very high temperature of about 1100°C.

2. Extracting the base oil from the cutting for reuse (TDU) and the cutting is used for the refilling of mud pits and road construction. Here, the treatment is done in the thermal desorption unit (TDU). In the TDU, drilling wastes are fed into a high temperature processor through an inlet screw at 400°C.

In the processor, oil based mud is heated and the hot oil passes through pipe into a boiler. The oil and water will evaporate as steam into condensation chamber. The condensate oil and water are separated\textsuperscript{104}. Finally, the cuttings come out from the processor through the outlet screw and are collected as clean cuttings which can be used for road construction and refilling of mud pits\textsuperscript{104}. 

2.14.1. Gas Chromatography (GC)

The GC major components are: Injectors, Columns and Detectors. Detectors include: flame ionization detectors (FID), electron capture detectors (ECD), thermal conductivity detectors (TCD) and nitrogen-phosphorus detectors (NPD)\textsuperscript{105}.

2.14.2 Graphite Furnace Atomic Absorption Spectrometry

An atomic absorption spectrophotometer equipped with a graphite furnace or an electrically heated atomizer, instead of a standard burner head, offers better sensitivity and a much lower detection limit compared to the flame method. The sensitivity of electro thermal AAS or graphite furnace AAS (GrAAS) makes it ideal for trace metals analysis\textsuperscript{106}. It is also much more automated than the other techniques in this field. The entire process is automated once the sample has been introduced and the furnace program initiated. With the use of automatic samplers, a completely unattended operation is possible. An additional benefit of the GrAAS technique is the use of microliter sample sizes. Routine determination at the microgram-per-liter (ppb) level for most elements makes it ideal for environmental applications, but it is also suitable for biological and geological samples, and many clinical analyses\textsuperscript{106}.

2.15. Sampling

Sampling is an indispensable step in carrying out analytical experiment; good sampling produce good result\textsuperscript{107, 108}.

2.16. Sample Preparation

Many spectroscopic analytical methods require samples in the form of solutions which employ straightforward preparatory methods like mixing, dilution and separation. On the other hand, solid samples require more complicated preparatory methods like grinding, pulverizing and


2.16.1. Sample Preparation for Metal Analysis

Samples containing particulate or organic materials like oil, blood, urine and liquid fuels generally require pretreatment before analysis. For clean samples/single phase like clean water, direct analysis with Atomic absorption spectrophotometer is done without digestion. Sewage water, requires digestion before analysis\(^\text{106}\). The two most widely used methods for the destruction of organic matter are wet ashing/digestion and dry ashing\(^\text{106}\).

**Wet Digestion**

Wet digestion as a sample preparation technique entails digestion of the sample with strong acid and heat, and re-dissolving the residue in dilute acid prior to analysis so that all metal species are converted wholly to the same metal compound. Nitric acid (HNO\(_3\)) will digest most samples adequately. Nitrate is an acceptable matrix for both flame atomic absorption spectrophotometer (FAAS) and graphite furnace atomic absorption spectrophotometer (GrAAS). Some samples may require the addition of perchloric, hydrochloric or sulfuric acids for complete digestion\(^\text{106}\). These acids may interfere in the analysis of some metals and all provide a poor matrix for GrAAS analysis.

As a general rule:

1. HNO\(_3\) alone is adequate for clean samples or easily oxidized materials.

2. HNO\(_3\) - H\(_2\)SO\(_4\) or HNO\(_3\) - HCl digestion is adequate for readily oxidizable organic matter.

HNO\(_3\) - HClO\(_4\) or HNO\(_3\) - HClO\(_4\) - HF digestion is necessary for difficult-to-oxidize organic matter or minerals\(^\text{106}\).

**Dry Ashing**
Dry ashing involves subjection of the organic matter to decompose at very high regulated temperature in the presence of atmospheric oxygen. The procedure involves weighing the sample into a clean silica or porcelain crucible, covered with a crystallizing dish and dried under a heat lamp until the water has evaporated and the sample has a brittle charred appearance after which the ash is dissolved with a dilute mineral acid and filtered. For a careful heating, the sample dish is placed in a muffle furnace at 800°C until the digestion is complete. After cooling, the ash residue is taken up on dilute mineral acid. Dry ashing procedure is not favorable for metals like mercury and selenium due to their high volatilities.

2.17. Precautions taken During Sample Preparation for Metal Analysis

1. Care was taken not to introduce metals into samples during preliminary treatment.

2. Contact with rubber, metal base paints, paper tissues, and all metal products, including those made of stainless steel, galvanized metal and brass was avoided during pretreatment.

CHAPTER THREE

3.0 EXPERIMENTAL

3.1. Study Area

The untreated and treated oil based mud samples were formulated by ANA Industries Limited and used at Nembe creek 74 offshore well, in Bayelsa State, Nigeria.
Ijaw regions including Nembe Coordinates at Latitude: 4°26’21″N and Longitude: 6°17’35″E. Nembe is located in Bayelsa State, Nigeria.

3.2. Sampling

The agitators installed in the mud pits help to homogenize the mud. For the purpose of sampling, the mud pits of 20 feet length, 10 feet wide and 10 feet deep were further taped into ten (10) grid plots, each measuring $4^1 \times 5^1 \times 10^1$ cubic feet. The untreated and treated samples of oil based drilling mud each was collected by dipping a fabricated analysis cup into the gridded plots of the pits. The composite samples were homogenized, transferred in clean polyethylene cans and stoppered to avoid volatilization of some analytes especially the poly aromatic hydrocarbons (PAHs).

3.3 Apparatus and Reagents

1. Weighing balance (Sartorius model ED623S).
2. Tared porcelain crucible.
3. Muffle furnace
4. 100ml, 50ml and 25ml pyrex volumetric flasks.
5. Measuring cylinders (50 and 100 cm$^3$).
6. 100 cm$^3$ conical flask.
7. 50 ml, 100 ml and 250 ml pyrex beakers
8. 3 cm$^3$ plastic sample bottles
9. 5 ml GC vial bottle
10. Hamilton 1 µl syringe
11. Buck scientific atomic absorption spectrophotometer, model 210/211 VGP Atomic absorption spectrophotometer, with graphite furnace model 220GF Graphite furnace and 220AS auto sampler.
13. Filter paper.
14. 5 ml pyrex pipette
15. Retort stand.
16. 125 ml pyrex separatory funnel
17. Crystallizing dish
18. 1:1 HNO$_3$ acid.
19. 2% HNO$_3$ acid – water solution.
20. Dichloromethane.
22. Primary stock solutions of nickel, iron, chromium, cadmium, manganese and vanadium.
23. Distilled water.

All the analytical grade chemicals were purchased from Sigma and used without further purification. The glass wares, sample bottles and syringe were washed with detergent, 2% HNO$_3$.
acid – water and dichloromethane where necessary and rinsed carefully with distilled water. All the instruments like weighing balance, atomic absorption spectrophotometer and gas chromatography were calibrated with reference standard to avoid systematic error\(^{107}\). Weighing balance was calibrated with standard mass after internal calibration. Graphite furnace atomic absorption spectrophotometer was calibrated using 2\%HNO\(_3\) acid – water solution as a blank or reference standard and finally with secondary standard solutions prepared in the following concentrations: 150ppb, 100ppb and 50ppb. Finally, the gas chromatography was calibrated with 1\(\mu\)l of poly aromatic hydrocarbon standard manufactured under Restek’s ISO 9001 Registered quality system certificate #FM80397.

3.4 Sample Preparation for AAS Analysis

**Dry Ashing Method of Digestion**

2 g of both the untreated and treated oil based mud samples were weighed separately in tared porcelain crucibles. The dishes containing the samples were placed in a muffle furnace at 800°C for 4 hours in order to obtain a brittle charred residue indicating that complete digestion is achieved. The ash residues obtained were cooled and dissolved with 1:1 HNO\(_3\) acid and filtered into 100ml volumetric flasks each. The filter papers used were washed down with excess distilled water. 2\%HNO\(_3\) acid – water solution was also added to make up to mark.

3.5 Sample Preparation for GC/FID Analysis

**Extraction for GC/FID Analysis using Separation Funnel**

20ml of both the untreated and treated oil based mud samples were measured each with
measuring cylinder and transferred into separating funnels. 50ml of dichloromethane was added. The solutions were gently shaken for 30 minutes and vented every 2 minutes to allow the fume/vapour to evaporate. The mixtures were allowed to settle and later filtered into 100ml conical flask each and transferred into clean sample bottles rinsed with dichloromethane.

3.6 Preparation of Standard Solution

Stock solutions were diluted to specific concentrations to produce absorbance verses concentration curve. Using 2%HNO₃ acid – water solution as a blank or reference standard and to prepare 2%HNO₃ acid – water solution, twenty milliliter (20ml) concentrated HNO₃ was measured into a 1000ml standard flask and made up to mark with distilled water. i.e 2/100 x 1000/1 = 20ml.

3.7. Preparation of Secondary Standard Solution

The secondary standard solutions used were prepared from primary stock solutions (Buck Scientific) grade.

3.7.1. Preparation of 1ppm Concentration from Primary Stock Solution for the Analyzing Metals.

Primary stock solution ≡ 1000ppm.

Secondary standard solution ≡1ppm ≡ 1000ppb.

To prepare 1ppm of Cd, Cr, Mn, Fe, V and Ni secondary standard solution from 1000ppm primary stock solution, 0.05ml of primary stock solutions of each of these metals were measured separately into 50ml standard flask and were made up to mark with 2%HNO₃ acid – water solution.

i.e  \[ C_1 V_1 = C_2 V_2 \]

\[ V_1 = \frac{C_2 V_2}{C_1} \]
\[ V_1 = ? \]
\[ V_2 = 50 \text{ml} \]
\[ C_1 = 1000 \text{ppm} \]
\[ C_2 = 1 \text{ppm} \]
\[ V_1 = 1 \text{ppm} \times 50 \text{ml} / 1000 \text{ppm} \]
\[ V_1 = 0.05 \text{ml}. \]

### 3.7.2. Preparation of 150ppb, 100ppb and 50ppb Concentration from Secondary Standard Solution for all the Analyzing Metals.

To prepare 150ppb of Cd, Cr, Mn, Fe, V and Ni from 1ppm/1000ppb secondary standard solution, 3.75ml of each of the secondary standard solutions of these metals were pipetted separately into 25ml standard flask and were made up to mark with 2\%HNO_3 acid – water solution.

i.e \[ C_1 V_1 = C_2 V_2 , \]
\[ V_1 = C_2 V_2 / C_1 \]
\[ V_1 = ? \]
\[ V_2 = 25 \text{ml} \]
\[ C_1 = 1000 \text{ppb} \]
\[ C_2 = 150 \text{ppb} \]
\[ V_1 = 150 \text{ppb} \times 25 \text{ml} / 1000 \text{ppb} \]
\[ V_1 = 3.75 \text{ml}. \]

To prepare 100ppb of Cd, Cr, Mn, Fe, V and Ni from secondary standard solution, 2.5ml of each of the secondary standard solutions of these metals were pipetted separately into 25ml standard
flask and were made up to mark with 2%HNO₃ acid – water solution.

i.e  \[ C_1 V_1 = C_2 V_2, \]

\[ V_1 = \frac{C_2 V_2}{C_1} \]

\[ V_1 =? \]

\[ V_2 =25\text{ml} \]

\[ C_1 = 1000\text{ppb} \]

\[ C_2 =100\text{ppb} \]

\[ V_1 = 100\text{ppb} \times 25\text{ml}/1000\text{ppb} \]

\[ V_1 = 2.5\text{ml} \]

To prepare 50ppb of Cd, Cr, Mn, Fe, V and Ni from secondary standard solution, 1.25ml of each of the secondary standard solutions of these metals were pipetted separately into 25ml standard flask and were made up to mark with 2%HNO₃ acid – water solution.

i.e  \[ C_1 V_1 = C_2 V_2, \]

\[ V_1 = \frac{C_2 V_2}{C_1} \]

\[ V_1 =? \]

\[ V_2 =25\text{ml} \]

\[ C_1 = 1000\text{ppb} \]

\[ C_2 =50\text{ppb} \]

\[ V_1 = 50\text{ppb} \times 25\text{ml}/1000\text{ppb} \]

\[ V_1 = 1.25\text{ml} \]

3.8. Setting up the Equipments for the Analyses

3.8.1 Graphite Furnace Atomic Absorption Spectrophotometer

The flame assay was detached from the sample compartment and furnace assay was installed
back in the sample compartment. The auto sampler was attached to the GrFAAS instrument.

After the instrument has been powered, lamps were inserted into the lamp – turret position and the lamp connector was plugged as designated by the number on the cap connector of the lamp. The lamp was allowed to warm up for 15 minutes before the analysis. Library screen mode was opened and select button (SEL) was pressed until the lamp number matches the turret position used. The desired metal and method including the slit, wavelength and energy background were loaded and saved in the library window following below conditions.

**Cadmium**

Lamp:- Cd – furn 3 – 228.9nm and Slit: - 0.7 Å

**Chromium**

Lamp:- Cr – furn 3 – 357.9nm and Slit: - 0.7 Å

**Vanadium**

Lamp:- V – furn 3 – 318.4nm and Slit: - 0.2 Å

**Nickel**

Lamp:- Ni – furn 3 – 232.0nm and Slit: - 0.2 Å

**Manganese**

Lamp:- Mn – furn 3 – 279.5nm and Slit: - 0.7 Å

**Iron**

Lamp:- Fe – furn 3 – 248nm and Slit: - 0.2 Å

(Å ≡ Ammeter)

The blank (i.e 2%HNO₃ acid – water solution) was poured into the auto sampler cups. Then the standards were analyzed according to their concentrations starting from the highest (150ppb, 100ppb and 50ppb). The standards (150ppb, 100ppb and 50ppb) absorbances were used to plot
the calibration curve.

3.8.2 Gas chromatography – Flame Ionization Detector

Before running the analysis, the GC/FID was made free from impurities by allowing all the peaks in the column to elute until when a clear straight line on the base line was achieved. The standard for poly aromatic hydrocarbon obtained from Restek’s ISO 9001 Registered quality system certificate #FM80397 was run for the calibration of the GC/FID instrument (this was done to identify the particular peaks of interest in the sample).

3.9. Analysis of the metals using Graphite Furnace AAS

After the calibration, the digested oil based drilling mud samples each was aspirated and analyzed for the following metals cadmium, chromium, vanadium, manganese, nickel and iron. The concentration of each metal was read directly from the instrument read-out.

3.10 Analysis of PAHs using GC/FID

1µl of poly aromatic hydrocarbon standard was injected into the column for the calibration of the instrument. Finally, 1µl of the oil based mud samples each was injected into the column and analyzed for the PAHs present in the samples. The corresponding peaks obtained from the standards were used to identify the particular peak of each analyte in the samples.

CHAPTER FOUR

4.0 RESULTS

The results obtained from the analysis of heavy metals in the untreated and treated oil based drilling mud samples are given in Table 1 and Table 2 respectively. Table 3 shows the
concentrations of various components of polycyclic aromatic hydrocarbons in both the untreated and treated oil based mud samples. Table 4 and 5 gave the concentrations of the analyzed parameters, WHO and USEPA standards. Bar charts illustrating the variations of heavy metal concentrations and poly aromatic hydrocarbons in untreated and treated oil based mud samples are given in Figure 1 and 2. Graphs representing the calibration curves for the heavy metals analysis are shown in figures 3 to 8. The tables representing the values in the graphs are shown in Appendix 1. The chromatogram for the poly aromatic hydrocarbon standard is given in Appendix 2 while Appendix 3 and 4 show the chromatograms for both untreated and treated oil based mud samples respectively.

Table 1. The Concentrations of Heavy Metals in Untreated Oil Based Mud
Table 2. The Concentrations of Heavy Metals in Treated Oil Based Mud

<table>
<thead>
<tr>
<th>Parameters (ppb)</th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
<th>Cd</th>
<th>Mn</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>89.100</td>
<td>85.100</td>
<td>10.000</td>
<td>10.100</td>
<td>77.200</td>
<td>96.510</td>
</tr>
<tr>
<td></td>
<td>89.000</td>
<td>85.001</td>
<td>10.060</td>
<td>10.000</td>
<td>77.000</td>
<td>96.500</td>
</tr>
<tr>
<td></td>
<td>88.960</td>
<td>85.000</td>
<td>10.000</td>
<td>10.000</td>
<td>76.800</td>
<td>96.501</td>
</tr>
<tr>
<td>Mean</td>
<td>89.020</td>
<td>85.030</td>
<td>10.050</td>
<td>10.030</td>
<td>77.000</td>
<td>96.503</td>
</tr>
<tr>
<td>±0.072 ±0.057 ±0.050 ±0.057 ±0.140 ±0.005</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameters( ppb)</th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
<th>Cd</th>
<th>Mn</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>65.001</td>
<td>70.000</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>40.020</td>
<td>58.100</td>
</tr>
<tr>
<td></td>
<td>65.000</td>
<td>69.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>40.000</td>
<td>58.000</td>
</tr>
<tr>
<td></td>
<td>65.001</td>
<td>69.002</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>39.500</td>
<td>57.900</td>
</tr>
<tr>
<td>Mean</td>
<td>65.000</td>
<td>69.330</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>39.840</td>
<td>58.000</td>
</tr>
<tr>
<td>±0.001 ±0.576 ±0.294 ±0.100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Table 3. Concentrations of PAHs Components in the Untreated and treated Oil Based Mud.

<table>
<thead>
<tr>
<th>Parameters (ppb)</th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
<th>Cd</th>
<th>Mn</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Treated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S/N</td>
<td>Components</td>
<td>Concentrations (µg/ µl)</td>
<td>Concentrations (µg/ µl)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>-------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Naphthalene</td>
<td>21.47</td>
<td>0.48</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>2</td>
<td>2-Methylnaphthalene</td>
<td>32.60</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Acenaphthylene</td>
<td>18.99</td>
<td>0.61</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Acenaphthene</td>
<td>10.05</td>
<td>0.51</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Fluorene</td>
<td>2.59</td>
<td>0.31</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Phenanthrene</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Anthracene</td>
<td>2.58</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Fluorantracene</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Pyrene</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Benzo(a)anthracene &amp; Chrysene</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Concentrations of the analyzed heavy metals and standards given by standard regulatory bodies
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Untreated (ppb)</th>
<th>Treated (ppb)</th>
<th>Treated (ppm/mg/l)</th>
<th>Standards WHO(mg/l)</th>
<th>USEPA (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>89.020</td>
<td>65.000</td>
<td>0.065</td>
<td>0.500</td>
<td>0.300</td>
</tr>
<tr>
<td>Ni</td>
<td>85.030</td>
<td>69.330</td>
<td>0.069</td>
<td>-</td>
<td>0.200</td>
</tr>
<tr>
<td>Cr</td>
<td>10.050</td>
<td>&lt;0.001</td>
<td>N</td>
<td>0.050</td>
<td>0.100</td>
</tr>
<tr>
<td>Cd</td>
<td>10.030</td>
<td>&lt;0.001</td>
<td>N</td>
<td>0.050</td>
<td>0.050</td>
</tr>
<tr>
<td>Mn</td>
<td>77.000</td>
<td>39.840</td>
<td>0.039</td>
<td>-</td>
<td>0.050</td>
</tr>
<tr>
<td>V</td>
<td>96.503</td>
<td>58.000</td>
<td>0.058</td>
<td>-</td>
<td>0.100</td>
</tr>
</tbody>
</table>

N= Negligible
Table 4: Concentrations of the analyzed PAHs and standards given by standard regulatory bodies

<table>
<thead>
<tr>
<th>Parameter (µ g/ µl)</th>
<th>Untreated (µ g/ µl)</th>
<th>Treated (µ g/ µl)</th>
<th>Standards</th>
<th>Standards</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WHO (mg/l)</td>
<td>USEPA (mg/l)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total PAHs</td>
<td>88.28</td>
<td>1.91</td>
<td>0.2</td>
<td>0.7</td>
</tr>
<tr>
<td>PAHs profile</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Naphthalene</td>
<td>21.47</td>
<td>0.48</td>
<td>No guideline</td>
<td>No guideline</td>
</tr>
<tr>
<td>2-Methylnaphthalene</td>
<td>32.60</td>
<td>-</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>18.99</td>
<td>0.61</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>10.05</td>
<td>0.51</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Fluorene</td>
<td>2.59</td>
<td>0.31</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>-</td>
<td>-</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Anthracene</td>
<td>2.58</td>
<td>-</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Fluorantracene</td>
<td>-</td>
<td>-</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Pyrene</td>
<td>-</td>
<td>-</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Benzo(a)anthracene &amp; Chrysene</td>
<td>-</td>
<td>-</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
Bar chart showing Metal Analysis of Untreated and Treated Oil Based Mud
Bar chart showing various components of poly aromatic hydrocarbons in the Analysis of Untreated and Treated Oil Based Mud
Fig 1: Calibration Curve of Cd

\[ y = 0.000x \]

\[ R^2 = 0.999 \]
Fig2: Calibration Curve of Cr

$y = 0.000x$

$R^2 = 0.960$
Fig3: Calibration Curve of V

\[ y = 0.022x \]

\[ R^2 = 0.846 \]
Fig4: Calibration Curve of Ni

$y = 0.000x$

$R^2 = 0.872$
Fig5: Calibration Curve of Mn

\[ y = 0.031x \]

\[ R^2 = 0.829 \]
Fig 6: Calibration Curve of Fe

y = 0.000x
R² = 0.964
4.2 DISCUSSION

World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) previously prepared guidelines to the environmentally sound disposal of drilling waste (cuttings and mud) to land. The guidelines were based on disposal of water based mud. Recently some companies have re-introduced oil based mud operations. The base material for this is usually either diesel or crude oil/condensate, together with the various proprietary additives necessary for the particular drilling conditions. Generally, oil based mud systems are considered less environmentally friendly than water based mud in particular, they may contain aromatics especially polyaromatics which at various concentrations are toxic and some of which are carcinogenic.\textsuperscript{110}

The USEPA is more restrictive of OBM disposal than WBM. It was on this note that this research work was based on the contributions of oil based mud to environmental pollution to ascertain the concentrations of six heavy metals (Ni, Cr, Cd, Mn, V and Fe) and polyaromatic hydrocarbons which at certain threshold would be detrimental to personnel and environment.

The results obtained from the analysis showed that the untreated oil based mud sample contained higher concentrations of heavy metals and polyaromatic hydrocarbons when compared with the treated oil based mud sample. Table 1 showed the mean concentrations of heavy metals in the untreated oil based mud sample in this order: Fe (89.020ppb), Ni (85.030ppb), Cr (10.050ppb), Cd (10.030ppb), Mn (77.000ppb) and V (96.503ppb) while Table 2 gave the mean concentrations of heavy metals in the treated oil based mud as follows: Fe (65.000ppb), Ni (69.330ppb), Cr (>0.0001ppb), Cd (>0.0001ppb), Mn (39.840ppb) and V (58.000ppb). On the other hand, Table 3 gave the following concentrations of polyaromatics hydrocarbons in the untreated oil based mud: naphthalene (21.47 µg/µl), 2-methylnaphthalene (32.60 µg/µl), acenaphthylene (18.99 µg/µl), acenaphthene (10.05 µg/µl), flourene (2.59 µg/µl), and
anthracene (2.58 µg/µl), while naphthalene (0.48µg/µl), acenaphthylene (0.61µg/µl), acenaphthene (0.51 µg/µl) and flourene (0.31µg/µl) are the concentrations of PAHs components in the treated oil based mud sample.

Thus, this necessitated the establishment of waste management system in the oil industry. Waste management technology plays a vital role in the process of drilling, hence it helps to minimize, recycle or treat the drilling waste to make it less toxic when directly or indirectly discharged to aquatic and terrestrial environment\textsuperscript{110}. Options for handling the wastes can be organized into a three tier pollution prevention hierarchy:

- **Tier 1 – Minimization:** The generation of waste is minimized within the processes for drilling a well. This approach is mutually beneficial across all three objectives of minimizing the cost of drilling the well, meeting the technical of the drilling operation and minimizing the impacts on the receiving environment. When feasible, inhibitive drilling fluids and efficient mechanical solids control equipment can often save money for operators and result in greater protection of the environment.

- **Tier 2 – Treat/Reuse:** This is commonly applicable for oil based muds. The most common way to reuse drilling fluids is to recover the most valuable constituents of the drilling fluids from one location and move them to another drilling location. Substantial efforts are ongoing to develop economic methods to treat drilling fluids and drill cuttings so that, they can be beneficially reused in oilfield and non oilfield applications.

- **Tier 3 – Disposal:** When drilling waste must have undergone the stages of minimization and treatment, the operators can reuse or even dispose it off\textsuperscript{110}.

Although oil based muds are not deliberately discharged into the environment usually because of high cost of mud formulation, the base fluid and additives used to formulate the mud. However,
treated oil mud even though indirectly discharged must conformed to the heavy metals and polyaromatic hydrocarbon guidelines given by standard bodies such as WHO and USEPA.106, 111. In treated oil based mud sample analyzed, the occurrences of the following metals were recorded viz: iron, nickel, chromium, cadmium, magnesium and vanadium. The results generally indicated that Nickel (0.069 mg/l) is relatively higher in concentration than all the metals analyzed followed by iron (0.065 mg/l), vanadium (0.058 mg/l) and manganese (0.039 mg/l). Chromium and cadmium were found to be below the detection limit (<0.0001 ppb). The results of the analysed heavy metals shown in Table 3 of the treated oil based mud conformed to USEPA standard according to Maria, Csuros & Csaba Csuros (2002) report106, also in Gbadebo et al (2010) in the analysis of drilling muds and cuttings from Igbokoda onshore oil wells and Gbadebo et al (2010), in the analysis of drilling muds and cuttings from Dibi and Ewan offshore wells.1, 85.

The results indicated relative low components of the PAHs in the treated oil based muds. Although, FEPA (1991) guidelines for the disposal of petroleum exploration wastes into Nigerian environment has no limit for PAHs, however the PAHs values obtained in this study are far lower than the Canadian Interim Standards on PAHs in soils and water.1 The values are reported as follows: naphthalene (0.48 µg/µl), acenaphthylene (0.61 µg/µl), acenaphthene (0.51 µg/µl) and flourene (0.31 µg/µl).

4.3 CONCLUSION

The treated oil mud analyzed in this work conformed to the heavy metals and polyaromatic hydrocarbon guidelines as given by standard bodies. The mud cannot contribute to environmental pollution when directly or indirectly discharged to environment this is due to high mud treatment operations done. Based on the findings from the analysis conducted in this
research work, the researcher tends to report that treatment of drilling mud is vital before the wastes are discharged to the environment.

4.4 Contributions to Knowledge

• The results of this study have highlighted the awareness that both untreated and treated muds contain the heavy metals: Fe, Ni, Cr, Cd, Mn and V.

• The treatment reduced the concentration of Fe from 89.020 to 65.000 ppb, Ni from 85.030 to 69.330 ppb, Cr from 10.050 to < 0.001 ppb, Cd from 10.030 to < 0.001 ppb, Mn from 77.000 to 39.840 ppb and V from 96.503 to 58.000 ppb.

• The untreated mud contains more PAHs (µg/µl) than the treated mud, i.e. more in spread and concentration: naphthalene 21.47 vs 0.48, 2 – methylnaphthalene 32.60 vs nil, acenaphthalene 10.05 vs 0.51, fluorene 2.59 vs 0.31 and anthracene 2.58 vs nil.

• These data had not been published and will be quite useful to policy makers on environmental pollution and to stakeholders in drilling mud - their usefulness and hazards.

REFERENCES


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Ohio, USA.


House, Meerut.


Geochemistry. Postgraduate Institute. Newcastle Research Group, Drummond Building, University of Newcastle upon Tyne, UK NE1 7RU.


## APPENDICES

### Calibration Curve for Cr

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